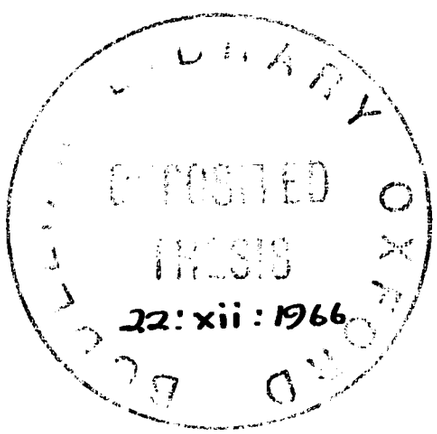
RADICAL REACTIONS OF SULPHUR COMPOUNDS

by

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A Thesis Presented for the Degree of
Doctor of Philosophy
in the University of Oxford

July,1966

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INTRODUCTION

This thesis falls into two main parts: the first consists of reactions of p-toluenesulphonyl iodide with a) quinones, b) polycyclic aromatic hydrocarbons and c) one olefin; the second is an attempt to detect free sulphinyl radicals by reaction with typical radical acceptors.

Several investigators have reported radical reactions of sulphonyl halides with olefins. Sulphonyl radicals have also been generated by other processes, of which the work of Waters and his collaborators seems to be the most interesting:

$$R\cdot + SO_2 \longrightarrow R\text{-}SO_2\cdot$$

$$RSO_2H + Ce^{4+} \longrightarrow RSO_2\cdot + Ce^{3+} + H^+$$

The sulphonyl halide used in this thesis to generate sulphonyl radicals was p-toluenesulphonyl iodide, which contains a weak S-I bond. Homolytic fission of this bond was expected, and seems to be the initial step in the reactions studied in this thesis.

Copper bronze and silver powder were found to accelerate the decomposition of the sulphonyl iodide.

The principal objective of the investigation was to react sulphonyl iodide with substracts othen than olefins, such as quinones and polycyclic aromatic hydrocarbons, so as to obtain conclusive evidence for the homolytic decomposition of the sulphonyl iodide.

The effect of light and inhibitors on the addition

of p-toluenesulphonyl iodide to acrylonitrile was also studied.

In the second part of the thesis an unsuccessful attempt to trap sulphinyl radicals is described. The production of such radicals was attempted by reaction of several sulphinyl chlorides with copper bronze and by decomposition of sulphenyl nitrates.

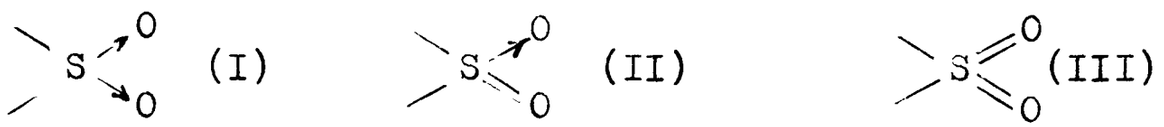
No kinetic studies were carried out in these investigations and the mechanisms proposed were induced from the nature of the products and conditions of reaction.

HISTORICAL SECTION

1. Some reactions of Sulphonyl Radicals

1.1 - Structure and characteristics of the sulphonyl group

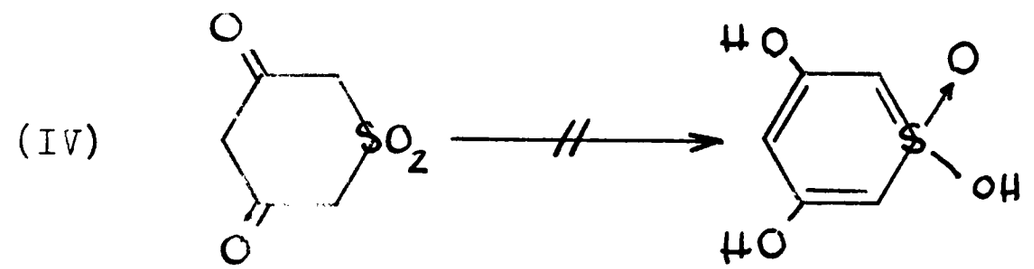
Three possible structures had been proposed to the sulphonyl group:



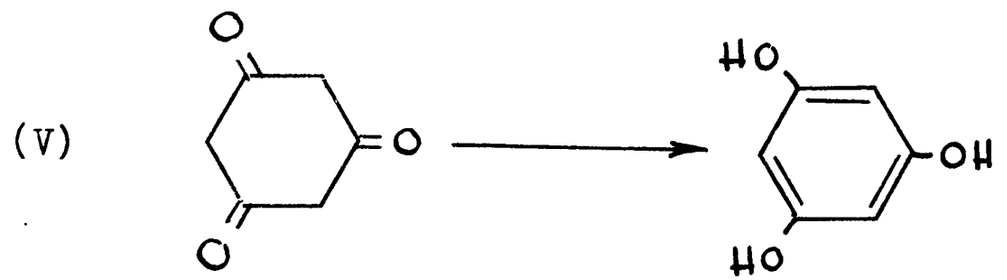
(I) (II) (III)

The truth is that all these structures must be considered to account for all the properties of the sulphonyl group.

Fehnel and Paul[1] showed that (IV) is unable to aromatize, whereas 1,3,5-cyclohexanetrione (V) converts to 1,3,5-trihydroxybenzene (phloroglucinol):



(IV)

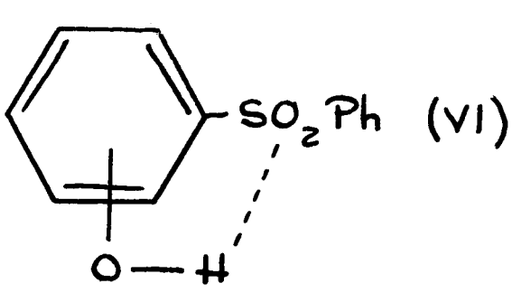


(V)

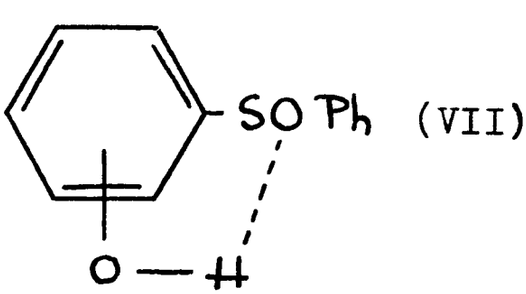
Arndt et al.[2] have also shown that the sulphonyl group

does not exist in the tautomeric enol form like the carbonyl group. It seems that the contribution of structure (III) is of very little importance [3, p.146] Structure (I) accords better with these facts.

The polar structure (II) in which sulphur possesses an electron dècet is more consistent with several indications. These indications are generally of a physical nature, like measurements of dipole moments [4], atomic distances [5] and spectrophotometrics [6]. Amstulz et al. [7] have studied the influence of the hydrogen bond in the infra red spectra of some hydroxyphenyl phenyl sulphones (VI) and sulphoxides (VII).

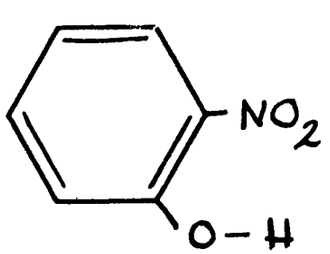
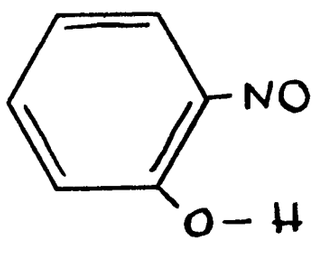


(VI)



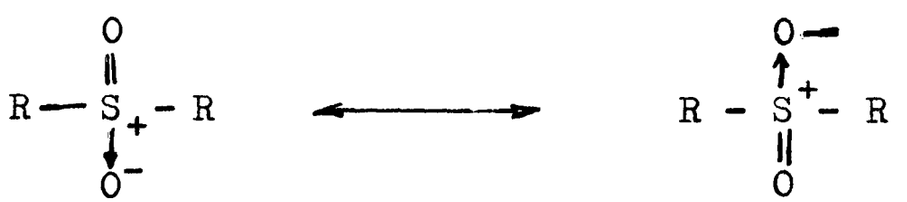
(VII)

A shift of the sulphoxide and sulphone (1,500 cm^{-1}) absorption bands towards lower frequencies was observed. Stronger hydrogen bond was observed in the case of the sulphoxide. The results were compared with those obtained with nitro and nitrosohydroxy benzenes (VIII). They interpret these spectral data by assuming that oxygens of the sulphone structure are considerably less basic than the

(VIII)

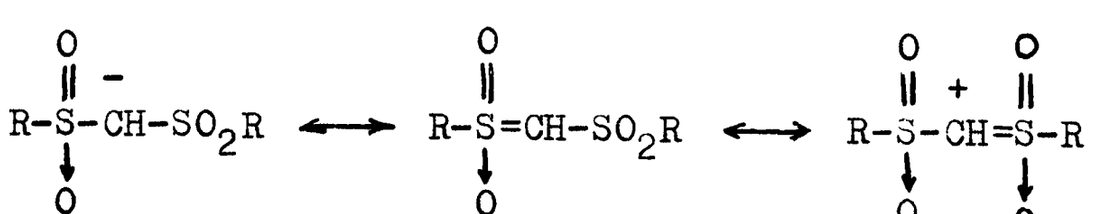
oxygen of the sulphoxide. They conclude that the difference between the sulphone and the sulphoxide can be explained by assigning to the sulphone a symmetrical structure (II) with resonance contributions from both S=O and S → O bonds.



(II)

This resonance structure was also proposed by Toussaint [8] who used X-rays diffraction measurements to support his argument.

This structure involves the expansion of the sulphur outer shell beyond the usual octet. The expansion of the sulphur outer shell had been proposed by several authors [9]. The sulphur atom of the sulphonyl group can expand its electronic configuration further than ten electrons [9,10]:



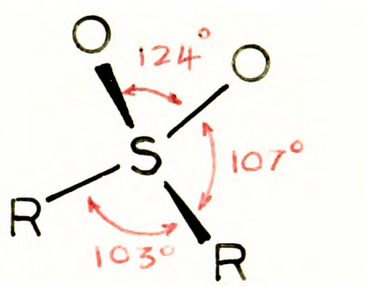
A.Burg (3 , p. 36) considered dimethylsulphone, $MeSO_2Me$, with a space orientation approximately tetrahedric. The sulphur-oxygen bonds are formed by a σ bond and two π bonds. These π bonds are formed by overlap of an oxygen 2p orbital and a hybrid sulphur orbital (with 3d, 4s and 4p character). The O-S-O bond angle is about 125°.

Cumper, Read and Vogel [11] studied some sulphones, RSO_2R, in benzenic solution, at $25^{\circ}C$ (R=methyl, ethyl, iso-propyl, n-propyl, n-buthyl, n-penthyl and benzyl) and the following valence angles were proposed:

$\hat{OSO}$ —— 124°

$\hat{OSR}$ —— 107°

$\hat{RSR}$ —— 103°



Dipole momenta were calculated for these sulphones and corresponding sulphoxides, RSOR, and they concluded that the S-O bond in sulphones is less polar than in sulphoxides. The sulphonyl group possesses basic properties to some extent as shown by freezing point depression in concentrated sulphuric acid [12] .

The properties of the sulphonyl group may be summarized as:

(a) The non-enolization

(b) The -I effect

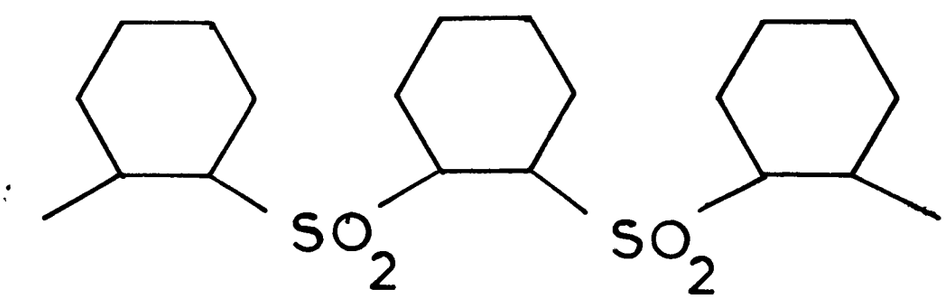
(c) The negative charge on the oxygen atom.

1.2. - The production of sulphonyl radicals.

1.2.1 - The reaction of sulphur dioxide with free radicals

1.2.1.1 - Reactions of liquid sulphur dioxide with unsaturated compounds.

This reaction was first reported by Solonina[13] who obtained copolymers of sulphur dioxide with allyl alcohol and with allyl ethers. Sayer and King[14] isolated polymers with the approximate formula $(C_6H_{10}O_2S)_x$ from a system of liquid sulphur dioxide and cyclohexene.

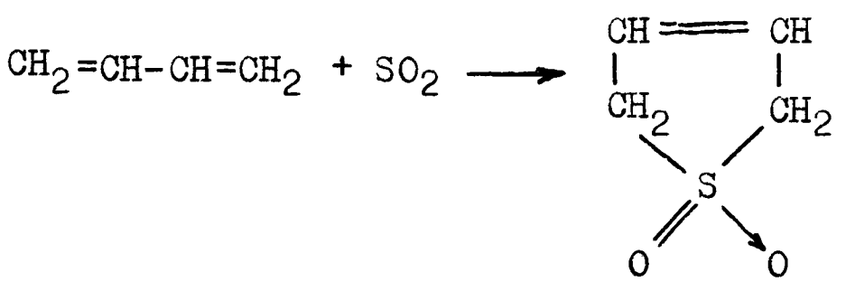


Marvel et al.[15] obtained similar reactions with a large number of unsaturated compounds but some exceptions were found (tri- and tetramethylethylene, ethyl crotonate, crotonaldehyde, methylacrylate, acrolein, vinyl chloride, acrylic acid, pinene, 1,4-dihydronaphthalene, chloroprene, trichloroethylene and oleyl alcohol). Polymers with molecular weights ranging from 100,000 to 200,000 have been obtained.

The reaction is catalysed by peroxides, u.v. light, oxygen, per-acids, ozone in chloroform, some metallic nitrates

and organometallic compounds. Polyhydric phenols have been reported to inhibit the reaction [16]. 1-Hexadecene has been polymerized with liquid sulphur dioxide in chloroform solution using a source of β-particles [17] and of γ-rays [18] as initiators.

Butadiene and many of its homologues react with sulphur dioxide under various conditions to give polymeric sulphones and cyclic monomeric sulphones:



The reaction has been carried out under various conditions including the use of aqueous ammonium sulphite at 120°C [19], water saturated with sulphur dioxide at room temperature [19], sulphur dioxide dissolved in ether ([19,20]) and liquid sulphur dioxide [21].

Snow and Frey [22] showed that there is always a sharp upper temperature limit above which copolymerization of olefins with liquid sulphur dioxide will not take place. This temperature was called "ceiling temperature" and its value depends on the olefin used and also on the amount of olefin present in the reaction mixture.

1.2.1.2. Photochemical gas-phase reaction of sulphur dioxide with hydrocarbons.

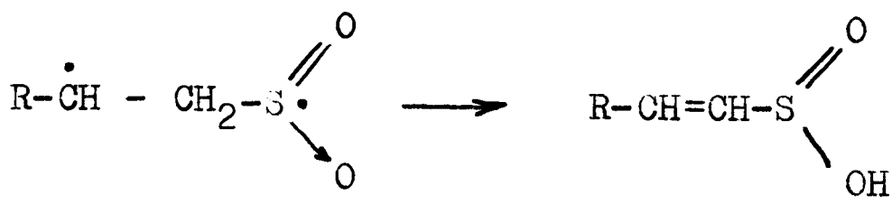
Gaseous sulphur dioxide reacts with hydrocarbons (olefins or paraffins) in the gas phase in the presence of u.v. light [23] :

$$RH + SO_2 \longrightarrow R.SO.OH$$

where RH is olefin or paraffin.

Spectroscopic studies [75] and the formation of C-S rather than C-O links in all reactions of sulphur dioxide and hydrocarbons induced by light [23] support the view that the excited molecule of sulphur dioxide reacts in the form $O=\dot{\underset{\cdot}{S}}=O$.

The reaction of sulphur dioxide and olefins in the liquid phase yielded high molecular weight polysulphones; in the gas phase sulphinic acids were obtained. This is because in the gas phase the diradical would rearrange to give an unsaturated sulphinic acid before collisions could occur:



The reaction proceeds most readily with long chain paraffins and tertiary carbon atoms are attacked more readily than secondary and secondary more readily than primary.

Olefins are less reactive than paraffins and they retard

the reaction of paraffins. This was explained [24] by their high quenching ability with respect to excited sulphur dioxide molecules:

$$SO_2^* + RH \longrightarrow SO_2 + RH$$

The following mechanisms have been suggested [24] from kinetic studies of the reaction with n-butane:

(a) $SO_2 + h\nu \longrightarrow SO_2^*$

(b) $SO_2^* + RH \longrightarrow RSO_2H$; R = m-butyl

(c) $SO_2^* + RH \longrightarrow SO_2 + RH$

(c') $SO_2^* + SO_2 \longrightarrow SO_2 + SO_2$

(d) $SO_2^* \longrightarrow SO_2$

where SO_2^* represents the excited sulphur dioxide molecule. Steps (c) and (c') are quenching processes and (d) is the process of internal deactivation.

For 1-butene the proposed mechanism was as follows:

$$SO_2 + h\nu \longrightarrow SO_2^*$$

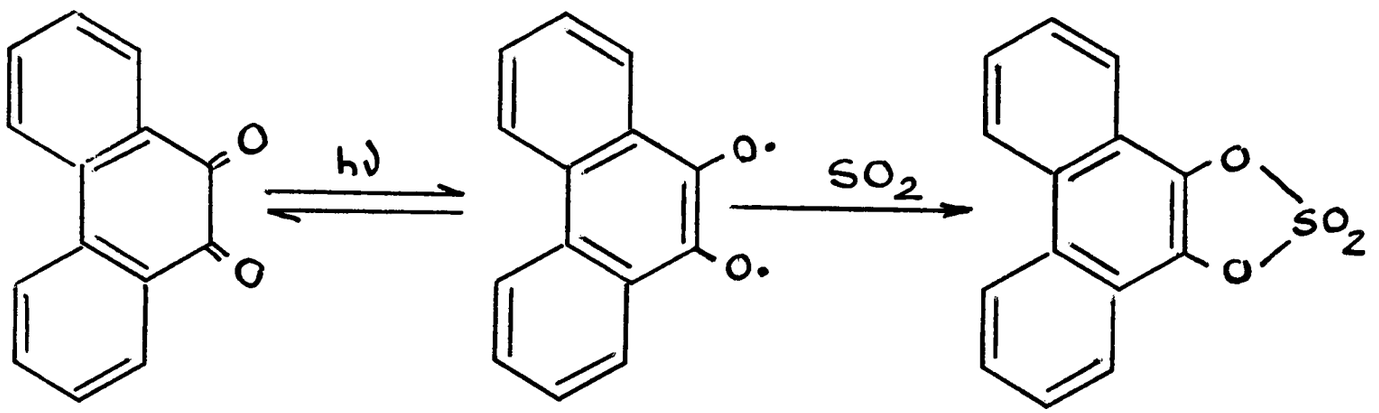
$$SO_2^* + B \longrightarrow SO_2 + B$$

$$SO_2^* + B \longrightarrow BSO_2$$

where B = 1-butene.

1.2.1.3. The photosynthesis of cyclic sulphuric acid esters by the addition of sulphur dioxide to o-quinones.

Schenck and Schmidt [25] has prepared several cyclic sulphuric acid esters by irradiating a mixture of sulphur dioxide and o-quinones in benzene and they suggested that the cyclic ester formation proceeded via intermediate photo-tropic diradicals:



Yields of the various cyclic esters obtained with different o-quinones are shown below:

Tetrachloro-o-quinone	57%
o-Naphthaquinone	33%
o-Chrysoquinone	81%
9,10-phenanthraquinone derivatives	17.5-65%

1.2.1.4 - The reaction of gaseous sulphur dioxide with phenyl radicals.

Ayscough et al. [26] studied by e.s.r. spectroscopy the action of gaseous sulphur dioxide on trapped hydrocarbon polymer radicals obtained by irradiation of polymers with γ-rays at low temperature. The spectrum obtained was attributed to sulphonyl radicals, $RSO_2^{\bullet}$, with the free electron largely on the sulphur atom. The spectrum was not changed when the sample was exposed to air.

Kuri et al. [27] also studied by using e.s.r. the action of gaseous sulphur dioxide on γ-irradiated P.V.C. and the spectrum obtained was attributed to $RSO_2^{\bullet}$ radicals. Waters and Squire ([28,29]) produced free sulphonyl radicals by reacting a free radical R- with gaseous sulphur dioxide in various solvents. The free radicals R. used were the 2-cyano-2-propyl and the phenyl radicals. It was seen that 2-cyano-2-propyl radicals were too stable to react with sulphur dioxide; 74% yield of dimer tetramethylsuccinonitrile was obtained (in a blank experiment a 77% yield was obtained).

Phenyl radicals were produced by the thermal decomposition of benzoyl peroxide in solution in the presence of sulphur dioxide. Clear evidence of the production of sulphonyl radicals could be obtained from the products of reaction.

A small yield (4%) of diphenyl sulphone was obtained when the solvent was benzene:

$$Ph. + SO_2 \longrightarrow PhSO_2.$$

$$2PhSO_2. \longrightarrow PhSO_2SO_2Ph$$

Chlorobenzene also did not take part in the reaction and a higher yield of dimer was obtained (13.8%).

Toluene and ethyl benzene took part in the reaction yielding other sulphone besides the dimer.

The mechanism suggested for the formation of phenyl-benzyl sulphone (15%) in toluene solution was:

$$Ph. + SO_2 \longrightarrow PhSO_2.$$

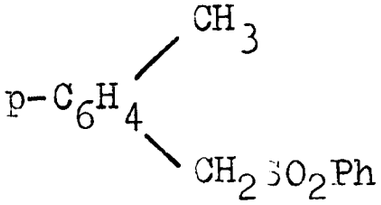
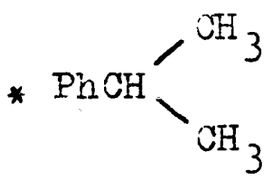
$$PhCH_3 + Ph. \longrightarrow PhCH_2. + PhH$$

$$PhCH_2. + PhSO_2. \longrightarrow PhCH_2SO_2Ph$$

$$PhCH_2. + SO_2 \longrightarrow PhCH_2SO_2.$$

$$PhCH_2SO_2. + Ph. \longrightarrow PhCH_2SO_2Ph$$

Lindsay [30] extended the work to other aromatic solvents. The products formed are shown in the table:

Solvent	Product	Yield
$p\text{-}C_6H_4(CH_3)_2$		18.3%
Ph_2CH_2	$Ph_2CH\text{-}SO_2Ph$	36.7%
$PhCOCH_3$	$PhCOCH_2\text{-}SO_2Ph$	5.5%
$PhCH_2CH_3$	Uncharacterized sulphone	-
* 	No sulphone formed	-

(*)Masters [31] has reported the isolation of phenyl cumyl sulphone in very small yield (0.08%) from the reaction of benzoyl peroxide and sulphur dioxide in cumene solution.

The mechanism proposed to account for the products of reaction in a solvent RH was the following:

$$Ph\cdot + SO_2 \longrightarrow PhSO_2\cdot \qquad (I)$$

$$RH + Ph\cdot \longrightarrow R\cdot + PhH \qquad (II)$$

$$R\cdot + PhSO_2\cdot \longrightarrow R\text{-}SO_2Ph \qquad (III)$$

$$R\cdot + SO_2\cdot \longrightarrow RSO_2\cdot \qquad (IV)$$

$$RSO_2\cdot + Ph\cdot \longrightarrow RSO_2Ph \qquad (V)$$

$PhSO_2\cdot + Ph\cdot \longrightarrow PhSO_2Ph$ (VI)

$PhSO_2\cdot + RH \longrightarrow PhSO_2H + R\cdot$ (VII)

It was suggested that the dominant mechanism was the addition of phenylsulphonyl radical to the solvent-derived radical R· (reaction I-III), rather than the addition of sulphur dioxide to the radical R·, and subsequent combination with a phenyl radical (reactions IV-V). Neither diphenyl sulphone $PhSO_2Ph$ nor benzenesulphinic acid $PhSO_2H$ were found in any of the experiments (VI,VII).

The reaction was studied in non-aromatic solvents by C.Correia [32]. It was seen that cyclohexanone, diethyl malonate, decalin and methylcyclohexane did not react with phenylsulphonyl radicals.

With t-butyl peroxide, toluene and sulphur dioxide no sulphone could also be obtained. The reaction mixtures obtained contained large amount of tar and high boiling point brown oils.

It seems that in non-aromatic solvents the solvent-radicals R· are not stable enough to remain in solution to react with sulphonyl radicals. It seems also that the presence of sulphur dioxide in solution originates side reactions yielding tar and oils.

1.2.2 - The oxidation of sulphinic acids with ceric sulphate.

The preparation of disulphones by oxidation of sulphinic acids with potassium permanganate was reported in 1908 by Hilditch ([33]).

Alimarin and Sotnikov ([34]) stated that ceric sulphate in acid solution oxidizes the benzenesulphinic acid; the reaction products being diphenyldisulphone, benzenesulphonic acid and an equivalent amount of cerous sulphate.

Forrest and Ryan ([35]) found similar results and reported that the end point of the titration of the sulphinic acid with ceric sulphate solution occurred at a molecular ratio $Ce^{4+}/PhSO_2H = 1.8$. This value is higher than that proposed by Alimarin [36], 1.1 - 1.2. Gringras and Sjostedt [37] proposed the equation:

$$4RSO_2^- + 6Ce^{4+} + 2H_2O \longrightarrow RSO_2SO_2R + 2RSO_3^- + 6Ce^{3+} + 4H^+$$

Correia [32] attempted some titrations of arylsulphinic acids in acid solution by adding an excess of standard ceric sulphate solution; the solution was then treated with potassium iodide solution and the liberated iodine was titrated with sodium thiosulphate. Results are given in the table:

RSO_2H	mols.Ce^{4+}/mols.RSO_2H
$PhSO_2H$	1.55
p-$TolSO_2H$	1.33
o-$ClC_6H_4SO_2H$	1.45

The oxidation of several arylsulphinic acids in a flow system by ceric sulphate was studied by Miss McMillan and Waters by using e.s.r. spectroscopy[38]. Arylsulphonyl radicals, $ArSO_2^{\bullet}$ were detected and this explained the formation of disulphones:

$$ArSO_2^- + Ce^{4+} \rightleftharpoons ArSO_2^{\bullet} + Ce^{3+}$$

$$2ArSO_2^{\bullet} \longrightarrow ArSO_2SO_2Ar$$

Correia[32] attempted some reactions of sulphonyl radicals so produced with olefins but no sulphones could be isolated. It was expected that the following reactions might occur:

$$ArSO_2^- + Ce^{4+} \longrightarrow ArSO_2^{\bullet} + Ce^{3+}$$

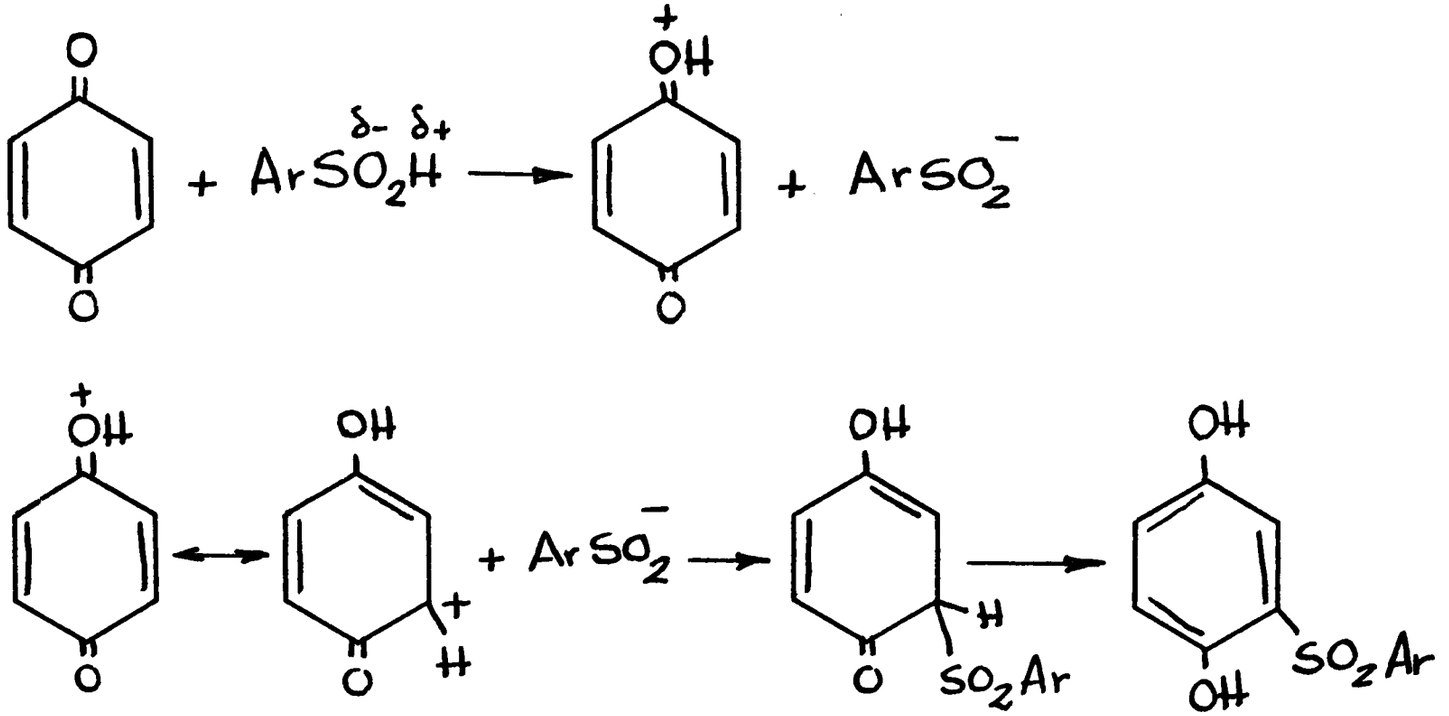
$$ArSO_2^{\bullet} + CH_2{=}CH{-}R \longrightarrow ArSO_2{-}CH_2\dot{C}HR$$

$$ArSO_2{-}CH_2\dot{C}HR \xrightarrow{ArSO_2^{\bullet}} ArSO_2{-}CH_2CH(R)SO_2Ar$$

and/or

$$ArSO_2{-}CH_2\dot{C}HR \xrightarrow{R^{\bullet}} RH + ArSO_2{-}CH{=}CH{-}R$$

An unsuccessful attempt was also performed with p-benzoquinone, but the only product formed was 2-arylsulphonyl-hydroquinone:



This is the well known heterolytic reaction between a sulphinyl anion, RSO_2^-, and a quinone molecule.

1.2.3 - The decomposition of sulphonyl halides.

Sulphonyl halides, RSO_2Hal, may decompose into free sulphonyl radicals and halogen atoms under suitable conditions. The formation of arylsulphonic anhydrides by photochemical decomposition of arylsulphonyl chlorides in the presence of oxygen reported by Olivier in 1916-18[39] may be a radical process since both peroxides[42] and ultraviolet light lower the temperature of decomposition of alkanesulphonyl[40,41] chlorides.

Herbrandson, Kelly and Versnel[43] studied the thermal decomposition of optically active 2-octanesulphonyl chloride,

$C_6H_{13}CH(CH_3)SO_2Cl$, under ultraviolet light and in the presence of peroxides. Racemic 2-chlorooctane and sulphur dioxide were obtained and they proposed the mechanism:

$$\text{Initiating (and/or)} \begin{cases} RSO_2Cl \longrightarrow R. + .SO_2Cl \\ RSO_2Cl \longrightarrow RSO_2. + Cl. \\ RSO_2Cl + R'. \longrightarrow RSO_2. + R'Cl \end{cases}$$

$$\text{Propagation} \begin{cases} RSO_2Cl + R. \longrightarrow RSO_2. + RCl \\ RSO_2. \underset{2}{\overset{1}{\rightleftharpoons}} R. + SO_2 \qquad (I) \end{cases}$$

The decomposition of sulphonyl radicals $RSO_2.$ into sulphur dioxide and radical R.(I) was proposed by M.Kharash et al.[44] as a step of the chlorosulphonation of hydrocarbons. It is known that reaction 1 predominates over reaction 2 when the temperature is raised [44, 45]. 2-octanesulphonyl chloride however decomposes in N,N-dimethylphormamide, $HCON(CH_3)_2$, following an ionic path.

The decomposition of methane, ethane and propane-sulphonyl chlorides and bromides was studied kinetically by Geisler and Reinhardt[46]. The results lead to a radical chain mechanism similar to that of Herbrandson et al.[43]

Inamoto[47] decomposed α,α'-azobisisobutyronitrile, $Me_2C(CN)N_2C(CN)Me_2$ in liquid sulphonyl chlorides at 100°C. Very small quantities of crossed products were obtained. In the case of benzenesulphonyl chloride, 1.4% of α-cyanoisopropyl

phenyl sulphone, $Me_2C(CN)SO_2Ph$, was obtained. This product arose very likely from a combination of 2-cyano-2-propyl and phenylsulphonyl radicals:

$$Me_2\dot{C}(CN) + PhSO_2. \longrightarrow Me_2C(CN)SO_2Ph$$

Though $PhCH_2SO_2Cl$ decomposes thermally by itself, the thermal decomposition was accelerated by the presence of 2-cyano-2-propyl radicals.

The decomposition of sulphonyl halides in the presence of metals do not always give the same products.

Karrer et al.[48] showed that the reaction of p-toluenesulphonyl chloride with copper bronze in pyridine was a very fast and complex reaction. p-Tolyl-p-toluenethiosulphonate, $TolSO_2STol$, a small quantity of dimer di-p-tolyldisulphone, $TolSO_2SO_2Tol$, copper salts of p-toluenesulphonic acid and metallic pyridine complexes were obtained as reaction products.

p-Toluenesulphonyl chloride in toluene is converted to di-p-tolyldisulphone by action of sodium or potassium[49] with a 19.4% yield. Otto et al.[50] attempted to prepare disulphones by using sulphonyl chlorides and sodium but without success. When naphthalenesulphonyl iodide was treated with silver powder in anhydrous ether, naphthalenesulphonic anhydride and naphthyl naphthalenethiosulphonate were obtained instead of the expected disulphone[51] :

$$6\ RSO_2I + 6\ Ag \longrightarrow 2(RSO_2)_2O + RSO_2SR + 6AgI$$

The same result was obtained by Kohler and McDonald [52] when sulphonyl iodides were heated with finely divided silver. p-Toluenesulphonyl iodide reacts with di-p-tolylmercury, p-tolylsulphone being obtained [53] :

$$TolSO_2I + Hg\begin{matrix}\diagup Tol \\ \diagdown Tol\end{matrix} \longrightarrow TolSO_2Tol + Hg\begin{matrix}\diagup Tol \\ \diagdown I\end{matrix}$$

Most of the reported radical reactions of sulphonyl halides had been concerned with its addition to olefins.

The addition of p-chlorobenzenesulphonyl chloride to allyl acetate, isobutylene and ethylene in the presence of benzoyl peroxide was reported by Ladd in two U.S. Patents.[54]

M.Kharaš̆h and Mosher [55] showed that 1-octene and 1-decene in the presence of benzoyl peroxide added to N-chlorosulphonyl phthalimide.

A radical chain mechanism was proposed:

$$(C_8H_4O_2)NSO_2Cl + R'\ . \longrightarrow (C_8H_4O_2)NSO_2\ . + R'Cl$$

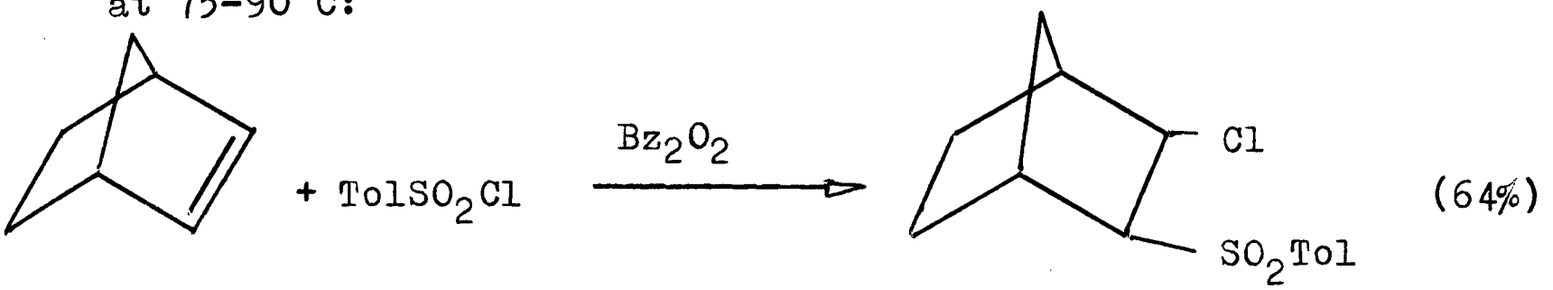
$$(C_8H_4O_2)NSO_2\ . + CH_2{=}CH{-}R \longrightarrow (C_8H_4O_2)NSO_2CH_2\dot{C}HR$$

$$(C_8H_4O_2)NSO_2CH_2\dot{C}HR + (C_8H_4O_2)NSO_2Cl \longrightarrow$$

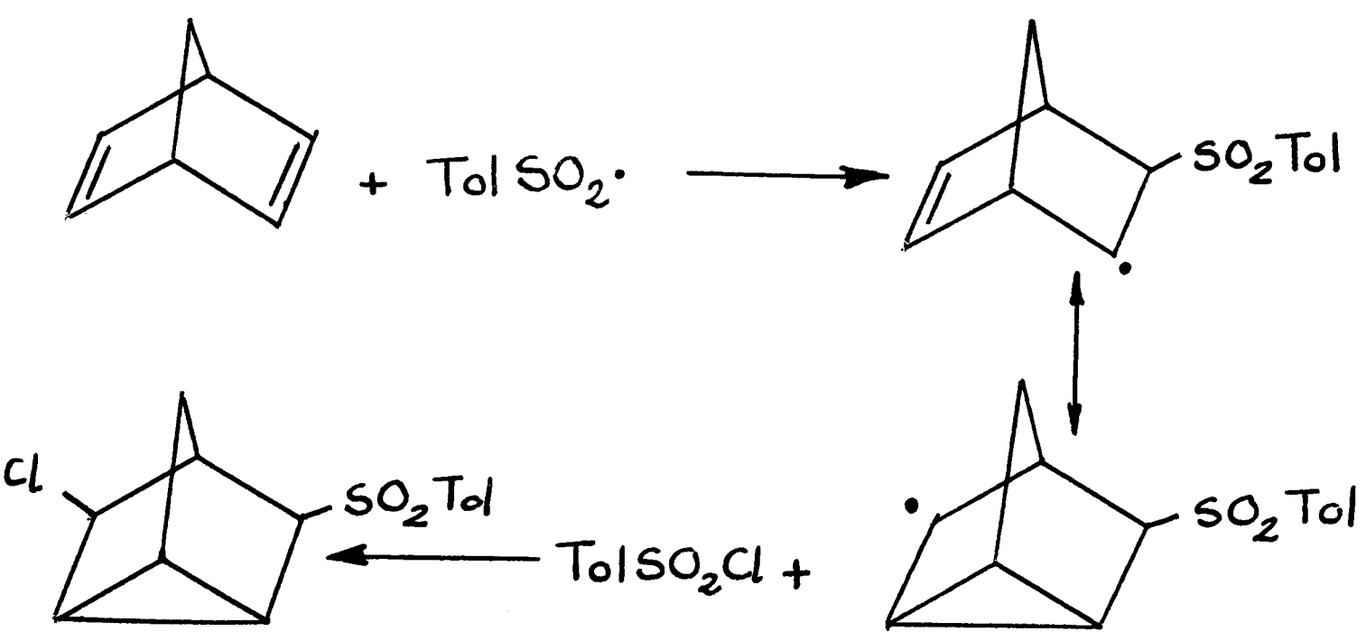
$$\longrightarrow (C_8H_4O_2)NSO_2CH_2CHCl\ R + (C_8H_4O_2)NSO_2\ \text{etc.}$$

Skell and McNamara [56], Skell, Woodworth and McNamara [57] and McNamara [58] reported similar additions of benzenesulphonyl halides to olefins under radical conditions (irradiation and peroxides). They found that the sulphonyl iodide is about ten times as reactive as the sulphonyl bromide and the sulphonyl chloride is much less reactive.

Cristol and Reeder [59] reported addition of p-toluenesulphonyl chloride to norbonene in the presence of benzoyl peroxide, at 75-90°C:



More recently, Cristol and Davies [60] studied the addition of sulphonyl halides to norbonadiene. In the presence of benzoyl peroxide for 24 h., at 75-82°C, a different addition product was obtained.



Recently Asscher and Vofsi [61] studied the addition of some aromatic sulphonyl chlorides to vinylic monomers and other olefins under copper (I and II) chloride catalysis.

The proposed mechanism of the addition was as follows:

$$X\cdot \text{ (from initiator)} + RSO_2Cl \longrightarrow RSO_2\cdot + XCl$$

$$RSO_2\cdot + CH_2{=}CH{-}R' \longrightarrow RSO_2CH_2\dot{C}HR'$$

$$RSO_2CH_2\dot{C}HR' + CuCl^+ \longrightarrow RSO_2CH_2CHClR' + Cu^+$$

$$Cu^+ + RSO_2Cl \longrightarrow CuCl^+ + RSO_2\cdot \text{ etc.}$$

The catalyst participates in the propagation step as a chlorine atom redox transfer agent [62].

Methanesulphonyl chloride added, under ultraviolet radiation, to 1-heptene to yield 2-chloro-1-methylsulphonyl-heptane [63]:

$$MeSO_2Cl + CH_2{=}CH{-}C_5H_{11} \longrightarrow MeSO_2{-}CH_2\underset{\displaystyle Cl}{\underset{|}{C}}H{-}\ C_5H_{11}$$

However, chloromethanesulphonyl chloride, $ClCH_2SO_2Cl$, reacts with 1-heptene in the presence of benzoyl peroxide to give 30-40% of 1,3-dichlorooctane [64]:

$$ClCH_2SO_2Cl \xrightarrow{Bz_2O_2} ClCH_2SO_2\cdot$$

$$ClCH_2SO_2\cdot \rightleftharpoons ClCH_2\cdot + SO_2$$

$$ClCH_2\cdot + R\text{-}CH{=}CH_2 \longrightarrow R\text{-}\dot{C}H\text{-}CH_2CH_2Cl$$

$$R\text{-}\dot{C}H\text{-}CH_2CH_2Cl + ClCH_2\text{-}SO_2Cl \longrightarrow R\text{-}CHCl\text{-}CH_2\text{-}CH_2\text{-}Cl + ClCH_2SO_2\cdot$$

Sulphur dioxide is also eliminated from the intermediate sulphonyl radical when trichloromethanesulphonyl chloride reacts with styrene at 160-170°C [65] :

$$X\cdot + CCl_3\text{-}SO_2Cl \longrightarrow CCl_3\text{-}SO_2\cdot + XCl$$

$$CCl_3\text{-}SO_2\cdot \rightleftharpoons \dot{C}Cl_3 + SO_2$$

$$\dot{C}Cl_3 + Ph\text{-}CH{=}CH_2 \longrightarrow Ph\text{-}\dot{C}H\text{-}CH_2\text{-}CCl_3$$

$$Ph\text{-}\dot{C}H\text{-}CH_2\text{-}CCl_3 + CCl_3\text{-}SO_2Cl \longrightarrow \text{Adduct} + CCl_3\text{-}SO_2\cdot$$

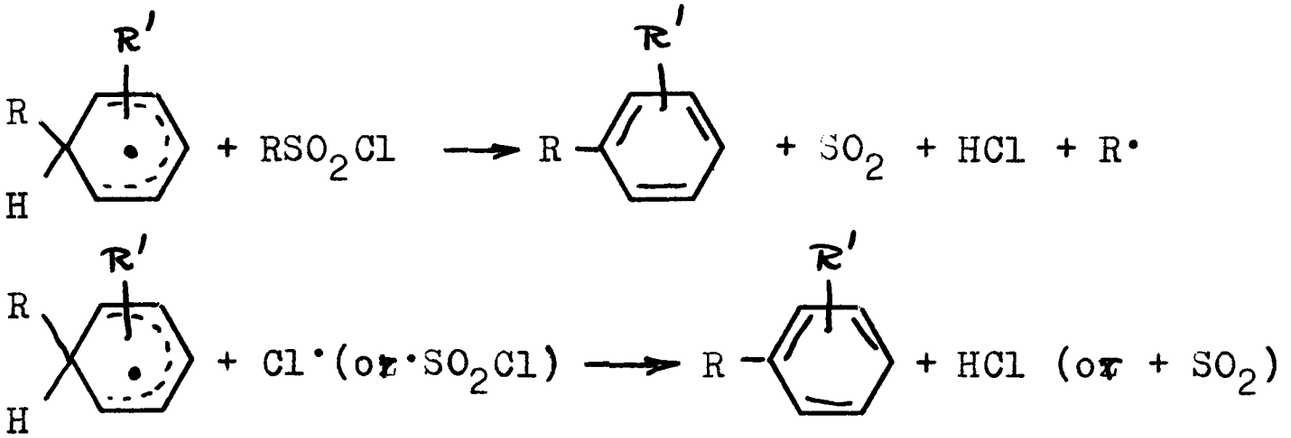
When sulphonyl chlorides are decomposed at about 250°C in aromatic substracts sulphur dioxide is lost and substitution in the aromatic nucleus occurs [45] :

$$RSO_2Cl \longrightarrow R\cdot + \cdot SO_2Cl$$

$$RSO_2Cl \longrightarrow RSO_2\cdot + Cl\cdot$$

$$RSO_2\cdot \longrightarrow R\cdot + SO_2$$





Reactions of trichloromethanesulphonyl bromide, $Cl_3C\text{-}SO_2Br$, with some hydrocarbons (cyclopentane, cyclohexane and toluene) under the influence of light were reported by Pinnell, Hüser and Kleissberg [66]. The hydrocarbon was brominated; chloroform and sulphur dioxide were formed. It was suggested that the hydrogen abstracter on the hydrocarbon was the radical $Cl_3C^{\bullet}$ obtained from decomposition of the sulphonyl radical:

$$Cl_3CSO_2Br \longrightarrow Cl_3CSO_2^{\bullet} + Br.$$

$$Cl_3CSO_2^{\bullet} \longrightarrow Cl_3C^{\bullet} + SO_2$$

$$RH + Cl_3C^{\bullet} \longrightarrow R^{\bullet} + Cl_3CH$$

$$R^{\bullet} + Br^{\bullet} \longrightarrow R\text{-}Br$$

$$R^{\bullet} + Cl_3CSO_2Br \longrightarrow R\text{-}Br + Cl_3CSO_2\cdot \text{ etc.}$$

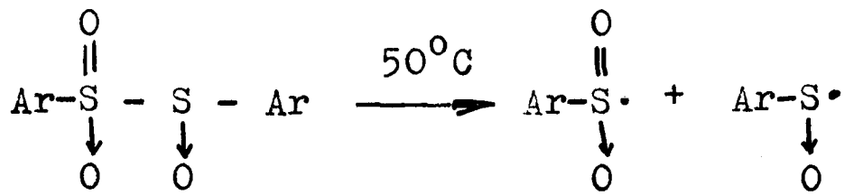
With trichloromethanesulphonyl chloride the hydrogen abstracter was proposed to be the sulphonyl radical [67]:

$$RH + Cl_3CSO_2^{\bullet} \longrightarrow R^{\bullet} + Cl_3CSO_2H$$

$$Cl_3CSO_2H \longrightarrow Cl_3CH + SO_2$$

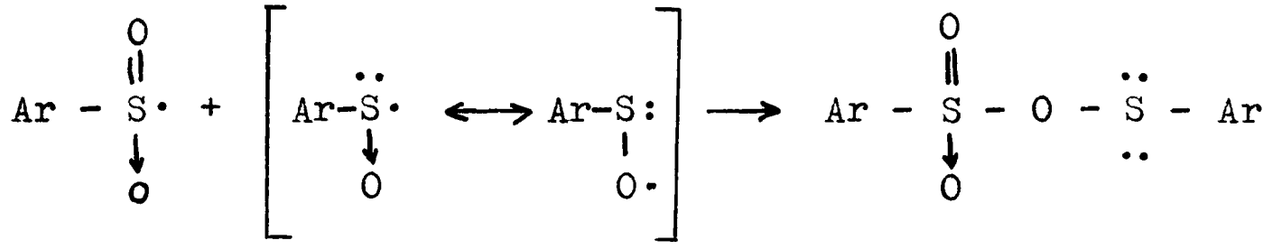
1.2.4 - Other processes

Some reactions had been explained by paths involving free sulphonyl radicals. An interesting result was that of Kice and Pawlowsky [68]. They showed that aromatic sulphinyl sulphones, $ArSO_2SOAr$, undergo rapid decomposition at 50°C:



The rate of decomposition is little affected by either solvent or the nature of the aryl group.

In an inert solvent these radicals then recombine yielding the sulphenyl sulphonate:



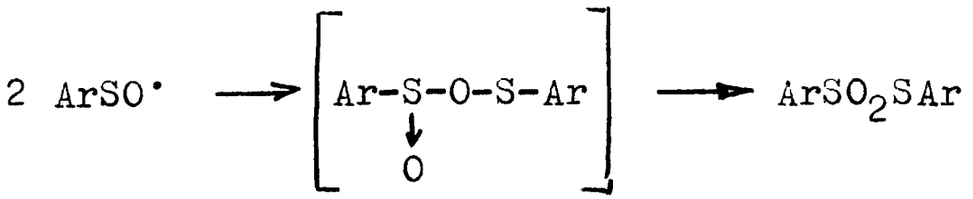
When the sulphinyl sulphones were allowed to decompose in the presence of 1,1-diphenylethylene, sulphonyl radicals were trapped:

$$ArSO_2SOAr \longrightarrow ArSO_2\cdot + ArSO\cdot$$

$$ArSO_2\cdot + Ph_2C{=}CH_2 \longrightarrow Ph_2\dot{C} - CH_2{-}SO_2Ar$$

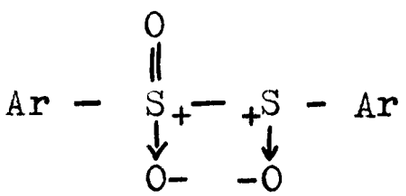
$$Ph_2\dot{C}{-}CH_2{-}SO_2Ar + R\cdot \longrightarrow Ph_2C{=}CH{-}SO_2Ar + RH$$

but sulphinyl radicals were too inactive to add to the olefine:



and dimerization occurred.

The explanation of the easy decomposition of sulphinyl sulphones was based on the repulsion of two electron-deficient sulphur atoms:



and also by assuming that radicals ArSO· are species of significantly lower energy than radicals $ArSO_2$·. This allowed us to understand the relative stability of disulphones, sulphinyl sulphones and disulphoxides:

$$ArSO_2 \div SO_2Ar \ll ArSO_2 \div SOAr \ll ArSO \div SOAr$$

Another interesting compound that decomposes in benzene or aromatic solvents to give sulphonyl radicals is phenyl phenylsulphonyldi-imide, $Ph-N_2-SO_2Ph$. The decomposition of this compound was studied by Rosenthal and Overberger [69] and they concluded that its decomposition involved a preliminary split into phenylazo and phenylsulphonyl radicals:

$$Ph-N_2 - SO_2Ph \longrightarrow PhN_2\cdot + PhSO_2\cdot$$

The phenyl-azo radical then loss nitrogen

$$PhN_2\cdot \longrightarrow Ph\cdot + N_2$$

The products of reaction with aromatic solvents may then arise by the attack of these radicals on the solvent:

$$R\cdot + PhH \longrightarrow R\text{-}Ph + H\cdot$$

$(R=Ph\cdot,\ PhSO_2\cdot \text{ or } PhN_2\cdot)$

by induced decomposition:

$$Ph\cdot + Ph\text{-}N_2\text{-}SO_2Ph \longrightarrow PhN_2Ph + PhSO_2\cdot$$

$$\text{or } PhSO_2Ph + PhN_2\cdot$$

by radical combination:

$$2R\cdot \longrightarrow R\text{-}R$$

or by radical attack on products:

$$R\cdot + PhN_2Ph \longrightarrow R\text{-}C_6H_4\text{-}N_2Ph$$

A.Lindsay [30] attempted to react sulphur dioxide with phenyl radicals produced by the thermal decomposition of phenyl phenylsulphonyl di-imide as a way of having a higher concentration of phenylsulphonyl radicals:

$$Ph\text{-}N_2\text{-}SO_2Ph \longrightarrow Ph\cdot + N_2 + PhSO_2\cdot \xrightarrow{SO_2} 2PhSO_2\cdot$$

but the attempt was unsuccessful.

Methylsulphonyl radicals, $CH_3SO_2^{\cdot}$, are thought to be formed from decomposition of bis-methylsulphonyl-isonitroso-methane, $(MeSO_2)_2C{=}NOH$, since the dimer dimethyldisulphone, $MeSO_2SO_2Me$, was one of the reaction products [70] :

$$(MeSO_2)_2C{=}NOH \longrightarrow MeSO_2^{\cdot} + MeSO_2{-}\dot{C}{=}NOH$$

$$2MeSO_2^{\cdot} \longrightarrow MeSO_2SO_2Me$$

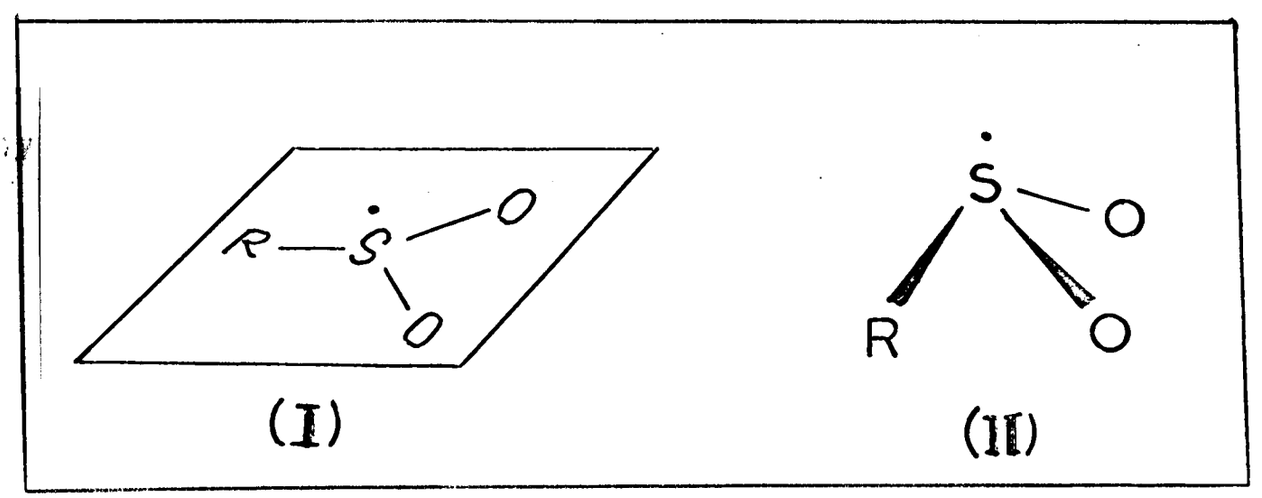
The reaction of dimethylsulphonyl-di-bromo-methane, $(MeSO_2)_2CBr_2$, with copper in boiling toluene [70] :

$$2(MeSO_2)_2CBr_2 \xrightarrow{Cu} [\,?\,] \xrightarrow{NH_3} (MeSO_2)_3CH \quad (20\%)$$

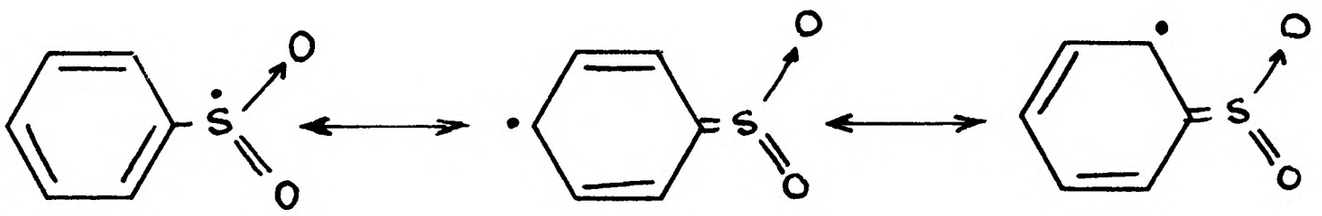
is supposed to be a radical reaction in which a free methyl-sulphonyl radical operates.

1.3 - Stereochemistry of sulphonyl radicals.

Sulphonyl radicals may have a planar (I) or a pyramidal (II) structure:

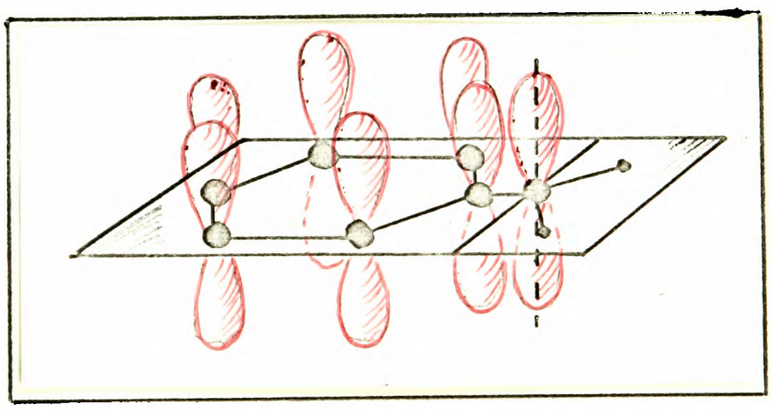


When R=Aryl, if radicals are planar it should be expected delocalization of the odd electron over the aromatic system:



If such radical was analysed by e.s.r. spectroscopy, the spectrum should show hyperfine splittings due to <u>orto</u>, <u>meta</u> and <u>para</u> hydrogens.

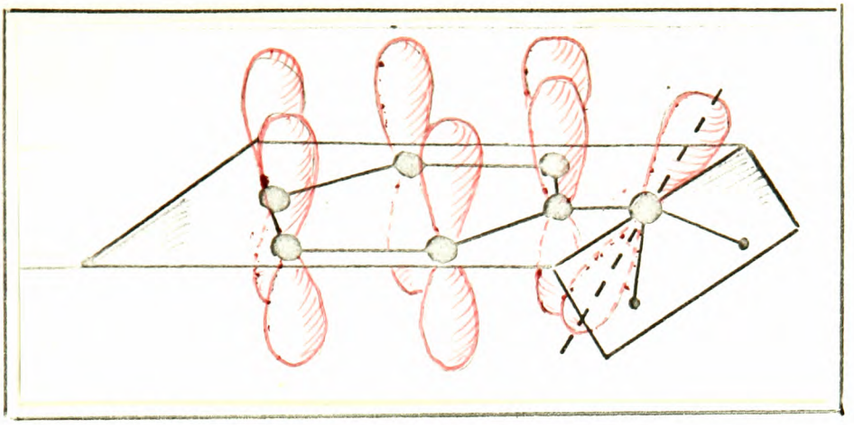
This had been obtained in radicals such as phenoxy [71] $Ph-\dot{O}$, and benzyl [72], $Ph-\dot{C}H_2$. The unpaired electron in these systems is oriented so as to hybridise completely with the aromatic π system:



The hyperfine splitting constants for hydrogens are as follows:

para > ortho > metha

If the radical is not planar (or near planar) but pyramidal (II) hybridisation with the aromatic π system is avoided:



and the e.s.r. spectrum should show interaction mostly with ortho hydrogens.

Miss McMillan and W.A.Waters [38] have studied the e.s.r. spectra of several arylsulphonyl radicals obtained by the oxidation of arylsulphinic acids with ceric sulphate in a flow system [73]. They found that spectra of those radicals showed only small hyperfine splittings; the coupling with aromatic ortho hydrogens was greater than with para hydrogen. They concluded that the radicals studied have a significant degree of σ character and a pyramidal structure was proposed.

The $(SO_3^{\cdot})^-$ radical-anion was studied in irradiated crystals by Whiffen et al. [74] and a definitely pyramidal shape was proposed.

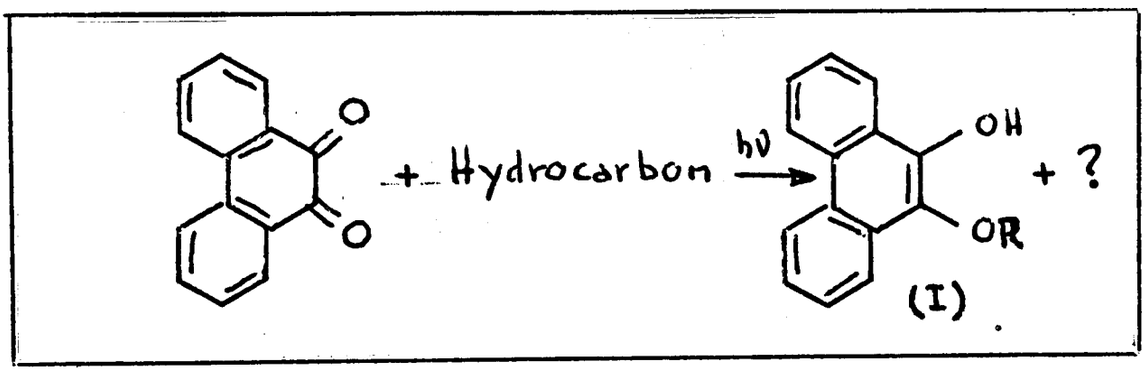
No other mention about the stereochemistry of sulphonyl radicals have been found in the literature.

2. Radical reactions and reactivity of quinones.

2.1. Free radical reactions of quinones.

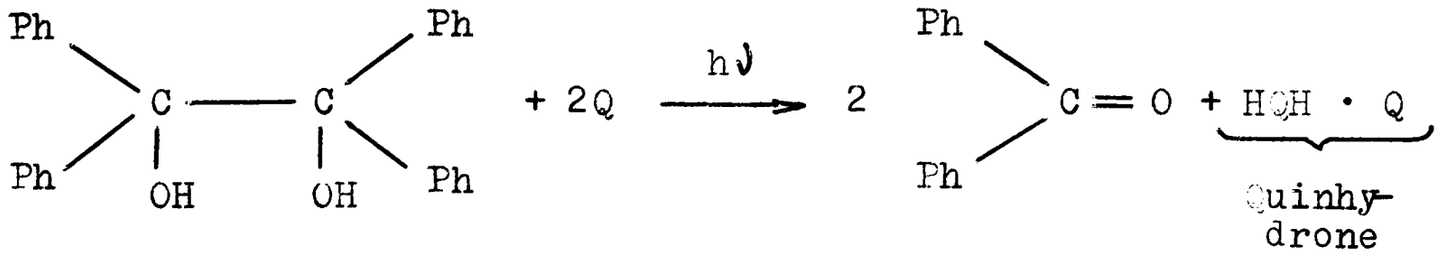
Photochemical dehydrogenations by quinones have been reported for many years. Ethanol and isopropylalcohol were converted to the respective aldehydes when exposed to the sunlight in the presence of p-benzoquinone.[76] Methanol was similarly oxidised to formaldehyde.[77]

Benrath and Von Meyer[78] showed that, on prolonged exposure to sunlight, phenanthraquinone reacted with o- and p-xylenes, and with cumene to give their phenanthrenediol monoether (I):

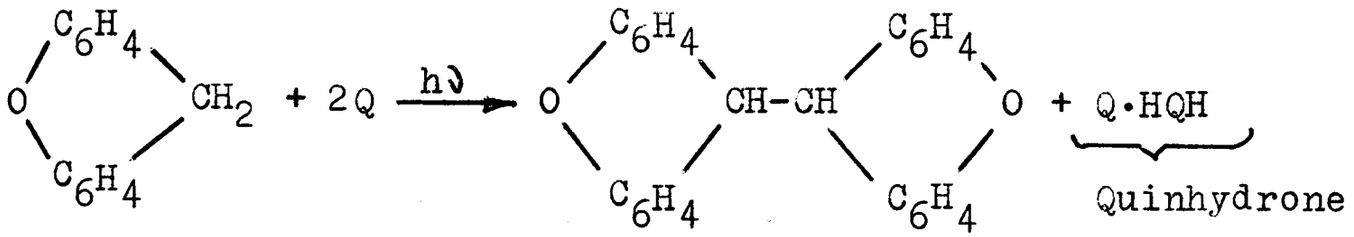


From the reactions with m-xylene, mesitylene and p-cumene they isolated only phenanthrenequinhydrone. The nature of the products derived from the hydrocarbons was not determined.

Diaryl ketones were obtained by photochemical dehydrogenation of aromatic pinacols:[79]



Methane derivatives (xanthene, diphenyl methane and others) were converted to the respective dimeric ethane derivatives when exposed to sunlight in the presence of quinones:[79]



xanthene dixanthyl

Waters[80] suggested that the high temperature thermal dehydrogenation of aromatic hydrocarbons by means of quinones involved a hydrogen atom transfer as shown below:



This view was supported by Dost and Van Nes.[171]

Moore and Waters[81] obtained further support for this mechanism by studying corresponding reactions at room temperature. The reactions of phenanthraquinone, chloranil and 1,4-naphtha-

quinone with p-xylene, cumene and tetralin were studied. under u.v. light in the absence of air. Dimeric hydrocarbons, R-R($MeC_6H_4CH_2CH_2C_6H_4Me$, and $PhCMe_2CMe_2Ph$) were isolated providing evidence for the formation of the free radicals, R·:

$$MeC_6H_4Me \xrightarrow{Q} MeC_6H_4CH_2\cdot$$

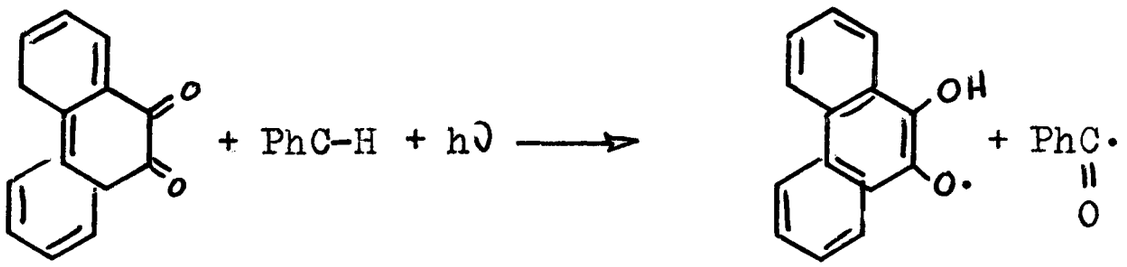
$$PhCHMe_2 \xrightarrow{Q} \underbrace{Ph\dot{C}Me_2}_{R\cdot}$$

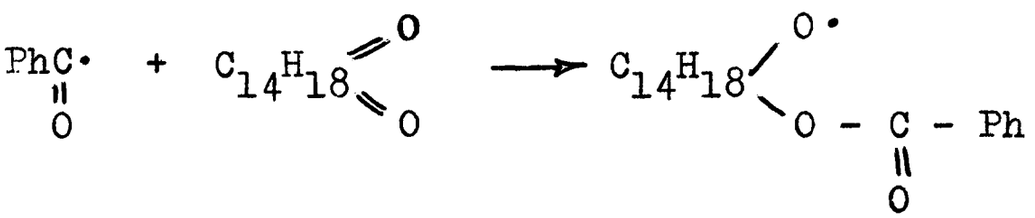
Quinhydrones were formed and regarded as the dimers of the semiquinone radicals, HQ·. p-Xylene gave a cross combination product, R-Q-H.

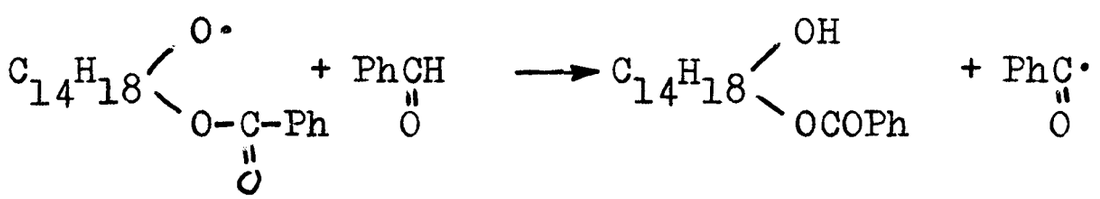
Other hydrocarbon radicals, which easily yield a stable olefin by the loss of a hydrogen atom, gave no cross-combination products:

$$Ph\dot{C}(Me)-Me + \cdot QH \longrightarrow Ph-C(Me)=CH_2 + H-Q-H$$

The photochemical reaction of phenanthraquinone and benzaldehyde was studied by Moore and Waters.[81] They suggested a chain reaction promoted by the activation of the quinone to a diradical capable of abstracting a hydrogen atom from the aldehyde molecule:





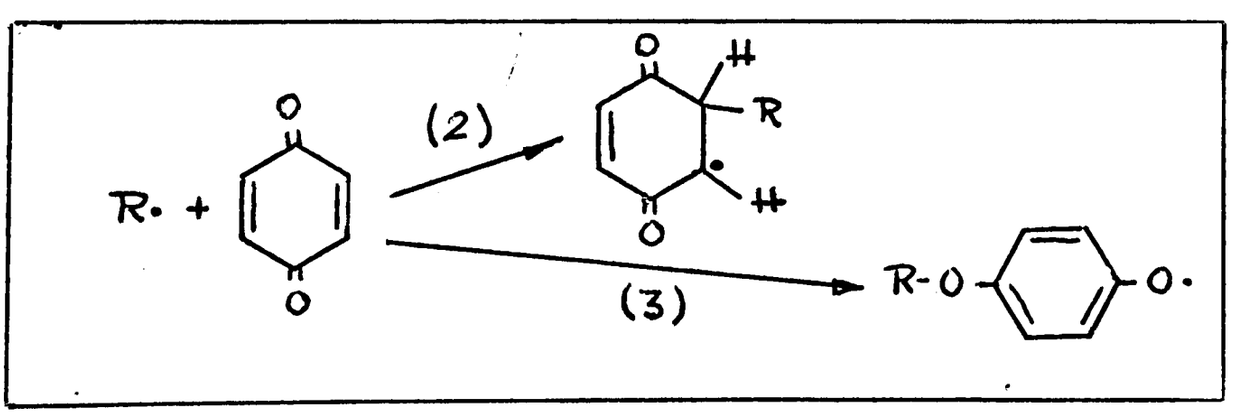


Q uinones possess pronounced reactivity toward free radicals, and it is this property which accounts for their inhibitory action on many chain processes.

It is generally accepted that free radicals react with quinones by an addition reaction (1)

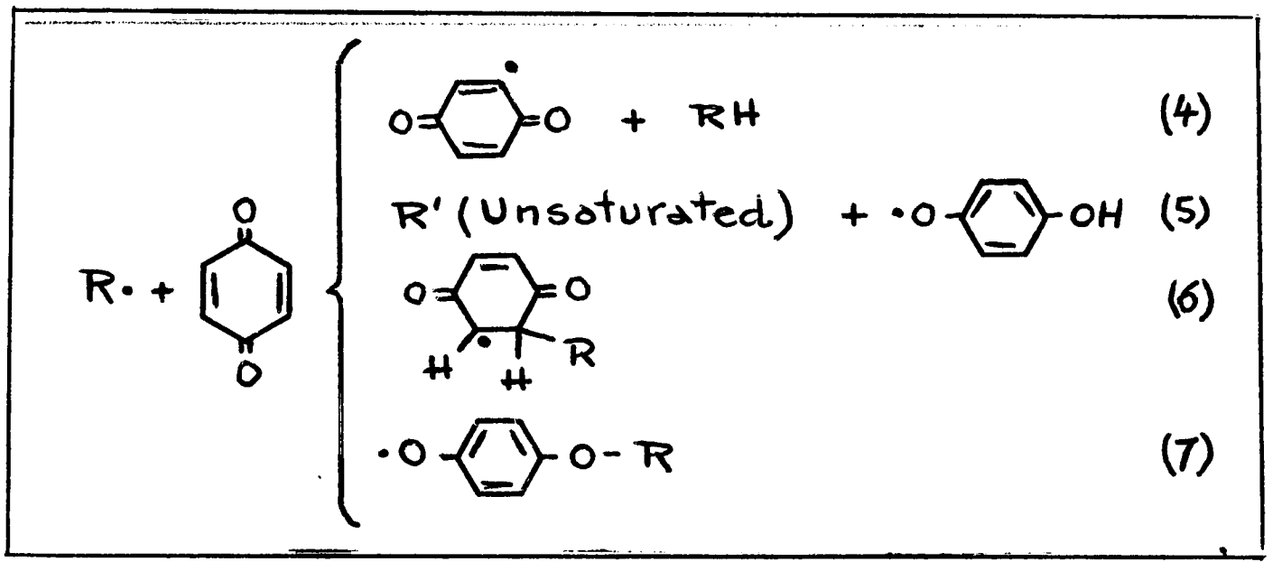
$$R\cdot + Q \longrightarrow R\text{-}Q\cdot \qquad (1)$$

Some investigators suggested the nuclear addition process (2) while others suggested that the attacking radicals might add to the oxygen (3):

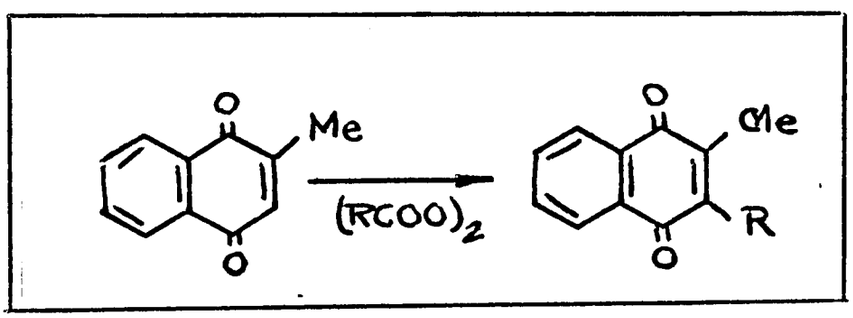


These conclusions are based on determination of the structure of the final products.

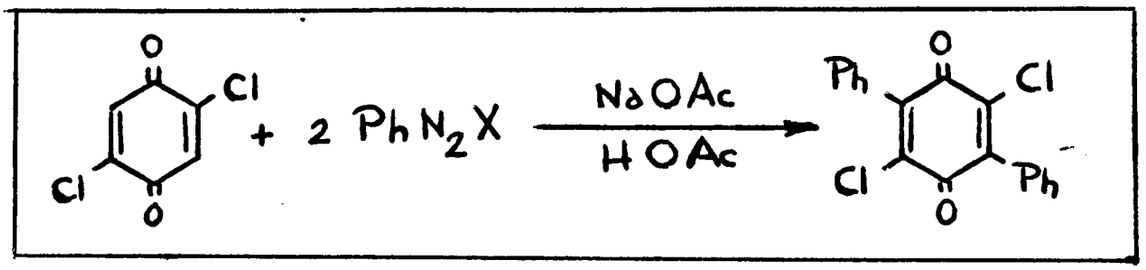
At least four initial reactions are possible between free radicals and quinones:[82]



Fieser and Oxford[83] found that p-benzoquinone and 1,4-naphthaquinone, which have a free position in the quinonoid ring, are alkylated by diacyl peroxides as shown below:

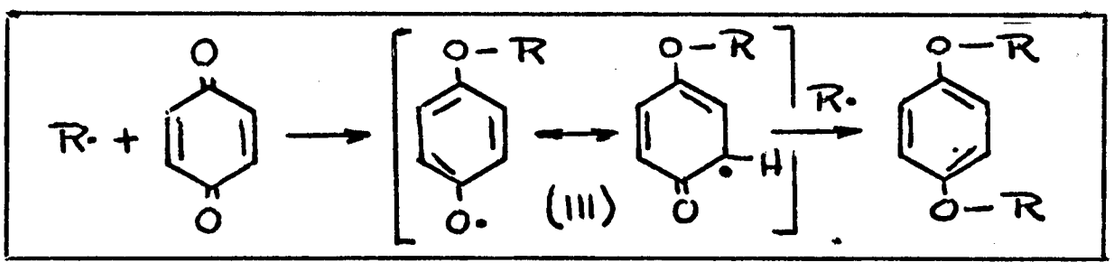


A similar nuclear attack was obtained when aromatic diazo compounds reacted with p-benzoquinones in the presence of sodium acetate and acetic acid:[84]

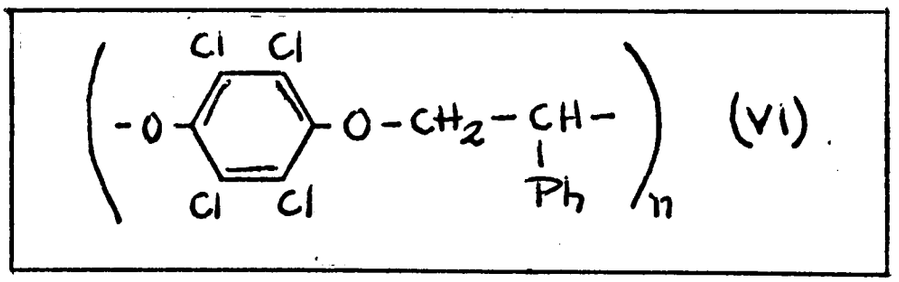


Cohen[85] has examined the polymerization of styrene in the presence of benzoyl peroxide and quinones. He found that, in the inhibition reaction, the quinone reacted with two radicals or growing chains and was converted to either a very weak retarder, or partly to inert products, and partly to products which may retard the subsequent polymerization.

The suggested formation of inert products is shown below:



Breitenbach and Renner[86] obtained a styrene-chloranil copolymer shown to have structure (VI) which indicated radical



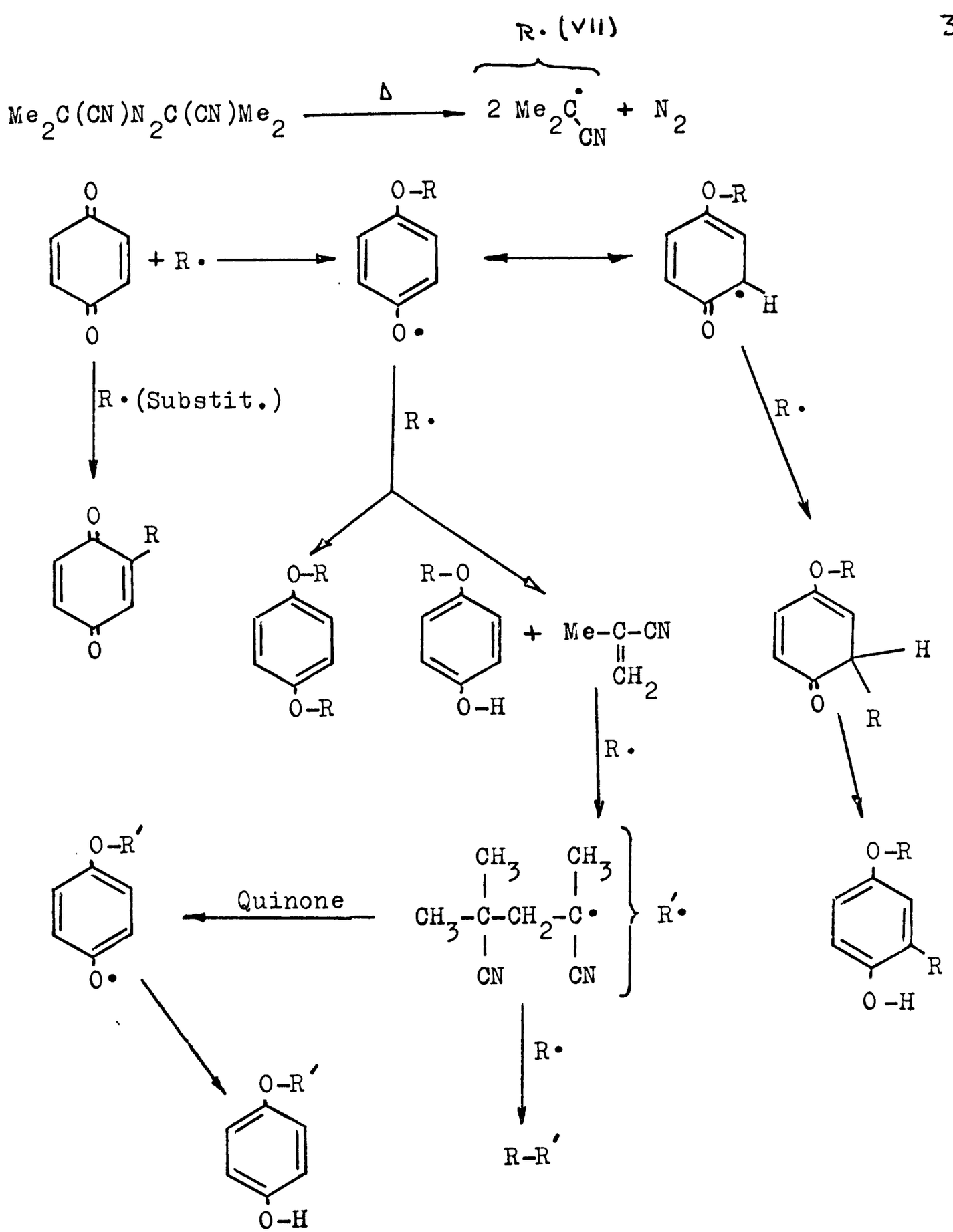
attack on the quinone oxygen.

Bickel and Waters[87] studied the decomposition of αα'-azoisobutyronitrile in the presence of p-benzoquinone and chloranil. Evidence was obtained for the attack by 2-cyano-2-propyl radicals on the oxygen of these quinones.

Phenolic products were formed by disproportionation reactions.

Similar results were obtained with dimethyl-αα'-azoisobutyrate, $Me_2C(CO_2Me)N_2C(CO_2Me)Me_2$.

The work of Bickel and Waters was continued by Aparicio and Waters[88] who studied the reaction of 2-cyano-2-propyl radicals (VII) with a series of quinones. The amount of dimer, $Me_2C(CN)C(CN)Me_2$, obtained in these reactions was taken as an indication of the reactivity of the various quinones towards radicals (VII). The mechanism proposed by Bickel and Waters was extended to a more general form:


R· (VII)
Me2C(CN)N2C(CN)Me2
Δ
2 Me2C·CN + N2
+ R·
O-R
O·
H
R·(Substit.)
R·
R·
R
O-R
R-O
O-H
+ Me-C-CN
CH2
H
R
O-R'
Quinone
CH3
CH3
CH3-C-CH2-C·
CN
CN
R'·
O-H
R-R'

The decomposition of αα'-azo-isobutyronitrile in the presence of hydroquinone gave a considerably higher yield of quinol mono-ether, R-Q -H. This gave an indication that quinol supplied hydrogen atoms to the semiquinone radical R-Q·.

$$R\cdot + Q \longrightarrow R - Q\cdot$$

$$R - Q\cdot + H\text{-}Q\text{ -}H \longrightarrow R\text{-}Q\text{-}H + H\text{-}Q\cdot$$

The reactivity of the quinones toward radicals (VII) was related to the normal redox potentials of the various quinones (p.44).

A kinetic study of the autoxidation of benzaldehyde was made by Dunn, Waters and Wickham-Jones [89].

The retarding effects of diphenoquinone and the respective quinol upon the benzoyl peroxide catalysed autoxidation were explained by assuming that the quinone acted as a chain terminating agent by combining with free benzoyl radicals:

$$PhCO\cdot + Q \longrightarrow PhCO\text{-}Q\cdot$$

$$PhCO\text{-}Q\cdot + Ph\text{-}\dot{C}O \longrightarrow PhCO\text{-}Q\text{-}COPh \quad (VIII)$$

An attempt to isolate the reaction products of this reaction [90] gave the dibenzoate (VIII) in a yield of only 5%.

9.2. The reactivity of quinones towards free radicals

The inhibition power of quinones in chain polymerization of vinyl monomers is an adequate measure of the reactivity of these compounds towards free radicals. The inhibition power can be measured by studying the kinetics of a chain reaction inhibited by quinones. If the quinone, Q, and the monomer, M, compete for the growing radical chain (R):

$$R + Q \xrightarrow{k_1} \text{Inactive products}$$

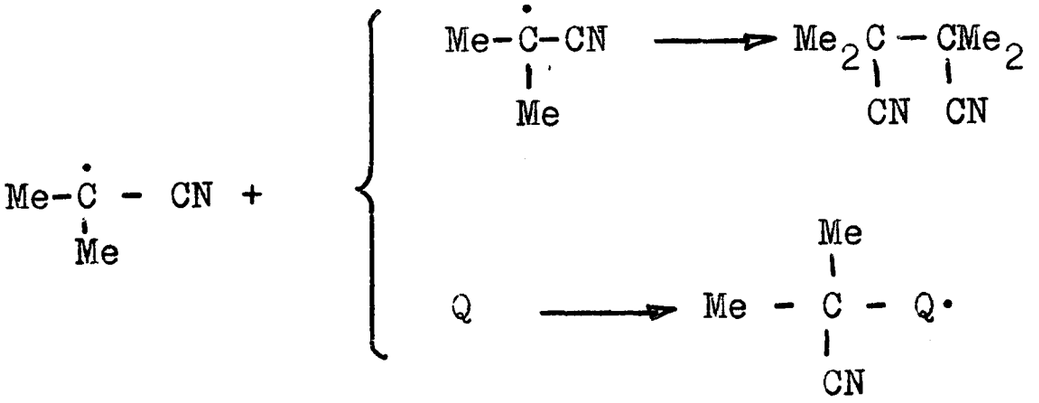
$$R + M \xrightarrow{k_2} R'\cdot$$

the values of k_1/k_2 for a series of quinones are an indication of the relative reactivity of the quinones. This technique was used by Breitenbach,[91] Bartlett et al.[92] and Kice[93]. Results relative to this paper are summarised below.

	Relative reactivity towards		
	Methyl radical	Styryl radical	Acetate radical
p-Benzoquinone	1.00	1.00	1.00
Toluquinone	0.68	0.37	-
p-xyloquinone	0.43	0.076	-
Duroquinone	0.05	0.0012	0.08
Chloranil	0.02	1.67	3.08

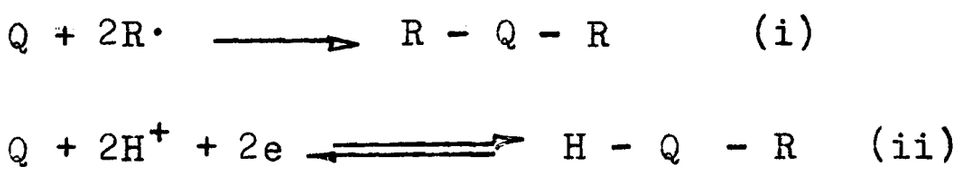
The reaction of 2-cyano-2-propyl radicals, MeCCN, with

several quinones was studied by Aparicio and Waters[88]. The reactivity of the quinones towards these radicals was measured from the amount of dimer, tetramethylsuccinonitrile, $Me_2C(CN)C(CN)Me_2$, formed in the reactions:



They found that the reactivity was dependent on the redox potential of the quinones. Steric effects were considered important in quinones with bulky groups adjacent to the oxygen atoms.

The irreversible reaction (i) and equilibrium (ii)



were considered to be similar in that they were both additions to the oxygen atoms of quinones, and both involved energy changes from the quinonoid to the benzenoid form. The driving force of both reactions was thought to be the gain in resonance energy in going to the aromatic QH_2 system from the

quinonoid Q-molecule, as was suggested many years ago by Branch and Calvin.[94]

As a result of quantum-mechanical calculations[95] this suggestion has been proved to be correct. A linear relationship was found to exist between the redox potential E_o of unsubstituted quinones and the difference in resonance energy between Q and H-Q-H.[95] This is a strong indication that in a series of unsubstituted quinones, the driving force for the reaction

$$2R\cdot + Q \longrightarrow R - Q - R$$

may be connected with the redox potential.

Aparicio and Waters[88] found this to be true in cases where the steric factor was absent. These steric factors can affect the rate of irreversible processes such as (i) but cannot affect the equilibrium constants of a reversible process such as (ii). Free radicals are considerably bulkier than are hydrogen atoms.

Rembaum and Szwarc[96] criticised the relating of reactivities of quinones to redox potentials, but agree that redox potentials and methyl affinities of quinones exhibited a parallel relationship.

The results of Aparicio and Waters are summarised in the following table:

Quinone	Yield: Di-ether (%)	Yield: Mono-ether (%)	Yield: Dimer (%)	Redox potential of quinone (volts)
p-Benzoquinones:				
2,5-diacetobenzoquinone	32	23	18.0	-
Benzoquinone	-	56	25.7	0.711
Toluquinone	46	31	26.0	0.653
m-xyloquinone	41	8.6	37.6	0.600
Chloranil	67	17	44.1	0.703
p-xyloquinone	35	5.9	47.5	0.597
Thymoquinone	32	1.0	49.2	0.589
2,5-Diethoxybenzoquinone	-	2.5	57.8	0.480
2,5-Di-tert-butylbenzo-quinone	100% of quinone recovered			0.554
Duroquinone	93% " " recovered		67	0.466
1,4-Naphthaquinones				
2,3-dichloronaphthaquinone	-	-	66.8	0.340*
Naphthaquinone	-	-	47.0	0.576*
Phenanthraquinone	-	-	49.0	0.460*
Anthraquinone	-	-	78.6	0.154*

* Rembaum and Szwarc [96].

The addition of methyl radicals to a series of quinones was investigated by Rembaum and Szwarc.[96] The relative reactivities were measured using the concept of "methyl affinity":

Methyl radicals, generated by the decomposition of acetyl peroxide, react with a solvent R-H with the liberation of methane

$$CH_3\cdot + R\text{-}H \xrightarrow{k_a} CH_4 + R\cdot \qquad (a)$$

If a quinone Q is added to the solvent R-H, the amount of methane evolved decreases, this is due to the reaction

$$CH_3\cdot + Q \xrightarrow{k_b} \dot{Q}CH_3 \qquad (b)$$

The ratio k_b/k_a is a measure of the reactivity of the quinone, Q, towards methyl radicals, and can be calculated from analysis of the gaseous products.

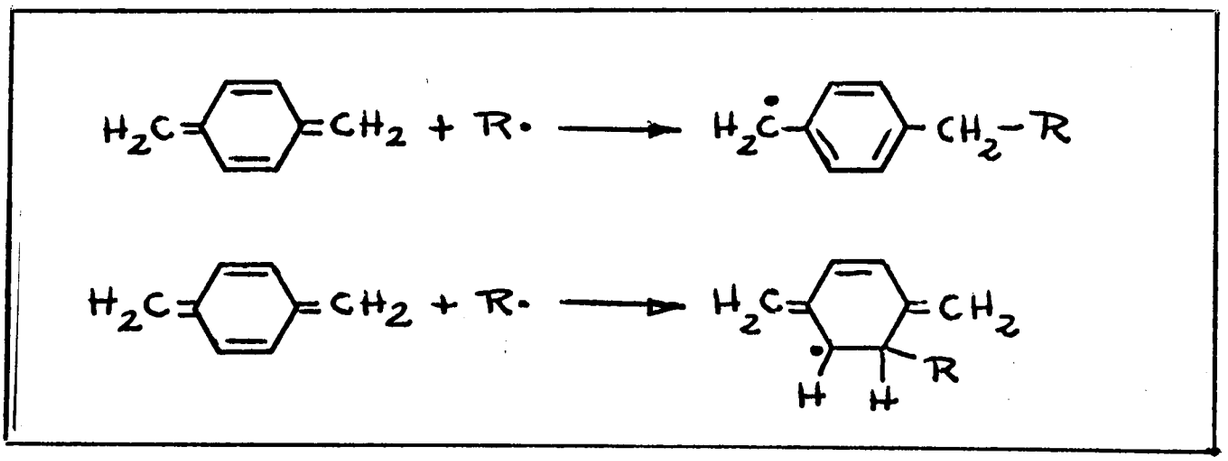
The reactions were carried out with toluene as R-H and the results are summarised below.

They suggested that the decrease in reactivity of quinones reflected the decrease in the "olefinic" character of the respective C=C double bonds. The initial attack by methyl radicals was suggested tentatively to be on the C=C double bond. These investigators were unable to isolate the final products of the reaction.

Quinone	Methyl affinity (p-benzo quinone = 1)	Quinone Redox potential (in EtOH) (volts)
p-Benzoquinone	1.00	0.715
Toluqinone	0.68	0.656
p-x yloquinone	0.41	0.598
Duroquinone	0.052	0.466
2-Methoxybenzoquinone	0.52	-
2-Chlorobenzoquinone	1.71	0.736
2,5-Dichlorobenzo quinone	2.50	0.740
2,6-Dichlorobenzoquinone	2.54	0.748
Chloranil	0.02	0.699
1,4-Naphthaquinone	0.32	0.484
2-Methyl-1,4-naphthaquinone	0.22	0.408
2,7-Dimethyl-1,4-naphthaquinone	0.27	0.407
2,3-Dimethyl-1,4-naphthaquinone	0.036	0.340
2,3-Dichloro-1,4-naphthaquinone	0.06	-
1,2-Naphthaquinone	0.225	0.576
Phenanthraquinone	0.046	0.460
2-t-Butylanthraquinone	0.006	-
A nthraquinone	not measureable	0.154

Fueno and Furukawa[97] computed the localization energies of several quinones both at the positions of oxygen and of the nuclear carbon atoms.

They assumed that the activation energy of an addition reaction parallelled the magnitude of the decrement in the π-electron energy, ΔE_{π}, on going from the parent compound to the addition product. Simple MO method was applied to the π-electron systems of the parent quinones and the addition products. The term ΔE_{π} obtained is equivalent to the localization energy of quinones at the position of methyl radical addition. The π-electron energies of quinones and the resulting adducts were approximated using those of the dimethide analogues of quinones and those of the related aromatic hydrocarbons. (First method of approximation):



The second method used (Second method of approximation) was based on the assumption that the Coulomb integral for the

oxygen and the resonance integral for the carbonyl π - bond are equal to $\alpha+2\beta$ and $\sqrt{2}\beta$ respectively.[99] α is the Coulomb integral for a carbon atom in benzene and β is the resonance integral for a π-bond in benzene. Their results are summarized as follows:

Quinone	Szwarc methyl affinity: r	log r/m	Position	1st Ap.	2nd Ap.
p-Benzoquinone	$15,200^{+}_{-}300$	3.88	1',4'	1.20	2.53
			2,3,4,5	2.20	-
1,4-Naphtha-quinone	$4,900^{+}_{-}230$	3.99	1',4'	1.31	2.64
			2,3	2.17	-
			5,8	2.39	-
			6,7	2.46	-
1,2-Naphtha-quinone	$3,400^{+}_{-}350$	3.53	1'	1.37	-
			2'	1.30	2.58
			4	2.18	-
9,10-Phenanthra-quinone	$700^{+}_{-}20$	2.54	9',10'	1.46	2.81
			1,8	2.43	-
			4,5	2.42	-
9,10-Anthra-quinone	-	-	9',10'	1.45	2.80
			1,4,5,8	2.38	-
			2,3,6,7	2.45	-

Notes: All the energies are given in units of $-\beta$.

m is the number of equivalent oxygens.

These results showed that a linear correlation holds between log r/m and ΔE_{π} , for the position of oxygen atoms. On the other hand, no relation seems to exist between the methyl affinity and the ΔE_{π} for the most reactive nuclear carbon atom.

From these results they concluded that ΔE_{π} for the oxygen atoms of quinones seems to be a satisfactory measure for their radical affinity. Thus, it was suggested that an attacking radical might first add to the oxygen atom of quinones, at least in the case of the four quinones studied. These results showed that Aparicio and Waters[88] were right and not Szwarc.[96]

3. A brief note on the free radical addition to olefins

A great number of compounds react with olefins by adding across the double bond as shown below:

$$A\text{-}B + RCH{=}CHR' \longrightarrow \underset{\displaystyle A}{\overset{\displaystyle |}{RCH}} - \underset{\displaystyle B}{\overset{\displaystyle |}{CHR'}}$$

Many of these reactions are non-radical processes that proceed by the formation of intermediate carbonium ions or carbanions.

As the π-electrons of the C=C double bond are the most readily accessible, attack by electrophilic reagents is the characteristic reaction of such a system.

In special cases, i.e. acrylonitrile, the presence of electron-withdrawing groups causes the π-electrons to become less accessible and attack by an anion then becomes possible. In either case, i.e., attack by an anion or by a cation, there is a preferred tendency to form a secondary (I) rather than a primary ion (II):

$$A^+ + CH_2{=}CH\text{-}R \longrightarrow A\text{-}CH_2\text{-}\overset{+}{C}H\text{-}R \qquad (I)$$

$$A^+ + CH_2{=}CH\text{-}R \longrightarrow CH_2\text{-}\underset{\displaystyle A}{\overset{\displaystyle +}{\underset{\displaystyle |}{CH}}}\text{-}R \qquad (II)$$

This is the theoretical justification of the empirical Markownikov rule.[99]

In 1933, Kharasch and Mayo[100] showed that "abnormal"

addition products could be obtained in several cases under radical conditions (peroxide effect).

In 1937, Hey and Waters[101] and Kharasch, Engelmann and Mayo[102] explained the "abnormal" addition of hydrogen bromide to olefins by the following mechanism:

$$H\text{-}Br + \underbrace{\text{Peroxide radical (or oxygen)}}_{R} \longrightarrow Br\cdot + RH \qquad (1)$$

$$Br\cdot + CH_2{=}CH\text{-}CH_3 \longrightarrow Br\text{-}CH_2\text{-}\dot{C}H\text{-}CH_3 \qquad (2)$$

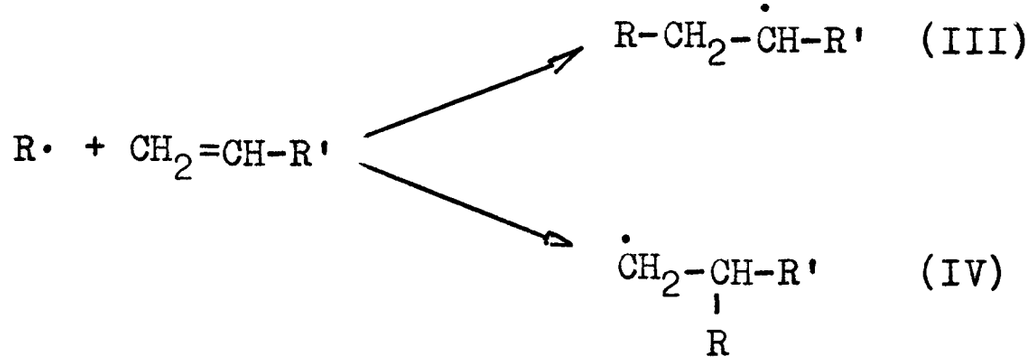
$$Br\text{-}CH_2\text{-}\dot{C}H\text{-}CH_3 + H\text{-}Br \longrightarrow BrCH_2\text{-}CH_2\text{-}CH_3 + Br\cdot \qquad (3)$$

i.e. atomic bromine formed in stage (1) adds on to the double bond (2) at the point of higher electron density, since it is an electrophilic reagent, to give the secondary radical. This radical abstracts hydrogen from a molecule of hydrogen bromide yielding a further bromine atom (3), etc.

This mechanism was confirmed by further studies that showed that the "abnormal" addition could be carried out in the absence of peroxides but in the presence of light, in the liquid or gas phase.[103]

The suggestion of Waters[104] concerning attack by an electrophilic halogen atom on the point of higher electronic density was seen not to be a general feature.[105] Mayo and Walling[106] suggested that the position of attack is determined by steric reasons, but this is a very special and limited factor.

Cadogan and Hey[107], and Mayo and Walling[108] supported the view that the position of attack by a radical R· depends on the relative stability of the two possible intermediate radicals (III) and (IV):



Haszeldine[109] showed that in olefins like $R\overset{\delta+}{-}CH=\overset{\delta-}{CH_2}$ (R=Me, Cl or F) and $R'\overset{\delta-}{-}CH=\overset{\delta+}{CH_2}$ (R'=CF_3, CN or CO_2Me) the polar nature of R or R' is not important in the position of attack by trifluoromethyl radicals.

Similar results were obtained by Henne and Nager[110] who showed that in the radical addition of hydrogen bromide, iodotrifluormethane and bromotrichloromethane to 3,3,3-trifluor-1-propene, radicals Br·, ·CF_3 and ·CCl_3 attack only the terminal carbon atom of the double bond:

$$CF_3\overset{\delta-}{-}CH=\overset{\delta+}{CH_2} \xrightarrow{R\cdot} CF_3-\dot{C}H-CH_2-R$$

R = ·Br, ·CF_3 or ·CCl_3

Tedder and Walton[111] studied recently the orientation of free radical addition to olefins. The reactions were carried out in the gas phase over a wide temperature range and the

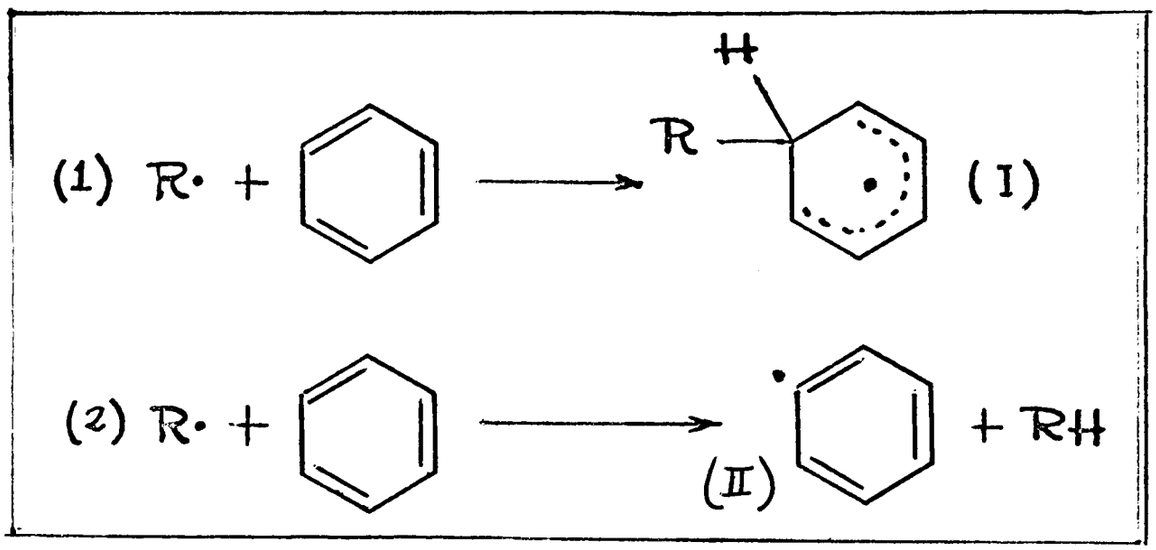
Arrhenius parameters for the rate of attack by trichloromethyl radicals at each end of four different olefins have been determined. It was found that the rate of addition is determined mainly by substituents on the carbon atom attacked and only to a small extent by the substituents attached to the carbon atom at which the unpaired electron is sited.

They suggested that the orientation of radical addition was determined principally by the relative strengths of the two possible bonds initially formed. They added that this must in general lead to exactly the same prediction of orientation as arguments about the stabilities of the products.

4. The reaction of free radicals with polynuclear aromatic hydrocarbons

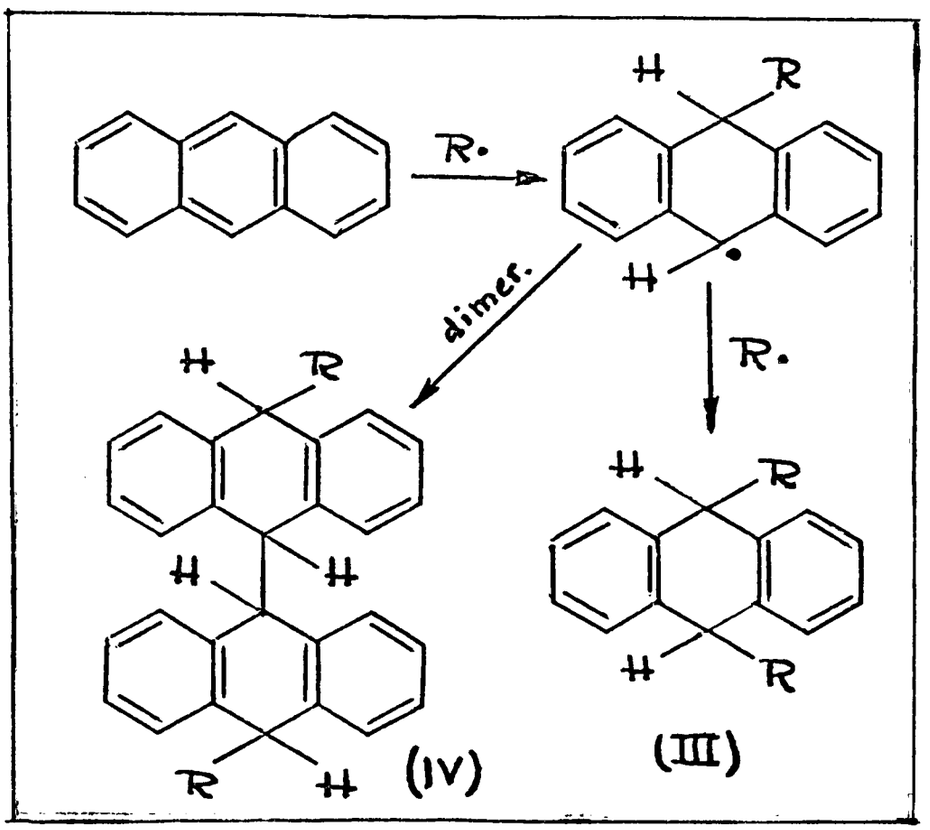
4.1. The mechanism of the reactions of free radicals with aromatic hydrocarbons

There are thought to be two different initial steps by which free radicals react with aromatic hydrocarbons. These steps are represented in equations (1) and (2):



The resulting radical (I) is a π-radical which is stabilised by the delocalisation of the unpaired electron throughout the ring system. Radical (II) is a localised σ-radical which is not stabilised by delocalisation.

Free radicals may react with aromatic hydrocarbons by an addition, the initial step of which is shown in equation (1). The isolation of products analogous to (III) and (IV) is a strong indication that the initial step is of the type described in equation (1)



Free radicals may also react with aromatic hydrocarbons by processes which result in substitution. This is shown in equations (3) - (5).

$$ArH + R\cdot \longrightarrow Ar\cdot + RH$$

$$Ar\cdot + R\cdot \longrightarrow Ar - R \qquad (3)$$

$$ArH + R\cdot \longrightarrow R - \dot{A}r - H$$

$$R - \dot{A}r - H + X \longrightarrow R - Ar + HX \qquad (4)$$

$$ArH + R\cdot \longrightarrow R - \dot{A}r - H \longrightarrow R - Ar + H\cdot$$

$$H\cdot + R\cdot \longrightarrow HR \qquad (5)$$

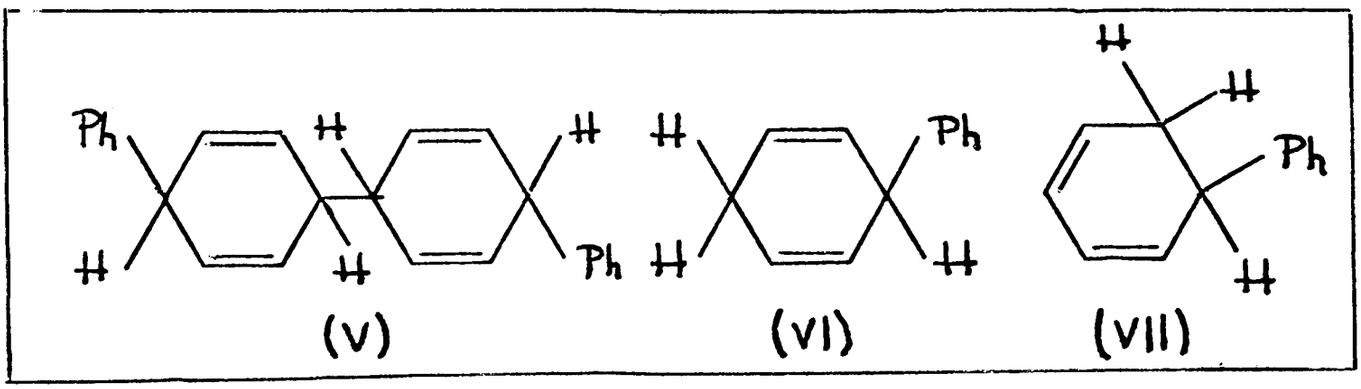
Homolytic aromatic substitution was reviewed by Sugood and Williams[112] and by Dermer and Edminson.[113] They concluded that except for specific cases (phenols, amines, methylbenzenes and anisole) the predominant mechanism for substitution was that shown in equation (5). Lewis and Symons[114] criticised this conclusion on the basis of several evidence. In fact the production of hydrogen atoms in the liquid phase is thermodynamically unlikely.[114] Also, phenylation of aromatic hydrocarbons with benzoyl peroxide in the absence of oxidising agents leads to formation of benzoic acid in high yield. The free hydrogen atom, produced in scheme (5) would be far too reactive to show such selectivity:

$$H\cdot + PhCOO\cdot \longrightarrow PhCOOH$$

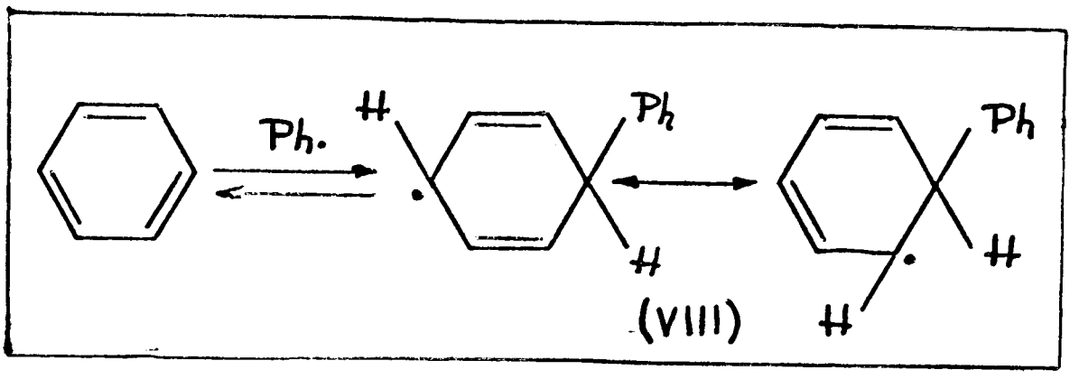
Rather, the benzoyloxy radical is thought to have abstracted hydrogen from an intermediate as shown in scheme (4).

Sheppard [115] studied the reaction of tritiobenzene and benzoyl peroxide. As they found no isotopic effect the C-H bond breaking cannot be part of the transition state. Similarly, in the reactions of p-nitrobenzoyl peroxide with benzene and toluene,[172] or in the reaction of benzoyl peroxide with dinitrotritio benzene[116] no isotopic effects were reported.

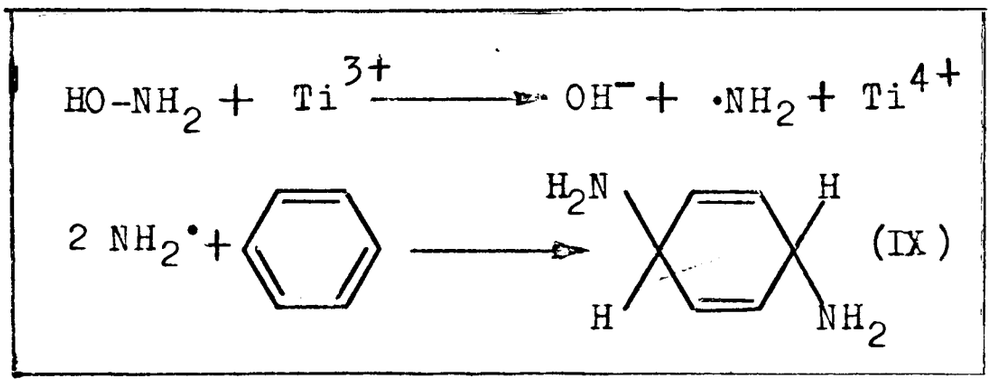
Addition reactions with benzene derivatives are less common than with hydrocarbons like anthracene. However addition of free radicals to benzene were reported by De Tar and Long.[117] They decomposed benzoyl peroxide in boiling benzene in relatively high dilution. Two significant new products were obtained: 1',4',1",4"-tetrahydro-p-quaterphenyl (V) and 1,4-dihydrobiphenyl (VI).



They also had evidence for 1,2-dihydrobiphenyl (VII). The formation of these products is a strong indication in favour of intermediate radicals (VIII):



Evidence for addition products (IX) in the reaction of amino radicals, $\cdot NH_2$, with benzene, toluene and cyclohexene was obtained by Waters et al.[118]



The hydrogen removal from a side chain often takes place (particularly with phenols and alkyl benzenes), sometimes to the exclusion of the nuclear substitution reaction,

$$R\cdot + R'CH_2Ph \longrightarrow RH + R'-\dot{C}H-Ph \qquad (X)$$

the intermediate radical (X) being stablised by resonance.

4.2. Reactions of free radicals with polynuclear aromatic hydrocarbons.

4.2.1. Reaction of benzoyl peroxide.

Davis, Hey and Williams[119] have reported that when benzoyl peroxide decomposes in naphthalene, dinaphthyls, phenylnaphthalenes and naphthyl benzoates are formed. The result can be interpreted either in terms of hydrogen abstraction in the α-position or in terms of the usual addition mechanism.

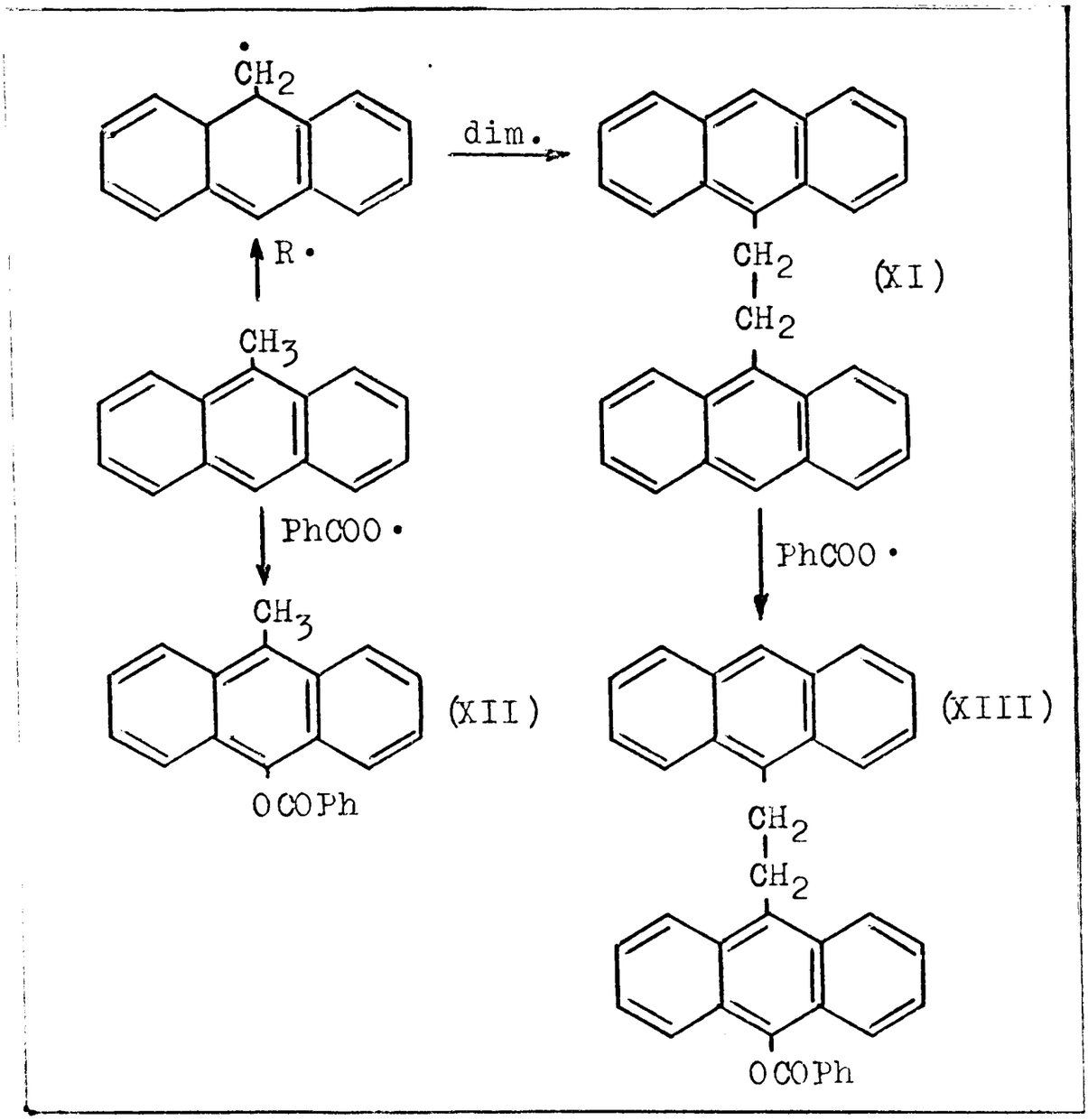
α-Halo- and α-nitronaphthalenes were substituted with benzoyloxy groups in the 2-, 4- and 5-position.[120]

The reaction of anthracene and other complex aromatic hydrocarbons with benzoyl peroxide was studied by Roitt and Waters.[121]

Attack on the aromatic hydrocarbon occurred before decomposition of the benzoyloxy radicals takes place. Anthracene gave 9-benzoyloxyanthracene and anthraquinone (oxidation product). Results are summarised as follows:

Aromatic hydrocarbon	Product
Anthracene	9-Benzoyloxyanthracene Anthraquinone
1,2-Benzanthracene	10-Benzoyloxy-1,2-benzanthracene
Phenanthrene	No reaction
1,2-5,6-di-Benzanthracene	No reaction
3,4-Benzopyrene	5-Benzoyloxy-3,4-benzopyrene
9-Methylanthracene	1,2-di-9'-Anthrylethane (XI) 9-Benzoyloxy-10-methylanthracene (XII) 1,9'-Anthryl-2(10-benzoyloxy-9-anthryl) ethane (XIII)

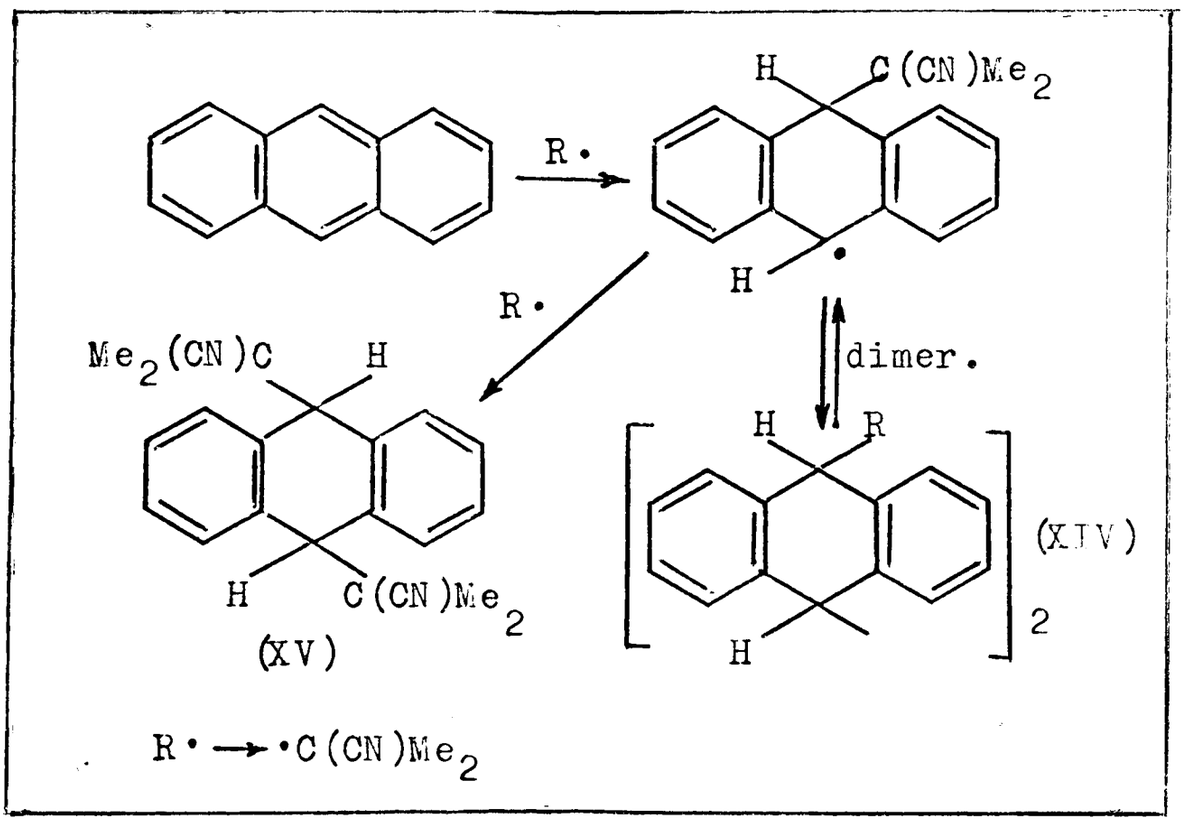
The reaction with 9-methylanthracene is of special interest as it was shown that hydrogen could be abstracted from the methyl group at a comparable rate to the substitution in the nucleus.



The relative order of reactivities, i.e. 3,4-benzopyrene $\gg$ anthracene, 1,2-benzanthracene $>$ 1,2-5,6-dibenzanthracene $>$ phenanthrene, follows the order of "free-valence numbers" at the reacting positions.

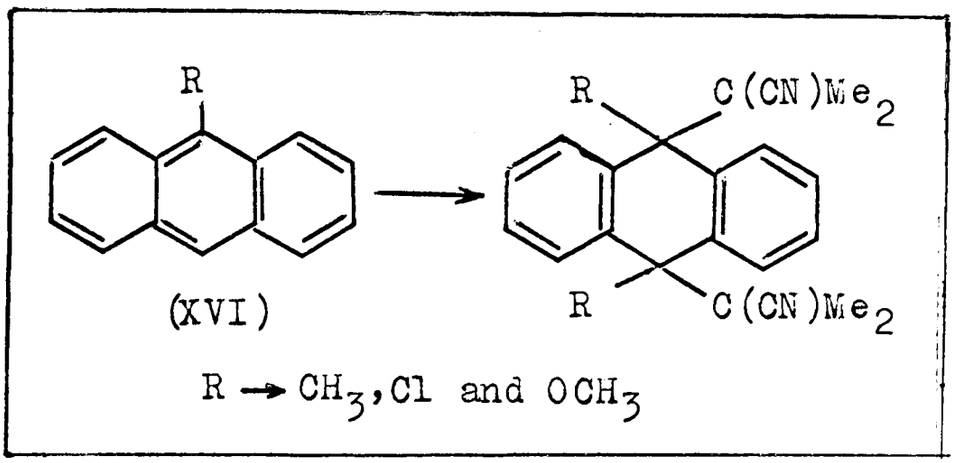
4.4.2. Reaction of 2-cyano-2-propyl radicals

Bickel and Kooyman[122] reported the reaction of 2-cyano-2-propyl radicals, generated by decomposition of α,α'-azo iso butyronitrile, with anthracene. 1,2-di-[9-(2-cyano-2-propyl)-10-anthryl]-ethane (XIV) and 9,10-di(2-cyano-2-propyl)-9,10-dihydroanthracene (XV) could be found:



Low temperature favours the formation of the dimer (XIV).

With 9-substituted anthracenes (XVI) no dimer was formed:



In the case of 9-methylanthracene no hydrogen abstraction from the side chain took place.

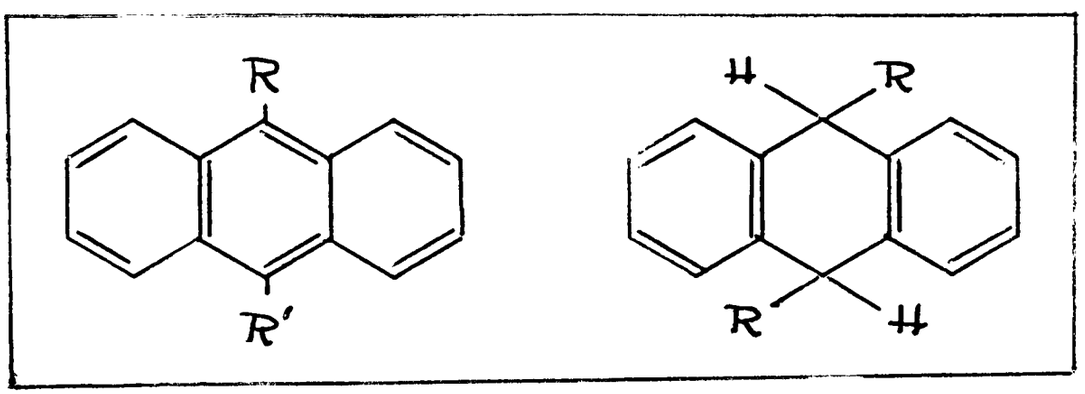
4.2.3. Reactions of thiyl radicals

Mikhailov and Blokhina [123] reported the reaction of thioacetic acid with some aromatic hydrocarbons in the presence of oxygen at room temperature.

This reaction was reviewed by Beckwith and Low [124] who repeated some of the experiments carried out by Mikhailov and Blokhina. They found that thioacetic acid and oxygen reacted with anthracene yielding 9,10-dihydro-9,10-di(acetylthio) anthracene (XVII) and 9-(acetylthio) anthracene (XVIII). Under similar conditions, thiobenzoic acid gave 9,10-dihydro-9,10-di(benzoylthio)anthracene (XIX) and 9-(benzoylthio)-anthracene (XX), Mercaptoacetic acid gave one isomer of

9,10-dihydro-9,10-di(carboxymethylthio)anthracene (XXI).

Toluene-ω-thiol, dimercaptopropanol and thiophenol did not react.

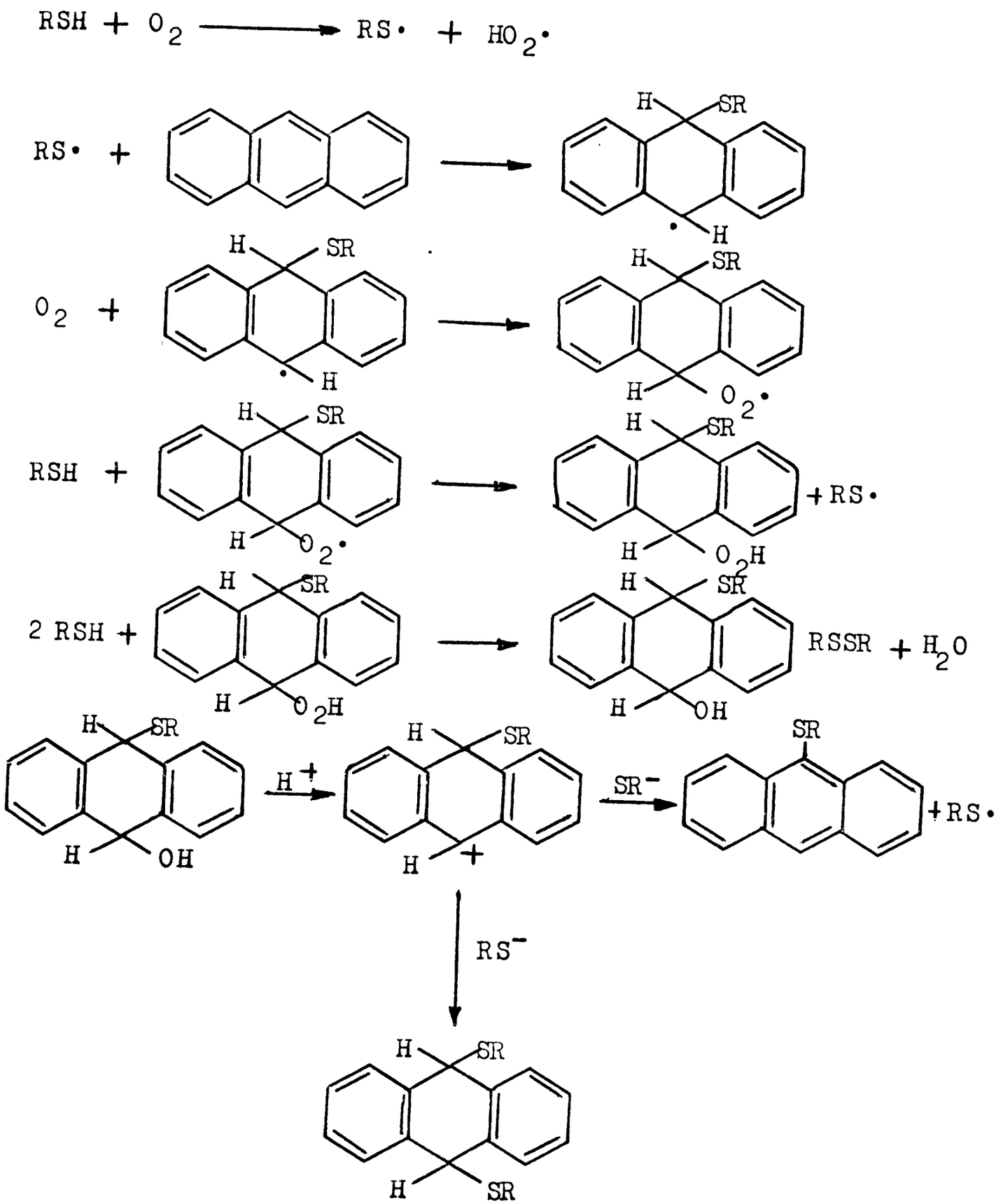


(XVIII) → R' = H; R = $SCOCH_3$ (XVII) → R = $SCOCH_3$

(XX) → R' = H; R = SCOPh (XIX) → R = SCOPh

(XXI) → R = SCH_2CO_2H

The following mechanism was proposed:


RSH + O2 → RS• + HO2•
RS• +
O2 +
RSH +
+RS•
2 RSH +
RSSR + H2O
H+
SR−
+RS•
RS−

In a second paper[125] Beckwith and Low reported the reaction of meso-substituted anthracenes with mercaptoacetic acid and oxygen. 3-Mercaptopropionic acid and S-(9-anthryl)-N-acethyl-l-cysteine reacted under similar conditions with anthracene and other polynuclear hydrocarbons.[126]

Beckwith and Low found no simple relationship between the ease with which polycyclic aromatic hydrocarbons reacted with thiols and oxygen and theoretical indices of reactivity. They stated that these indices are valid only when the initial combination of radicals with substrates is irreversible. When this step is reversible, the relative reactivities of different aromatic compounds, and of different positions within one molecule may be affected by such factors as steric hindrance and the relative thermodynamic stabilities of products.

Recently Beckwith and Low[127] reported the production of thiyl radicals by reaction of thiols with tert-butyl hydroperoxide in the presence of catalytic amounts of ferrous ion:

$$Fe^{2+} + {}^{t}Bu-O-O-H \longrightarrow Fe^{3+} + {}^{t}BuO\cdot + OH^{-}$$

$${}^{t}BuO\cdot + RSH \longrightarrow {}^{t}BuOH + RS\cdot$$

$$2RS\cdot \longrightarrow RSSR$$

$$2Fe^{3+} + 2RSH \longrightarrow 2Fe^{2+} + RSSR + 2H^{+}$$

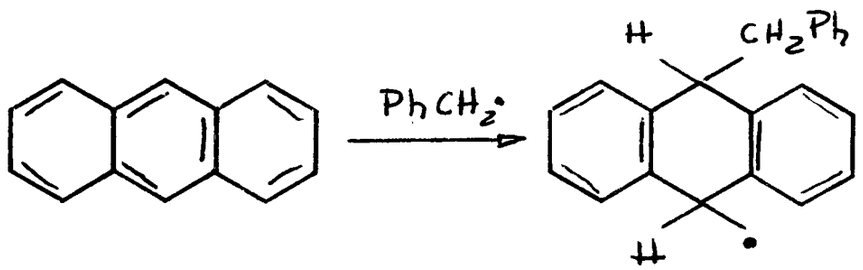
Thiyl radicals so produced undergo reactions with polycyclic aromatic hydrocarbons giving better yields than previous reactions, but yielding the same type of products.

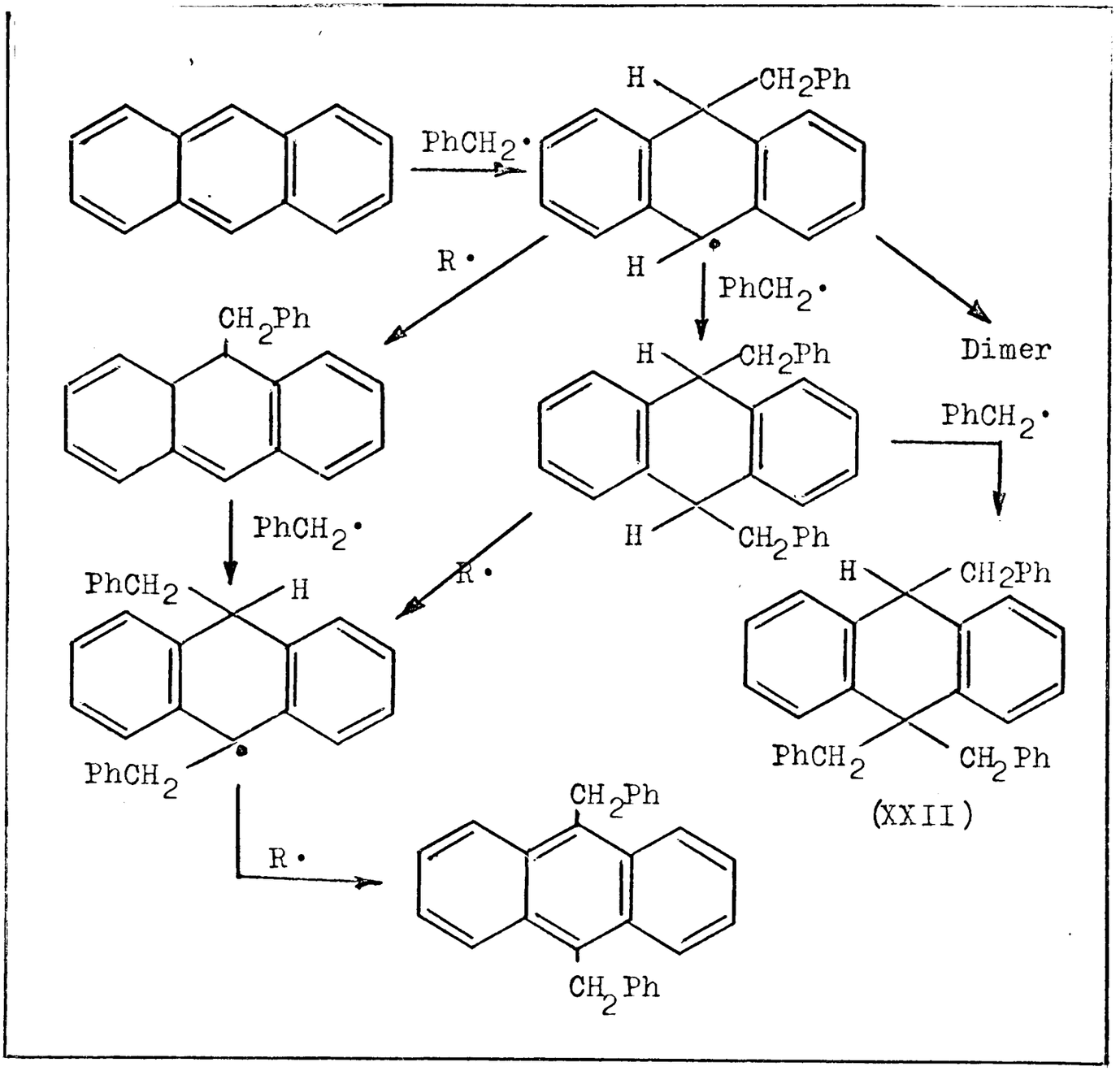
4.2.4. Reaction of benzyl radicals.

Beckwith and Waters[128] decomposed di-tert-butyl peroxide in toluene in the presence of anthracene. The reaction products arose from reaction of benzyl radicals, $PhCH_2\cdot$, with anthracene according:

$$Me_3C-O-O-CMe_3 \longrightarrow 2Me_3CO\cdot$$
$$Me_3CO\cdot \longrightarrow Me_2CO + Me\cdot \quad \Big\} \; R\cdot$$

$$R\cdot + PhCH_3 \longrightarrow RH + PhCH_2\cdot$$

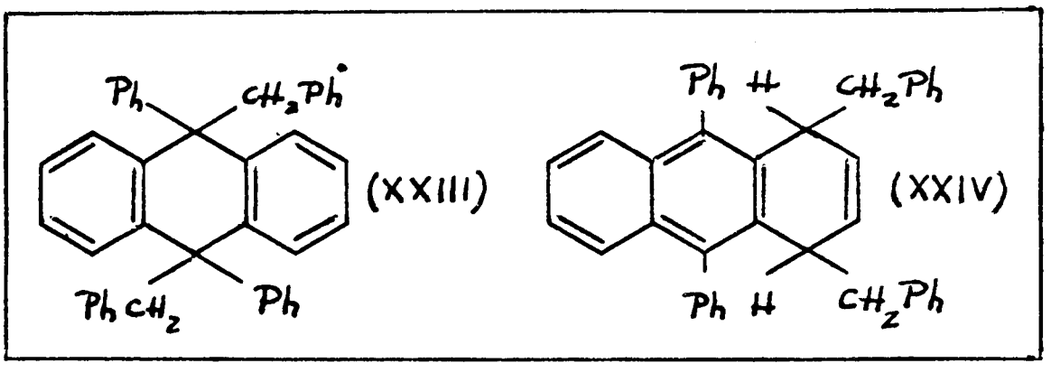




It was the first time that addition and substitution products were found in the reaction of radicals with anthracene. A very interesting feature is the formation of the tri-substituted product (XXII).

Benzyl radicals also reacted with 9,10-diphenylanthracene.[129] The products of reaction were the addition product, 9,10-dibenzyl-9,10-diphenyl-9,10-dihydroanthracene (XXIII) and

another compound very likely 1,4-dibenzyl-1,4-dihydro-9,10-diphenyl anthracene (XXIV).



The reaction of benzyl radicals produced from benzyl magnesium chloride and benzyl chloride under the catalytic action of cobaltous chloride were studied by Norman and Waters.[131]

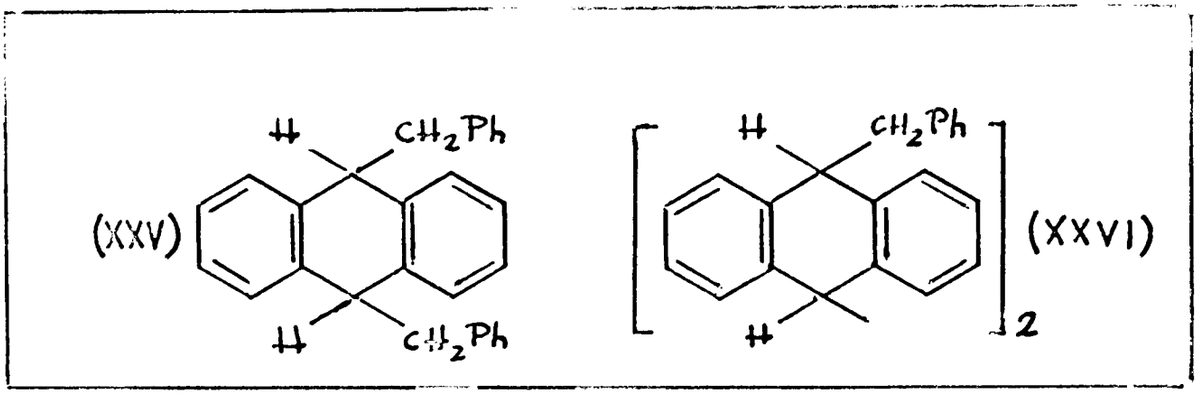
It is believed that the formation of benzyl radicals arose by the process:

$$PhCH_2MgCl + CoCl_2 \longrightarrow PhCH_2CoCl + MgCl_2$$

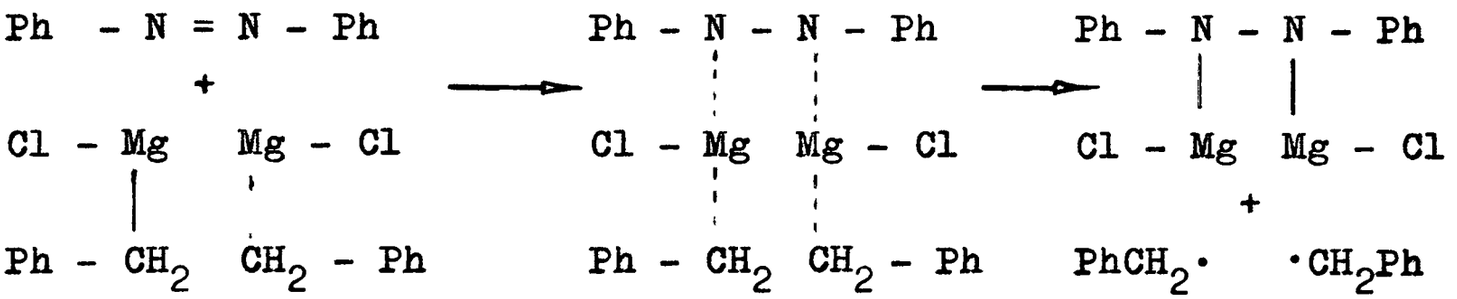
$$PhCH_2CoCl \longrightarrow PhCH_2\cdot + \cdot CoCl$$

$$\cdot CoCl + PhCH_2Cl \longrightarrow PhCH_2\cdot + CoCl_2$$

9,10-Dibenzyl-9,10-dihydroanthracene (XXV) and three isomers of 10,10'-dibenzyl-9,9',10,10'-tetrahydro-9,9'-dianthryl (XXVI) were the formed products.



Similar results were obtained when benzyl radicals were generated by reaction of benzyl magnesium chloride and azobenzene[131]:



Sisido, Udo and Nozaki,[132] obtained benzyl radicals from a mixture of benzyl chloride, iron powder and hot water:

$$PhCH_2Cl \xrightarrow{Fe,H_2O} PhCH_2^+ + Cl^-$$

$$2PhCH_2^+ + Fe \longrightarrow 2PhCH_2\cdot + Fe^{2+}$$

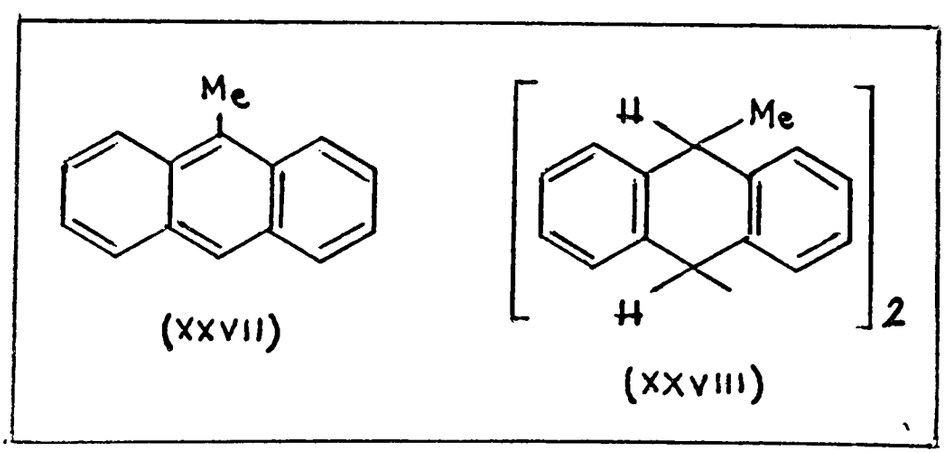
$$2PhCH_2\cdot \longrightarrow PhCH_2CH_2Ph$$

The benzyl radicals so produced reacted with anthracene yielding 9,10-di-benzyl-9,10-dihydroanthracene and two isomers of 10,10'-di-benzyl-9,9',10,10'-tetrahydro-9,9'-bianthryl among other products.

Benzyl radicals[133] produced by thermal decomposition of dibenzyl mercury, $(PhCH_2)_2Hg$, reacted with anthracene at the meso position to give the same products as other reactions of benzyl radicals with anthracene.

4.2.5. Reaction of methyl radicals

Beckwith and Waters,[134] used the thermal decomposition of di-tert-butylperoxide in boiling chlorobenzene and o-dichlorobenzene as a source of methyl radicals. Chlorobenzene, naphthalene, phenanthrene and pyrene reacted only to a small extent, but anthracene gave 9-methylanthracene (XXVII) and 9,9',10,10'-tetrahydro-10,10'-dimethyl-9,9'-dianthryl (XXVIII)



(XXVII) (XXVIII)

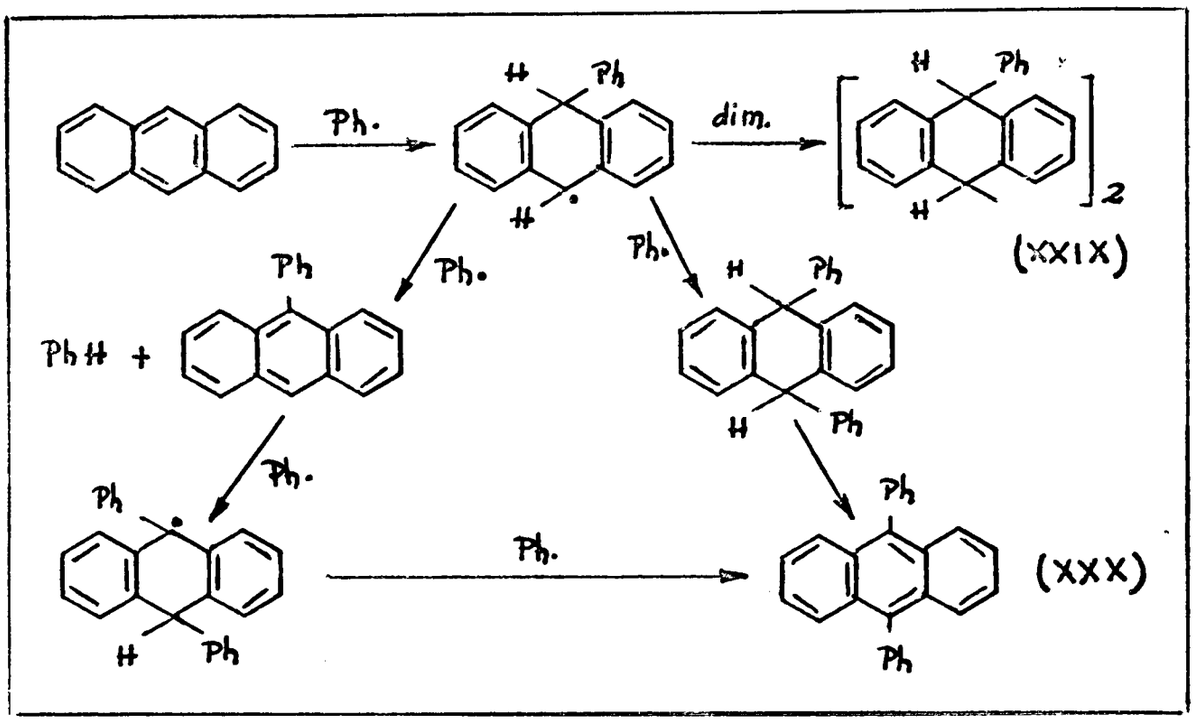
The results of Bickel and Kooyman[122] concerning formation of the dimer were confirmed, i.e., low temperatures favoured the formation of (XXVIII).

.4.2.6. Reaction of phenyl radicals

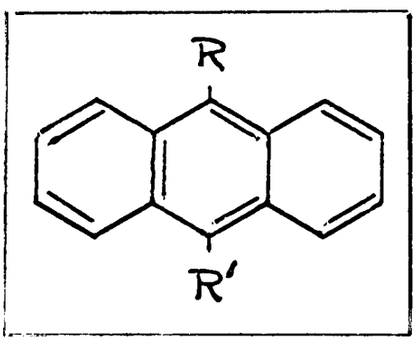
Norman and Waters[130] reacted anthracene and some meso-substituted anthracenes with phenyl radicals, obtained by the action of zinc powder on benzenediazonium salts suspended in acetone.

$$(PhN_2)_2ZnCl_4 + Zn \longrightarrow 2Ph\cdot + 2N_2 + 2\,ZnCl_2$$

Although phenyl radicals can be produced from benzoyl peroxide, this method could not be used in the reaction with anthracene as benzoyloxy radicals react before decomposition could take place.[121] 9,9',10,10'-tetrahydro-10,10'-diphenyl-9,9'-dianthryl (XXIX) and 9,10-diphenylanthracene (XXX) were the products isolated in the reaction with anthracene:



9-Methylanthracene reacted with phenyl radicals to give only 9-methyl-10-phenyl anthracene (XXXI). No addition product or dianthryl ethane were obtained. Both 9-methyl- and 9-phenylanthracene were much more reactive towards phenyl radicals. The latter yielded 9,10-diphenylanthracene (XXXII) only.



(XXXI) → R = Me, R' = Ph

(XXXII) → R = R' = Ph

Whereas both methyl [134] and benzyl [128] radicals react with anthracene to give meso-radical adducts, yet in the reaction

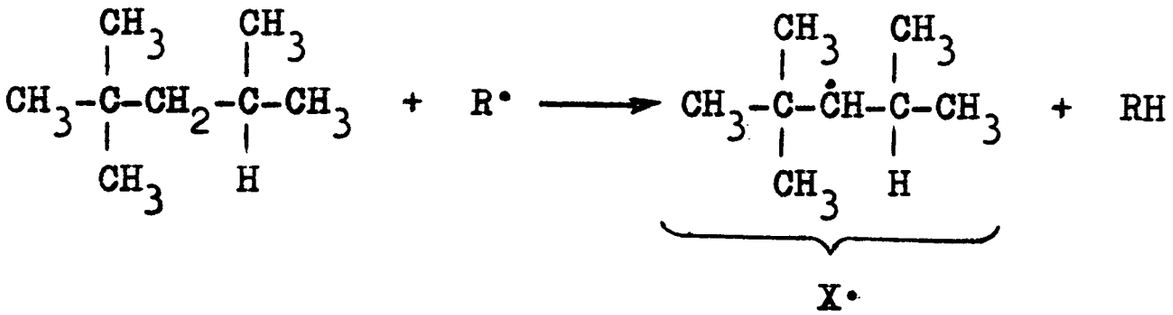
of phenyl radicals no 9,10-diphenyl-9,10-dihydroanthracene was formed.

Apparently phenyl radicals are incapable of adding at the meso-positions of 9,10-diphenylanthracene, probably for steric reasons.[129]

4.2.7. Reaction with other radicals.

Beckwith and Waters[128] decomposed di-tert-butyl peroxide in iso-octane in the presence of anthracene.

Abstraction of hydrogen did not occur at the tertiary position of iso-octane, but in the position 3:



The structure of all reaction products was not determined but it was proved that radicals X• added to anthracene since the dimeric dianthryl X• substituted was isolated.

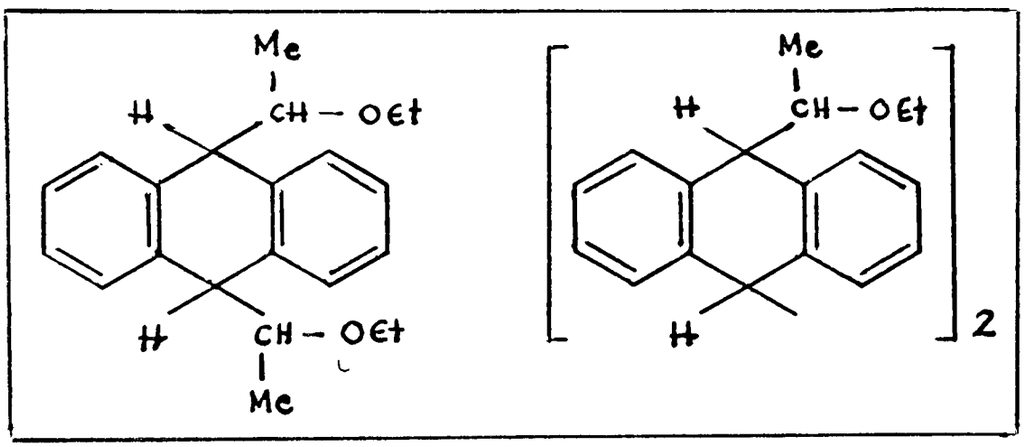
Triphenylmethyl radicals, produced by heating triphenylchloride and mercury in boiling benzene, reacted with 9,10-di-methylanthracene[136] to yield the addition product 9,10-

dimethyl-9,10-bis(triphenylmethyl)-9,10-dihydroanthracene and an insoluble high m.p. product thought to be the dianthryl derivative.

Alkyl radicals formed by hydrogen abstraction on ether reacted with anthracene, as Norman and Waters have shown:[131]

$$Ph\cdot + CH_3CH_2\text{-}O\text{-}Et \longrightarrow Ph\text{-}H + CH_3\dot{C}H\text{-}O\text{-}Et$$

to give the following products:



The reaction of phosphorus pentahalides with anthracene and 9-methylanthracene was said to be a radical reaction[137] proceeding by addition of atomic halogen and radical $\cdot PX_4$ across the meso position, followed by elimination of phosphorus trihalide and hydrogen halide.

4.3. Reactivity of polynuclear aromatic hydrocarbons towards free-radicals.

The most extensive study of reactivity of aromatic hydrocarbons is that of Szwarc and his collaborators[138] who have determined the relative rates of reaction of a number of aromatic compounds with methyl radicals derived from acetyl peroxide. These "methyl affinities" are a measure of the efficiency of the aromatic compound in competing with the solvent for methyl radicals. The reactions were conducted in iso-octane.

$$\cdot CH_3 + C_8H_{18} \xrightarrow{K_1} CH_4 + C_8H_{17}\cdot$$

$$\cdot CH_3 + ArH \xrightarrow{K_2} ArHCH_3\cdot$$

The relative magnitudes of rate constants K_1 and K_2 can be calculated from the composition of the gaseous mixture of the reaction products. The reaction is carried out in a very dilute solution of acetyl peroxide with a large excess of aromatic compound. Under these conditions, the errors caused by side reactions are greatly reduced. This method does not indicate the position of addition of methyl radicals.

Relationship between methyl affinity and theoretical indices

Compound	Position of attack	log R^*	πe	E_{loc}	F_{max}
Benzene	1-6	-0.8	-	2.31	0.081
Diphenyl	2,6,2',6'	0.10	2.10	2.06	0.118
Naphthalene	1,4,5,8	0.74	1.98	1.81	0.134
Phenanthrene	1,8,9,10	0.83	1.935	1.79	0.134
Chrysene	3,9	1.46	1.805	1.67	0.139
Pyrene	3,5,8,10	1.50	1.61	1.51	0.151
1,2-Benzanthracene	7	1.67	1.53	1.35	0.196
Stilbene	α,β	1.96	1.64	-	0.163
Anthracene	9,10	2.61	1.46	1.25	0.202
Naphthacene	5,6,11,12	3.37	1.135	1.03	0.212

R^* - Methyl affinity per reactive carbon atom.[138,134]

πe - Polarographic half-wave potential.[139,134]

E_{loc} - Minimum carbon-localisation energy.[140,134]

F_{max} - Maximum free-valence number.[141,134]

The relative rates of addition of free radicals to aromatic molecules can also be determined by measuring their retarding power towards free-radical catalysed processes. Kooyman and Farenhorst[142] studied the retardation of the peroxide catalysed additions of carbon tetrachloride to 1-hexadecene and bromotrichloromethane to styrene. They supposed that the retardation occurred by a bimolecular reaction of trichloromethyl radical , $\cdot CCl_3$, with the aromatic compound.

$$\cdot CCl_3 + \text{Retarder} \xrightarrow{k_r} \text{stabilised radical (incapable of participation in the chain reaction)}$$

$$\cdot CCl_3 + CH_2 = CH - R \xrightarrow{k_a} Cl_3C-CH_2-\dot{C}H-R$$

The relative reactivity of the retarders, $K_r = \frac{1}{2}(k_r/k_A)$ was calculated for several aromatic hydrocarbons. A linear relationship was found between log K_r/n and F_{max}, where $\underline{n}$ is the number of equivalent positions with maximum "Free Valence" number, and $\underline{F_{max}}$ is the Free Valence number at the most reactive position. Relative reactivities of some aromatic hydrocarbons are given below:

System carbon tetrachloride-hexadecene

Retarder	$K_r \times 10^2$
Benzene	0.1
Biphenyl	0.28
Phenanthrene	1.6
Naphthalene	4.0
Chrysene	6.6
Stilbene	98
Pyrene	132
Anthracene	almost complete inhibition
1,2-Benzanthracene	" " "

System bromotrichloromethane-styrene

Retarder	$K_r \times 10^2$
Stilbene	3.9
Pyrene	4.1
1,2-5,6-Dibenzanthracene	15
2,3-Benzanthracene	420

The effect of aromatic hydrocarbons on the peroxide-catalysed autoxidation of benzaldehyde was studied by Dunnaxxt and Waters.[143] They suggested that the retarding ability of a hydrocarbon could be related to its Free Valence number but later, Turner and Waters[144] who studied other aromatic hydrocarbons found exceptions and concluded that in order to find a simple relationship between reactivities and free valence number it is necessary to know a) the detailed reaction mechanism, and b) the chemical nature of the reaction products.

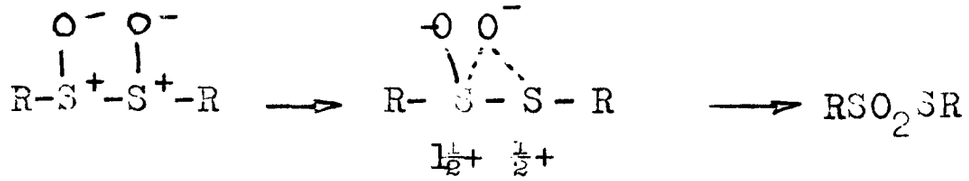
5. Sulphinyl Radicals

Very little evidence for the existence of sulphinyl radicals, R-SO•, has been reported.

However in 1957, Barnard[145] studied the reaction of benzenesulphinyl chloride, PhSOCl, with zinc dust:

$$2PhSOCl \xrightarrow{Zn} PhSO_2SPh$$

and this result could be explained either by (a) the rearrangement of the initially formed disulphoxide into the more stable thiosulphonate



or (b) oxygen transfer between sulphinyl radicals with subsequent coupling of the resulting sulphonyl and sulphinyl radicals:

$$2RSOCl + Zn \longrightarrow 2RSO\cdot + ZnCl_2 \qquad (1)$$

$$2RSO\cdot \longrightarrow RSO_2\cdot + RS\cdot \longrightarrow RSO_2\text{-}SR \qquad (2)$$

In this case formation of disulphide, RSSR, and disulphone, RSO_2SO_2R should be expected.

The non-occurrence of disproportionation (2) can be

explained by the theory that the transfer of negatively charged oxygen, from one sulphinyl radical to another occurs to give ions.

$$2RSO\cdot \longrightarrow \overset{-}{R}SO_2 + \overset{+}{R}S \longrightarrow RSO_2 — SR$$

Barnard and Percy [146] studied the oxidation of thiosulphinates, RSOSR, by organic hydroperoxides, peracids and hydrogen peroxide.

$$Ar\text{-}SO\text{-}S\text{-}Ar \xrightarrow{[O]} Ar\text{-}SO_2\text{-}S\text{-}Ar$$

(I) (II)

They suggested that the major path by which (I) was converted into (II) does not involve direct oxidation at S but an induced disproportionation with S-S bond cleavage and recombination of the various fragments. They suggested that the disproportionation was caused by the presence of sulphinyl radicals.

Sulphinyl radicals would be produced in the spontaneous disproportionation of the small amount of disulphoxide, Ar-SO-SO-Ar formed by direct oxidation of thiosulphinate.

$$Ar\text{-}SO\text{-}S\text{-}Ar \xrightarrow{[O]} Ar\text{-}SO\text{-}SO\text{-}Ar \longrightarrow 2ArSO\cdot$$

Topping and Kharasch [147] reported the decomposition of sulphenylnitrates, $ArS\text{-}O\text{-}NO_2$, by an homolytic process leading

to nitrogen dioxide and sulphinyl radicals:

$$Ar\text{-}S\text{-}O\text{-}NO_2 \longrightarrow Ar\text{-}SO^{\bullet} + NO_2$$

The only product obtained besides nitrogen dioxide was thiosulphonate, $Ar\text{-}SO_2\text{-}S\text{-}Ar$ and this was thought to be formed by "coupling" of sulphinyl radicals:

$$2\,Ar\text{-}SO^{\bullet} \longrightarrow \left[Ar\text{-}\underset{\underset{O}{\downarrow}}{S} - O - S - Ar\right] \longrightarrow Ar\text{-}SO_2\text{-}S\text{-}Ar$$

(III) (II)

A path for the formation of (II) from (III) was based on the work of Stirling[148], who showed that sulphenyl chlorides and sulphinic acids reacted to yield the corresponding thiosulphonate

$$RS\text{-}Cl + H\text{-}\underset{\underset{O}{\downarrow}}{O}\text{-}S\text{-}R \longrightarrow \left[R\text{-}S\text{-}\underset{\underset{O}{\downarrow}}{O}\text{-}S\text{-}R\right] + HCl$$

$$\left[R\text{-}S\text{-}\underset{\underset{O}{\downarrow}}{O}\text{-}S\text{-}R\right] \longrightarrow RS\text{-}SO_2R$$

The "coupling" of sulphinyl chlorides to give thiosulphonate was recently supported by Kice and Pawlowski[149] who studied the kinetics of the decomposition of sulphinyl sulphones (IV) at 50°, (The rate of decomposition is little affected either by the solvent or the nature of the aryl group.)

$$ArSO_2SOAr \longrightarrow ArSO_2\cdot + ArSO\cdot$$

(IV) (V)

When the decomposition of (IV) was performed in the presence of 1,1-diphenylethylene (VI), sulphonyl radicals (V) were able to add to the olefin:

$$Ph_2C{=}CH_2 + Ar\text{-}SO_2\cdot \longrightarrow Ph_2\text{-}\dot{C} - CH_2\text{-}SO_2Ar$$

$$Ph_2\dot{C}\text{-}CH_2\text{-}SO_2Ar \xrightarrow{R\cdot} Ph_2C{=}CH\text{-}SO_2Ar + RH$$

but sulphinyl radicals dimerized:

$$2ArSO\cdot \longrightarrow [ArSO\text{-}\underset{\underset{O}{\downarrow}}{S}\text{-}Ar] \longrightarrow ArSO_2SAr$$

(III)

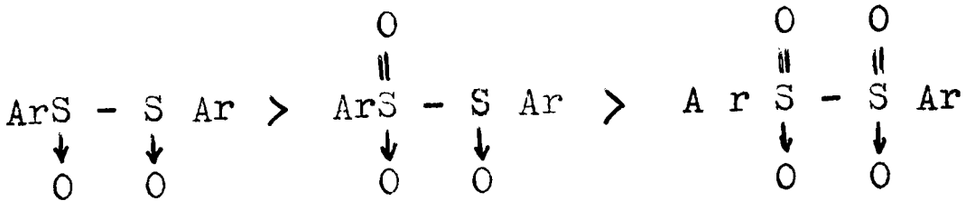
The facile decomposition of sulphinyl sulphones (IV) was explained by the repulsion of the two electron-deficient sulphur atoms:

$$Ar\text{-}\overset{\overset{O^-}{|}}{\underset{\underset{O^-}{|}}{S^{++}}} - \overset{\overset{}{|}}{\underset{\underset{O^-}{|}}{S^{+}}} - Ar \longrightarrow ArSO_2\cdot + ArSO\cdot$$

and also by assuming that sulphinyl radicals, ArSO·, are species of significantly lower energy than sulphonyl radicals, $ArSO_2\cdot$.

These two facts are in accord with the relative facility

of decomposition of the following compounds:



No reactions of sulphinyl radicals with typical free radicals substrates have been reported in the literature.

DISCUSSION

DISCUSSION

1. Some reactions of p-toluenesulphonyl iodide.

1.1 The decomposition of p-toluenesulphonyl iodide.

1.1.1. Decomposition in the presence of copper bronze.

p-Toluenesulphonyl iodide is a yellow crystalline solid which decomposes to p-toluenesulphonic acid when exposed to the air for several days. On heating to its melting point under an atmosphere of nitrogen, iodine is liberated with the formation of a tarry residue. The decomposition of p-toluenesulphonyl iodide in solution is a slower process. When the sulphonyl iodide was refluxed in carbon tetrachloride for nine hours, about 90% of unreacted sulphonyl iodide was recovered. This difference in behaviour of the halide in solution and in the solid state may be due to a reversible decomposition reaction:

$$TolSO_2I \rightleftharpoons TolSO_2\cdot + I\cdot \qquad (1)$$

which occurs more easily when the halide is in solution.

The possibility of accelerating the rate of decomposition by the use of a free radical or metal, R, capable of combining with the iodine liberated during the reaction was next considered.

$$TolSO_2I \rightleftharpoons TolSO_2\cdot + I\cdot$$

$$TolSO_2I + R \longrightarrow TolSO_2\cdot + IR$$

$$R\cdot + I\cdot \longrightarrow IR$$

The expected product of decomposition in an inert solvent was the dimer, di-p-tolyldisulphone, $TolSO_2SO_2Tol$. However, when p-toluenesulphonyl iodide was refluxed in carbon tetrachloride for six hours with a small excess of copper bronze the products of the reaction were p-toluenesulphonic anhydride, $(TolSO_2)_2O$, (69%) and p-tolyl-p-toluenethiosulphonate, $TolSO_2STol$, (57.5%).

The molar ratio of these two products was

$$\frac{\text{Formed } (TolSO_2)_2O}{\text{Formed } TolSO_2STol} = 2.13$$

i.e., two molecules of p-toluenesulphonic anhydride were formed per molecule of p-tolyl-p-toluenethiosulphonate:

$$6\ TolSO_2 \longrightarrow 2(TolSO_2)_2O + TolSO_2STol$$

(II) (III)

It seems that oxygen was transferred between particles:

$$6TolSO_2 \left\{ \begin{array}{l} 2(TolSO_2)_2 \\ 2\ TolSO_2 \end{array} \right. \longrightarrow \left\{ \begin{array}{ll} 2\ (TolSO_2)_2O & (II) \\ TolSO_2STol & (III) \end{array} \right.$$

The formation of p-toluenesulphonic anhydride (II) may also be explained by assuming a reaction between sulphonyl radicals and gaseous oxygen viz.

$$TolSO_2\cdot + O^2 \longrightarrow TolSO_2\text{-}O\text{-}O\cdot$$

$$TolSO_2\text{-}O\text{-}O\cdot + TolSO_2\cdot \longrightarrow TolSO_2\text{-}O\text{-}O\text{-}SO_2Tol$$

$$TolSO_2\text{-}O\text{-}O\text{-}SO_2Tol \longrightarrow 2TolSO_2\text{-}O\cdot$$

$$TolSO_2\text{-}O\cdot + TolSO_2\cdot \longrightarrow (TolSO_2)_2O \quad (II)$$

which is known to occur with sulphonyl chlorides.[39]

However, this mechanism does not account for the formation of (III).

1.1.2. Decomposition in the absence of oxygen

The solvent, carbon tetrachloride, was thoroughly dried and fractionated in a distillation system filled with nitrogen. The decomposition of the sulphonyl iodide was carried out in an atmosphere of nitrogen under identical conditions to those described in 1.1.1. p-Toluenesulphonic anhydride (69.5%) and p-tolyl-p-toluenethiosulphonate (72%) were once again obtained, but none of the dimer, di-p-tolyldisulphone, was found in the reaction mixture.

This experiment shows that the sulphonic anhydride must have been formed with oxygen derived from the system itself and not from an external source. The yields of (I) and (II) were calculated from equation (2).

The same results were obtained when the decomposition was carried out with powdered silver in place of copper bronze.

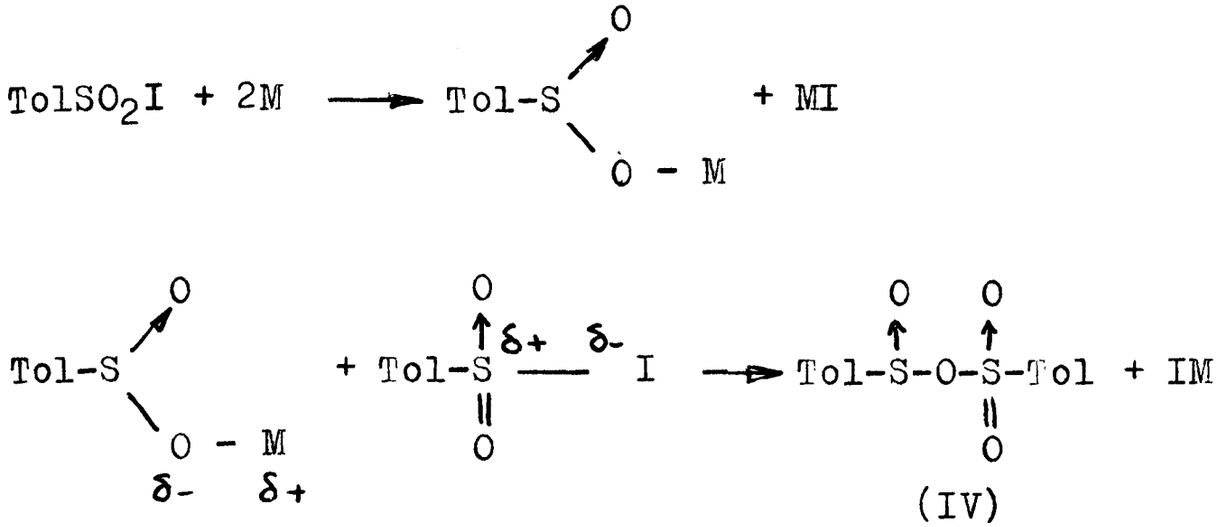
1.1.3. The stability of the dimer, di-p-tolyldisulphone, under the conditions of the previous experiments.

The decomposition of the sulphonyl iodide in the presence of copper bronze yielded none of the dimer, di-p-tolyldisulphone. This sulphone is very stable under non-alkaline conditions[150] and should be easily detected if formed during the decomposition.

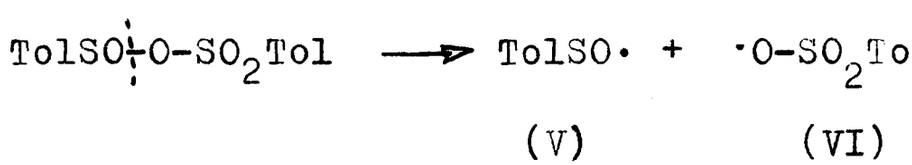
In order to confirm the stability of the disulphone, it was subjected to the experimental conditions described in 1.1.1. p-Tolyldisulphone was refluxed in carbon tetrachloride in the presence of copper bronze for seven hours. The disulphone was recovered in 90% yield but no trace of p-toluenesulphonic anhydride or p-tolyl-p-toluenethiosulphonate was detected. This indicates that oxygen is transferred between the various intermediates before dimerisation can take place.

1.1.4. Decomposition under ultra-violet radiation.

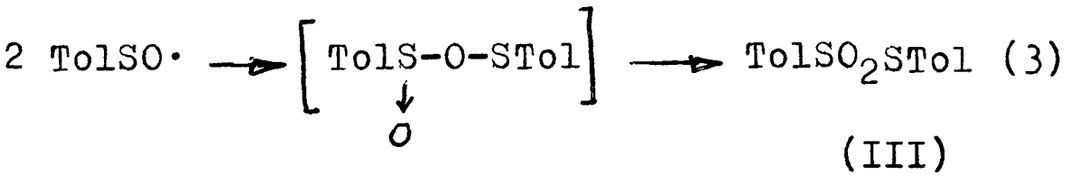
These experiments were carried out in order to ascertain whether the formation of p-toluenesulphonic anhydride, $(TolSO_2)_2O$, was dependent upon the presence of metals. In the presence of a metal, (M), the formation of this product may follow a mechanism similar to that shown below:

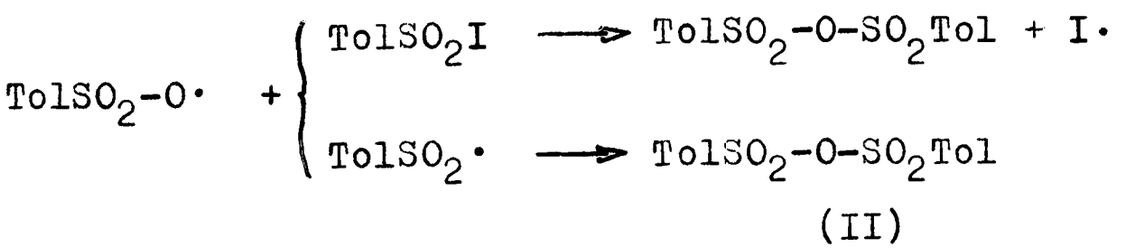


If product (IV) then decomposes into two free radicals (V) and (VI):



the formation of the sulphonic anhydride (II) and thiosulphonate (III) can be explained thus

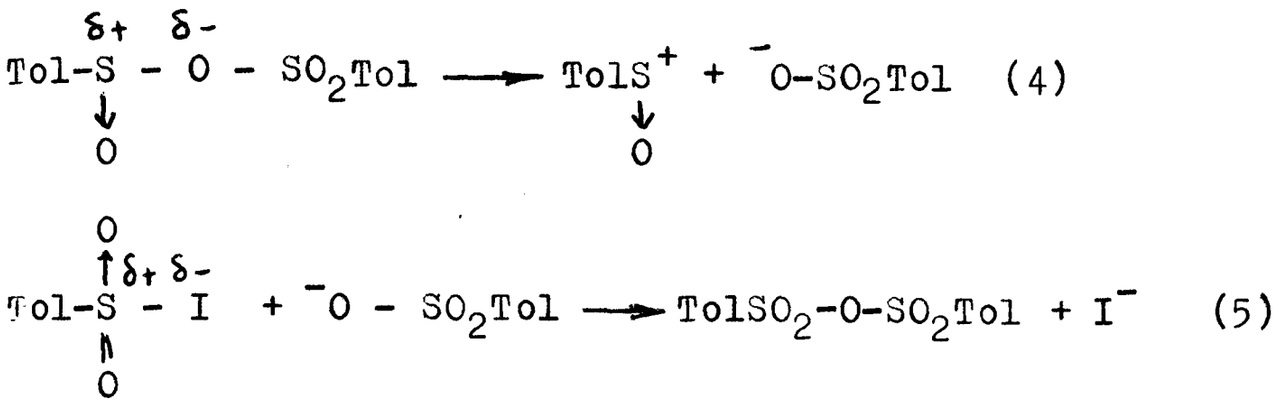




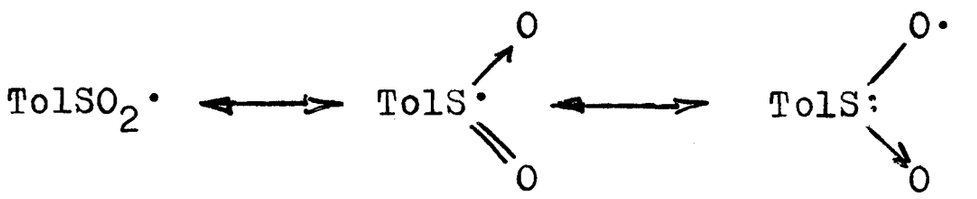
The process invoked in equation (3) is established. [146,147,149]

If product (IV) decomposes heterolytically (4), the formation of the anhydride is still explained (5) but not that of the

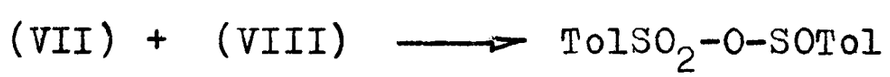
thiosulphonate:



In the absence of metal the formation of product (IV) is unlikely, unless a free radical process is involved:



(VII) (VIII)



(IV)

p-Toluenesulphonyl iodide was dissolved in benzene and irradiated for seven hours. The products of the decomposition were p-tolyldisulphone (5.3%) and p-toluenesulphonic anhydride (23%), but analysis was difficult owing to the presence of a substantial quantity of tar and iodine in the reaction mixture. This experiment proves that anhydride is also formed in the absence of metals. The smaller yield of the product

may be due to the fact that:

(a) some anhydride was lost when the reaction mixture was washed with sodium dithionite to remove iodine.

(b) the yield was based upon its phenylammonium p-toluenesulphonate derivative.

(c) the decomposition of the sulphonyl halide under u.v. light may be slower than in the presence of metals.

1.1.5. Reaction of p-toluenesulphonyl iodide with sodium-p-toluenesulphinate.

This experiment was undertaken in an attempt to obtain those products formed during the decomposition of the sulphonyl iodide in the presence of metals via product (IV)

$$\overset{\delta+\ \delta-}{TolSO_2I} + \overset{+\ -}{NaO\text{-}SOTol} \longrightarrow \underset{(IV)}{TolSO_2\text{-}O\text{-}SOTol} + Na^+I^- \qquad (6)$$

p-Toluenesulphonyl iodide and sodium p-toluenesulphinate (dihydrate) in ether were stirred in the dark for ten hours. Unreacted sodium sulphinate (89%) was recovered from the reaction mixture, but the presence of p-toluenesulphonic anhydride and the corresponding acid was not detected.

The reaction was also carried out in boiling carbon tetrachloride, for three hours. p-Tolyldisulphone (7.3%) was formed in this reaction, but no sulphonic anhydride or acid

were obtained.

These experiments indicate that the intermediate (IV), $TolSO_2$-O-SOTol, was not formed, or if formed, did not decompose to give the same products of decomposition as the sulphonyl iodide.

1.1.6. Decomposition in the presence of free radicals.

It was thought that some free radicals might accelerate the decomposition of the sulphonyl iodide by reacting with the iodine as illustrated below to yield sulphonyl radicals, $TolSO_2\cdot$:

$$\text{Radical source} \longrightarrow R\cdot$$

$$R\cdot + TolSO_2I \longrightarrow RI + TolSO_2\cdot$$

$$TolSO_2I \rightleftharpoons TolSO_2\cdot + I\cdot$$

$$R\cdot + I\cdot \longrightarrow RI$$

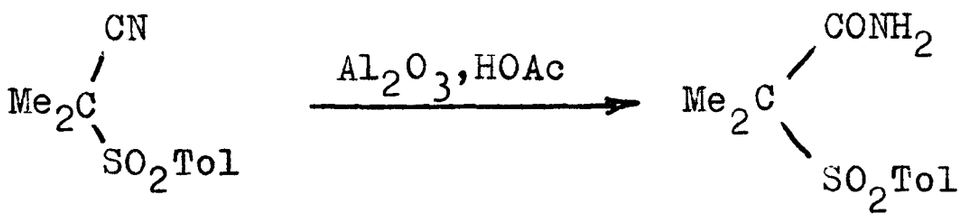
The purpose of the following experiments was to see if the $TolSO_2\cdot$ radicals would yield the sulphonic anhydride and thiosulphonate, as well as crossed products of the type $R\text{-}SO_2Tol$.

A - Decomposition in the presence of 2-cyanomethyl-2-propyl radicals.

An equimolecular mixture of azo-bis(2-cyanomethyl-2-propyl) and p-toluenesulphonyl iodide in benzene was heated under reflux for six hours.

The products formed were: p-toluenesulphonic anhydride (37.4%), p-tolyldisulphone (17.8%) and 2-iodo-2-methylpropionitrile, $Me_2CI(CN)$, (35%).

A similar reaction in carbon tetrachloride using excess of the azo-compound yielded p-toluenesulphonic anhydride (26.7%), p-tolyldisulphone (3.04%), 2-iodo-2-methylpropionitrile (32%), tetramethylsuccinonitrile (29.1%), $Me_2C(CN)C(CN)Me_2$, and a solid product that was not completely characterized but which was thought to be the amide derivative of the crossed product, 2-methyl-2-p-tolylsulphonylpropionitrile, $Me_2C(CN)SO_2Tol$, (12.3%). It is believed that the amide was formed during chromatography on an alumina column:



These experiments indicated that the sulphonic anhydride may be formed by a free radical reaction. A mechanism to account for the formation of the reaction products is shown below:

$$Me_2C(CN)N_2C(CN)Me_2 \xrightarrow{\Delta} 2Me_2\dot{C}(CN) + N_2$$

$$TolSO_2I \rightleftharpoons TolSO_2\cdot + I\cdot$$

$$Me_2\dot{C}(CN) + TolSO_2I \longrightarrow Me_2CI(CN) + TolSO_2\cdot$$

$Me_2\dot{C}(CN) + I\cdot$ (or I_2) $\longrightarrow Me_2CI(CN)$

$Me_2\dot{C}(CN) + TolSO_2\cdot \xrightarrow{?} Me_2C(CN)SO_2Tol$

$2Me_2\dot{C}(CN) \longrightarrow Me_2C(CN)C(CN)Me_2$

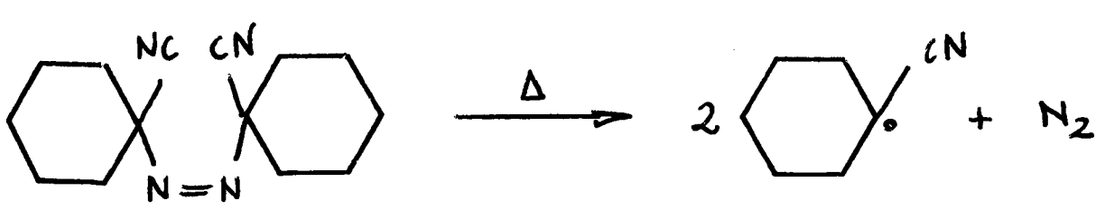
$2TolSO_2\cdot \longrightarrow TolSO_2SO_2Tol$

$m\ TolSO_2\cdot \longrightarrow$ Products of the decomposition of $TolSO_2I$ in 1.1.1.

B - Decomposition in the presence of 1-cyanomethylcyclohexyl radicals.

An equimolecular mixture of the sulphonyl iodide and azo-bis(1-cyanomethylcyclohexane) in benzene was refluxed for fortythree hours. The half-life of decomposition of the azo-compound at 80° in toluene is approximately 28 hours.[151]

The products of reaction were p-toluene-sulphonic anhydride (94%), p-tolyldisulphone (4.6%), 1,1'-bis(1-cyanomethylcyclohexyl), $C_6H_{10}(CN)C_6H_{10}(CN)$, (3.66%) and 1-iodo-1-cyanomethylcyclohexane, $C_6H_{10}(CN)I$, (13.3%). The following mechanism would explain the formation of these products:



$$C_6H_{10}(CN)\cdot + \begin{cases} TolSO_2I \longrightarrow C_6H_{10}(CN)I + TolSO_2\cdot \\ I\cdot \longrightarrow C_6H_{10}(CN)I \end{cases}$$

$$2C_6H_{10}(CN)\cdot \longrightarrow C_6H_{10}(CN)C_6H_{10}(CN)$$

$$2\ Tol\ SO_2\cdot \longrightarrow TolSO_2SO_2Tol$$

$$m\ TolSO_2\cdot \longrightarrow \text{Products of decomposition of the sulphonyl iodide in 1.1.1.}$$

p-Toluenesulphonic anhydride was again formed in the absence of metals.

1.1.7. Conclusions

p-Toluenesulphonyl iodide decomposed quantitatively in solution at about 80° in the presence of metals (copper bronze or silver) in 3-4 hours. The products of the decomposition were p-toluenesulphonic anhydride and p-tolyl-p-toluenethiosulphonate. The dimer, p-tolyldisulphone, was not formed. The same results were obtained when the decomposition was carried out in the absence of oxygen.

During the decomposition in the absence of metals (under u.v. light or in the presence of free radicals) appreciable amounts of tar and iodine were formed which made the isolation of products more difficult. p-Toluenesulphonic anhydride

was formed under these conditions as well as the dimer, p-tolyldisulphone. p-Tolyl-p-toluenethiosulphonate was not isolated but it is thought that this was due to experimental difficulties.

It is impossible to say why none of the disulphone was formed when the decomposition was carried out in the presence of metals.

The mechanism proposed for the decomposition of p-toluenesulphonyl iodide in solution in the presence of metals is shown below:

$$TolSO_2I \rightleftharpoons TolSO_2\cdot + I\cdot \quad (7)$$

$$TolSO_2I + M \longrightarrow TolSO_2\cdot + MI \quad (8)$$

$$I\cdot + M \longrightarrow MI \quad (9)$$

$$2I\cdot \longrightarrow I_2 \quad (10)$$

$$\tfrac{1}{2}I_2 + M \longrightarrow MI \quad (11)$$

$$2TolSO_2\cdot \longrightarrow TolSO_2SO_2Tol \text{ (not isolated)} \quad (12)$$

$$2TolSO_2\cdot \longrightarrow TolSO_2\text{-}O\cdot + TolSO\cdot \quad (13)$$

$$2TolSO_2\cdot \longrightarrow TolSO_2STol \quad (14)$$

$$TolSO_2\text{-}O + TolSO_2\cdot \longrightarrow (TolSO_2)_2O \quad (15)$$

In this mechanism step (13) is a disproportionation process in which oxygen is transferred from one radical to another.

1.2.The reaction of p-toluenesulphonyl iodide with quinones

1.2.1 Reaction with p-benzoquinone

It was expected that the decomposition of p-toluenesulphonyl iodide in the presence of copper bronze and quinones would yield di-p-toluenesulphonates (I) via a free radical mechanism:

$$TolSO_2I \rightleftharpoons TolSO_2\cdot + I\cdot$$

$$I\cdot + Cu \longrightarrow \text{Copper iodide}$$

$$TolSO_2I + Cu \longrightarrow TolSO_2\cdot + \text{Copper iodide}$$

$$TolSO_2\cdot + Q \longrightarrow TolSO_2\text{-}Q\cdot \quad (Q\text{-Quinone})$$

$$TolSO_2\text{-}Q\cdot + TolSO_2\cdot \longrightarrow TolSO_2\text{-}Q\text{-}SO_2Tol \quad (I)$$

A mixture of p-toluenesnlphonyl iodide, p-benzoquinone and copper bronze in carbon tetrachloride was heated under reflux for seven hours. p-Toluenesulphonic anhydride (12.3%) and hydroquinone-di-p-toluenesulphonate (46.5%) were the only reaction products. The yield of the anhydride was calculated from the weight of derivative phenyl ammonium-p-toluene sulphonate, $TolSO_3^-\overset{+}{N}H_3Ph$, according to the stoichiometry of the equation:

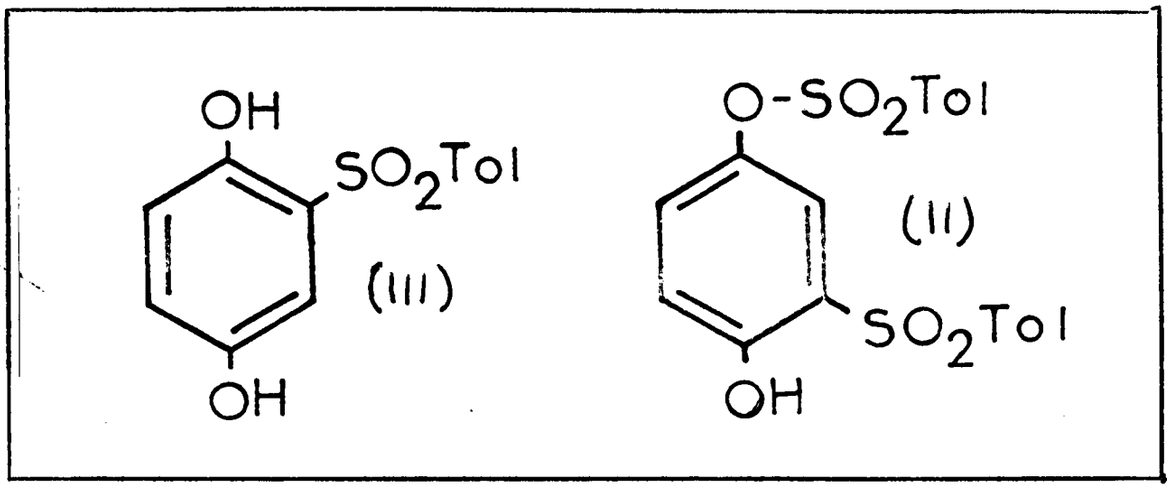
$$(TolSO_2)_2O + 2\ PhNH_2 \longrightarrow TolSO_3^-\overset{+}{N}H_3Ph + TolSO_2NHPh$$

Hydroquinone-di-p-toluenesulphonate was identified by comparison with an authentic specimen prepared by the method of Drahowzal & Klaman [154]:

$$2\ TolSO_2Cl + HO\text{-}C_6H_5\text{-}OH \longrightarrow TolSO_3\text{-}C_6H_5\text{-}OSO_2Tol\ (I)$$

The structure of this di-ester was confirmed by n.m.r. spectroscopy.

Phenolic products such as (II) and (III) were not formed in the reaction.



In a blank experment product (III) was dissolved in aqueous sodium hydroxide solution and acidified with hydrochloric acid.Product (III) was recovered almost quantitatively.

1.2.2 - Reaction with hydroquinone

This experiment was carried out to see whether Hydroquinone-di-p-toluenesulphonate (I) could be formed by reaction of the sulphonyl iodide with hydroquinone under the conditions of the previous experiment:

$$2\ TolSO_2I + HO\text{-}C_6H_5\text{-}OH \longrightarrow \underset{(I)}{TolSO_2C_6H_5O\text{-}SO_2Tol} + 2\ HI \quad (1)$$

Any hydroquinone present in the reaction mixture would yield the di-ester (I) plus hydrogen iodide.If hydrogen iodide reacted with the quinone

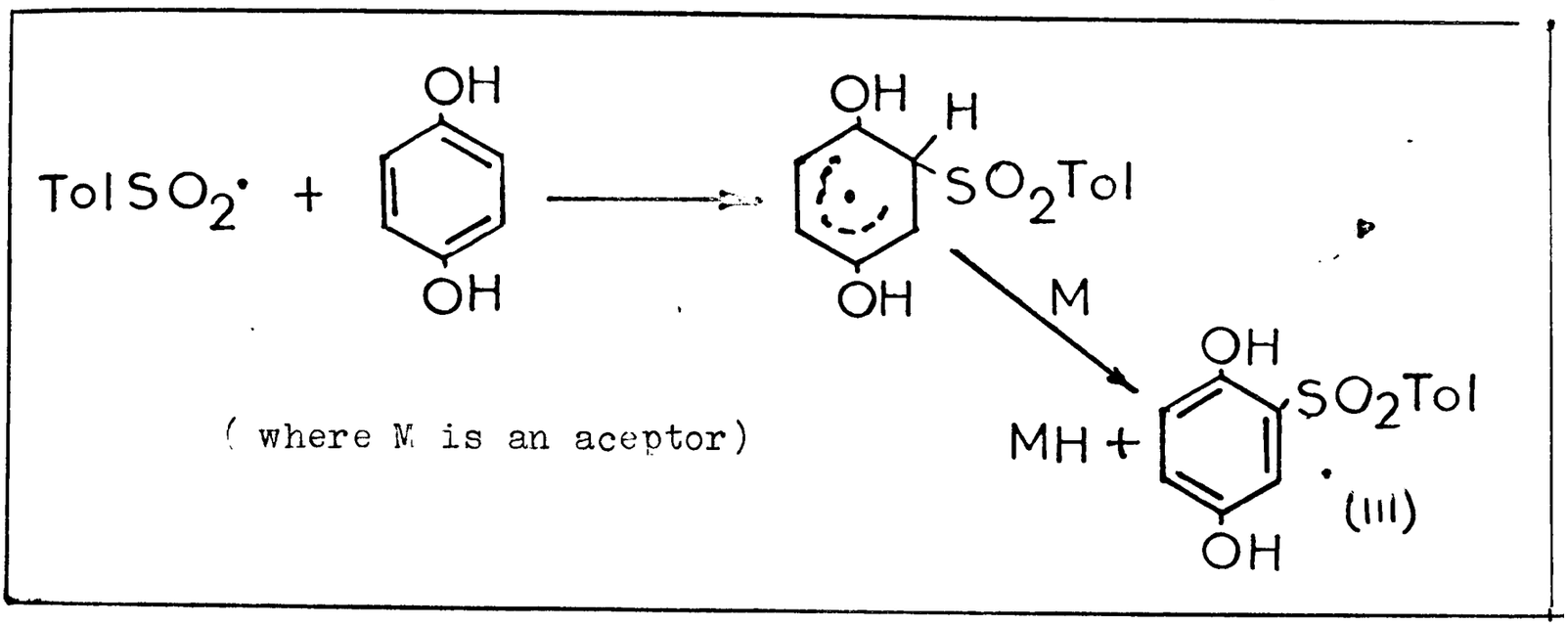
$$O{=}C_6H_4{=}O + 2\ HI \longrightarrow HO\text{-}C_6H_4\text{-}OH + I_2$$

further amounts of hydroquinone should be formed which would undergo reaction (1).

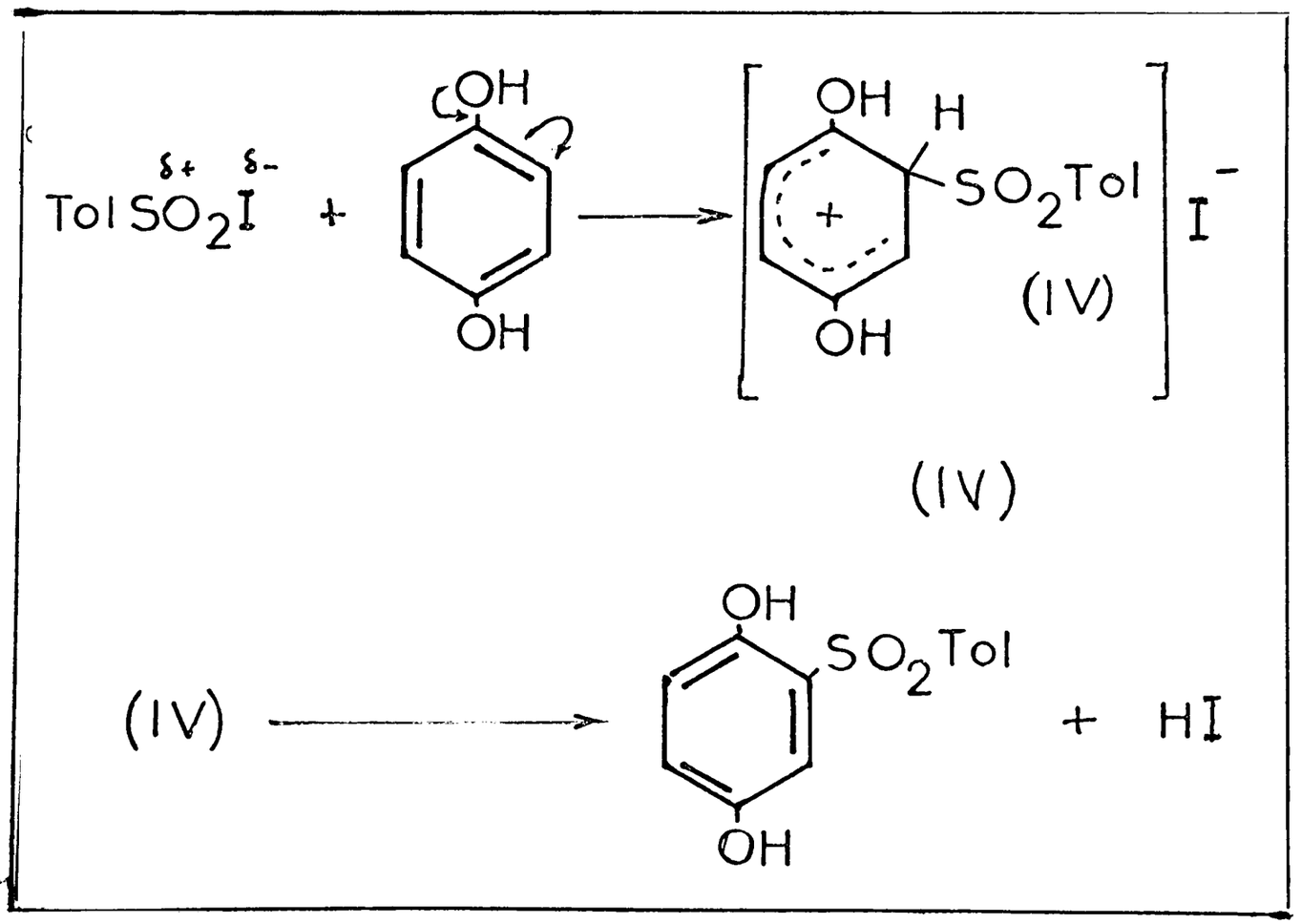
p-Toluenesulphonyl iodide was refluxed in dry benzene with an equimolecular amount of hydroquinone and a small excess of copper bronze for four hours.

The only product of reaction was 2-p-tolylsulphonylhydroquinone (III), identified by comparision with an authentic specimen prepared by reaction of p-toluenesulphonic acid with p-benzoquinone (p.288).

Product (III) may be formed either by a radical process:



or by an ionic process:



No attempt was made to distinguish between these two processes.

1.2.3 - Reaction with p-benzoquinone in the absence of copper bronze.

A mixture of p-toluenesulphonyl iodide and p-benzoquinone in carbon tetrachloride was heated under reflux for seven hours. p-Toluenesulphonyl iodide (76%) was recovered from the reaction mixture. Unreacted p-benzoquinone was removed by washing with an alkaline sodium dithionite solution. No hydroquinone-di-p-toluenesulphonate was found in the reaction mixture. The failure of the reaction may be explained in two ways:

Radical reaction-The decomposition of the sulphonyl iodide in solution in solution in the absence of copper bronze is very slow and is a reversible process

$$TolSO_2I \rightleftharpoons TolSO_2\cdot + I\cdot$$

Without copper bronze the number of sulphonyl radicals in solution is very small and so the rate of the reaction

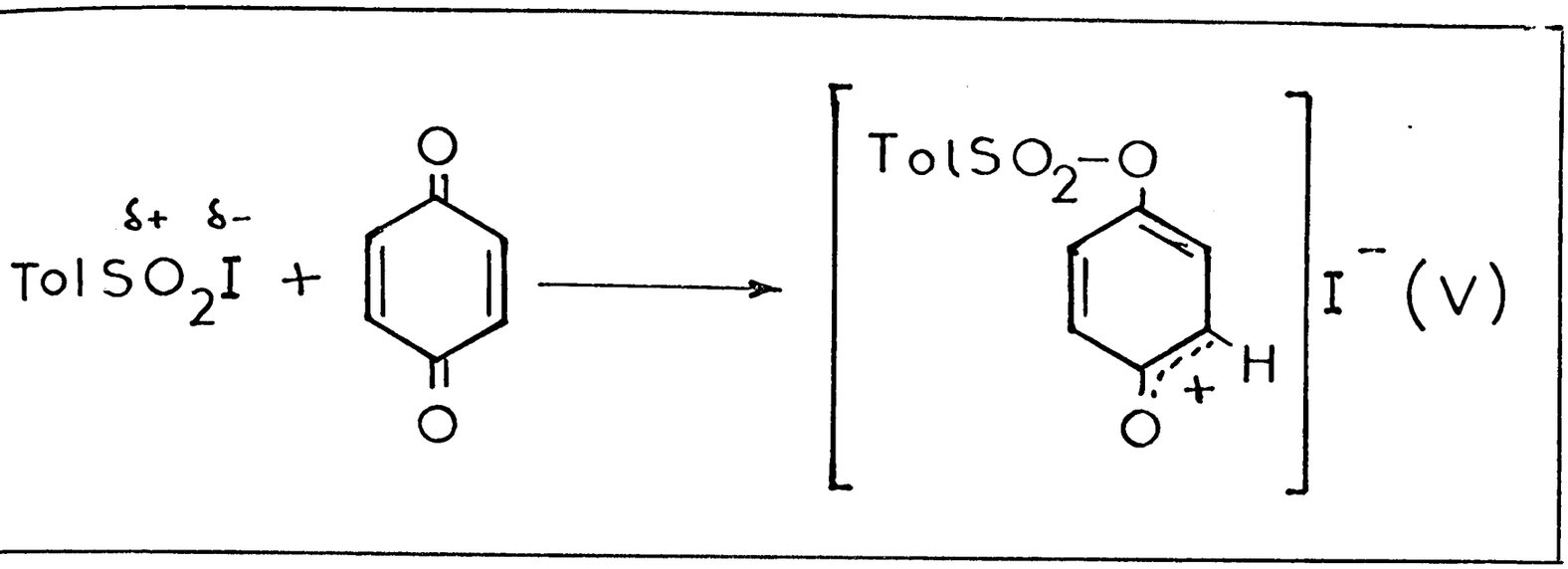
$$TolSO_2\cdot + Q \longrightarrow TolSO_2\text{-}Q\cdot \longrightarrow (I)\ TolSO_2\text{-}Q\text{-}SO_2Tol \longrightarrow TolSO_2\cdot$$

is also very small, and after seven hours of reaction no detectable di-ester (I) was obtained.

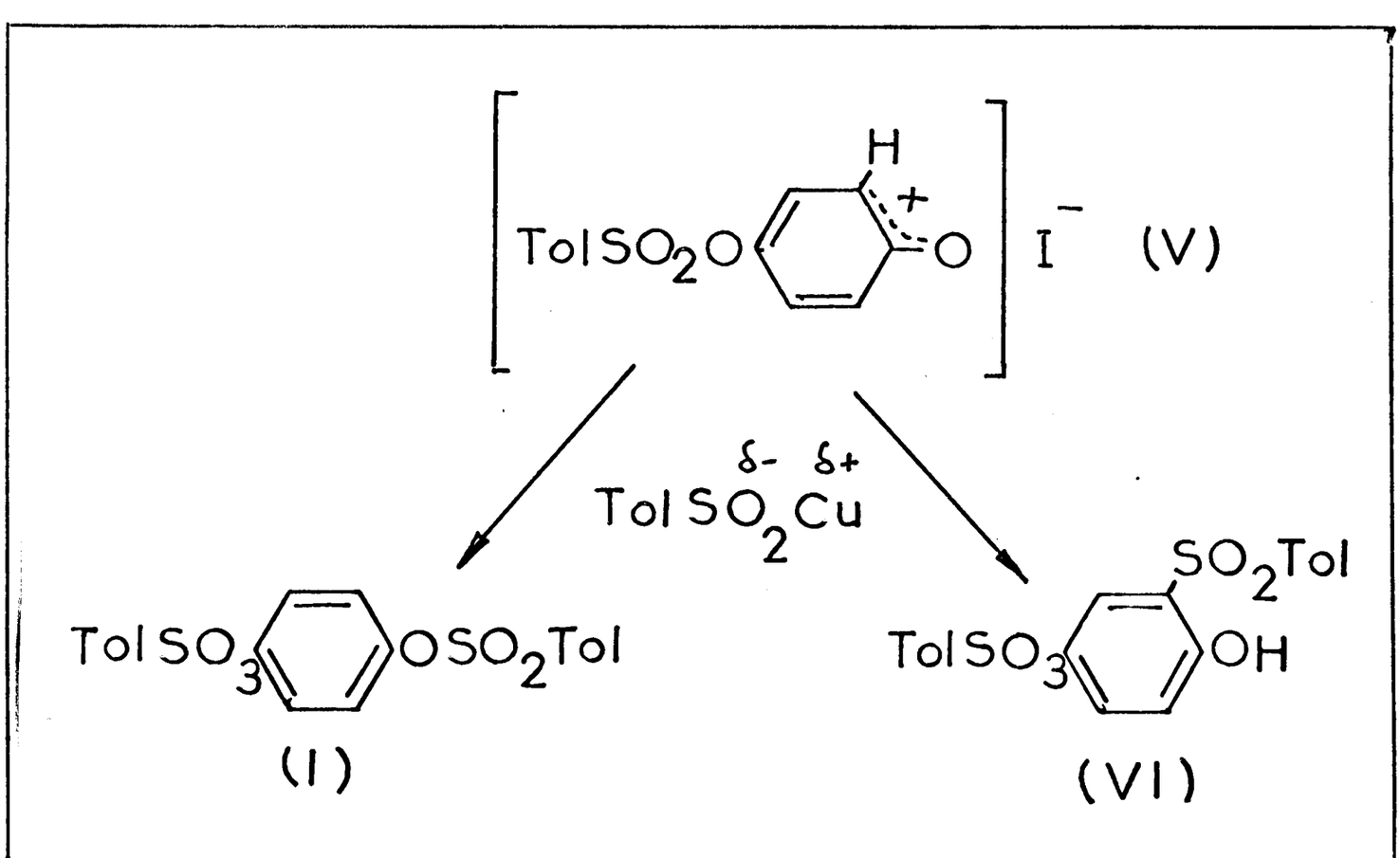
Heterolytic reaction-In the presence of copper bronze, copper sulphinate could be formed

$$TolSO_2I \xrightarrow{Cu} TolSO_2^{\delta-}\text{-}Cu^{\delta+} + \text{Copper iodide}$$

The sulphonyl iodide could attack an oxygen atom of the quinone:



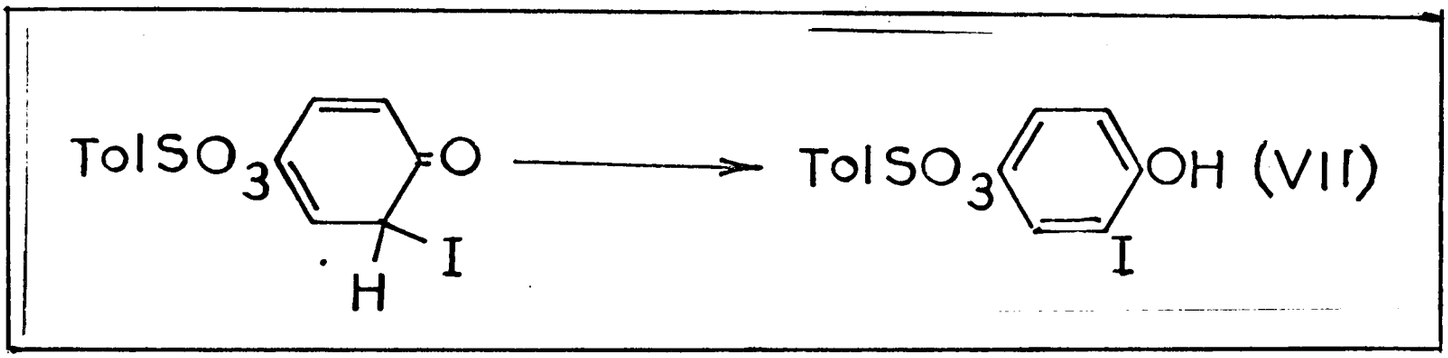
followed by reaction of intermediate (V) with copper sulfinate:



If this heterolytic process ocurred, product (VI) should be formed as well as (I).

The formation of product (VI) might be more likely than the formation of (I) because the positive charge in (V) may be more localised on the carbon than on the powerful electron attracting oxygen.

If the initial attack on the quinone oxygen atom was made by the $TolSO_2^{\delta+}\text{--}I^{\delta-}$ to yield the intermediate (V), product (VII) should be also formed:



but this product was never isolated in the reaction of p-toluenesulphonyl iodide with quinones.

It may be concluded that a radical process is more likely to operate.

1.2.4 - Blank tests

1.2.4.1 - Effect of washing the reaction mixture with an alkaline solution of a reducing agent.

p-Toluenesulphonyl iodide was decomposed by copper bronze in boiling carbon tetrachloride. Most of the sulphonic anhydride was separated and p-benzoquinone was added to the reaction mixture which was then washed with an alkaline sodium dithionite solution.

No hydroquinone-di-p-toluenesulphonate was formed during the washing procedure.

This experiment indicated that under the conditions of the reaction with p-benzoquinone:

a) the concentrations of unreacted p-toluenesulphonyl iodide and p-toluenesulphonic anhydride in the cold carbon tetrachloride filtrate are too small for the product to be detected, or

b) the rate of reaction is too low for appreciable product to be formed during the washing procedure.

$TolSO_2I$, $(TolSO_2)_2O$
Quinone, Sodium dithionite
Sodium hydroxide
$\longrightarrow$ Di-ester

It was concluded that the di-ester collected from the reaction mixture washed with an alkaline sodium dithionite solution (exp. 1.2.1) was already present.

1.2.4.2 - Reaction of p-toluenesulphonic anhydride with p-Benzoquinone.

Hydroquinone-di-p-toluenesulphonate could be formed by reaction of p-toluenesulphoniç anhydride with the quinone or hydroquinone:

$(TolSO_2)_2O$ + $HO-C_6H_4-OH$ or $O=C_6H_4=O$ $\xrightarrow{\text{Copper salts, Cu}}$ $TolSO_2$ > Q, $TolSO_2$ >

Two experimentes were carried out, one of which was in the presence of a mixture of copper bronze and copper iodide.

No hydroquinone-di-p-toluenesulphonate was formed in either of these reactions.

1.2.5 - The Reaction of p-Toluenesulphonyl iodide with other quinones.

Reactions were carried out in the same manner as the reaction of p-toluenesulphonyl iodide with p-benzoquinone(1.2.1).

Results are summarized in the following table:

Quinone	Yield of di-ester
p-Benzoquinone	46.5%
Toluquinone	28.0%
p-Xyloquinone	12.0%
Thymoquinone	2.8%
Chloranil	2.4%
9,10-Phenanthraquinone	2.4%
m-Xyloquinone	0.00%
Duroquinone	0
9,10-Anthraquinone	0
1,2-Acenaphthaquinone	0

1.2.6 - Results

p-Toluenesulphonyl iodide was reacted with several quinones in the presence of copper bronze to yield di--p-toluenesulphonates.The reaction is probably a radical reaction by attack of sulphonyl radicals on the oxygen atoms of quinones.

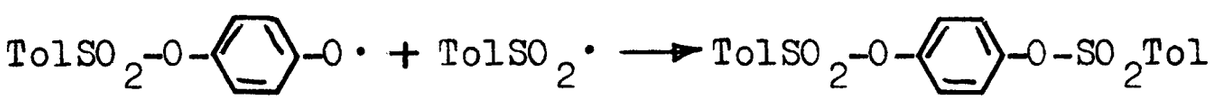
The mechanism proposed to the reaction is as shown next page:

$$TolSO_2I \rightleftharpoons TolSO_2\cdot + I\cdot$$

$$I\cdot + Cu \longrightarrow \text{Copper iodide}$$

$$TolSO_2I + Cu \longrightarrow TolSO_2\cdot + \text{Copper iodide}$$





1.2.7 - Relation between the redox potential of quinones and yields of reaction.

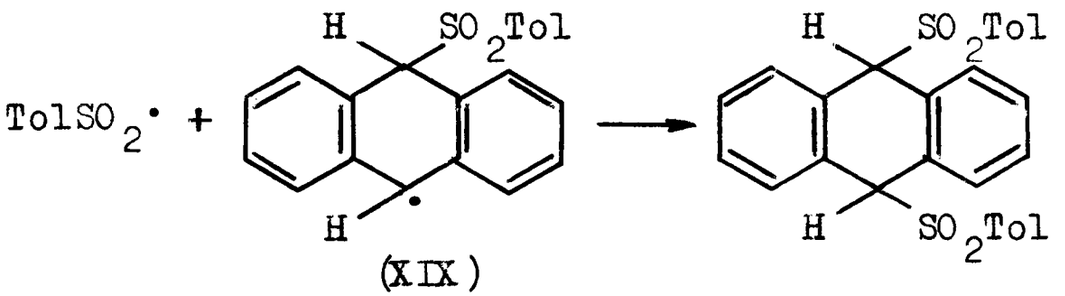
The reaction of p-toluenesulphonyl iodide with quinones in the presence of copper bronze gave:

Quinone	Di-ester %	Redox potential of quinone (volts)
p-Benzoquinone	46.5	0.711
Toluquinone	28.0	0.653
p-Xyloquinone	12.0	0.597
Thymoquinone	2.8	0.589
Chloranil	2.4	0.703
9,10-Phenanthraquinone	2.4	0.471
m-Xyloquinone	0.66	0.600
Duroquinone	0	0.466
9,10-Antraquinone	0	0.150
1,2-Acenaphthaquinone	0	--

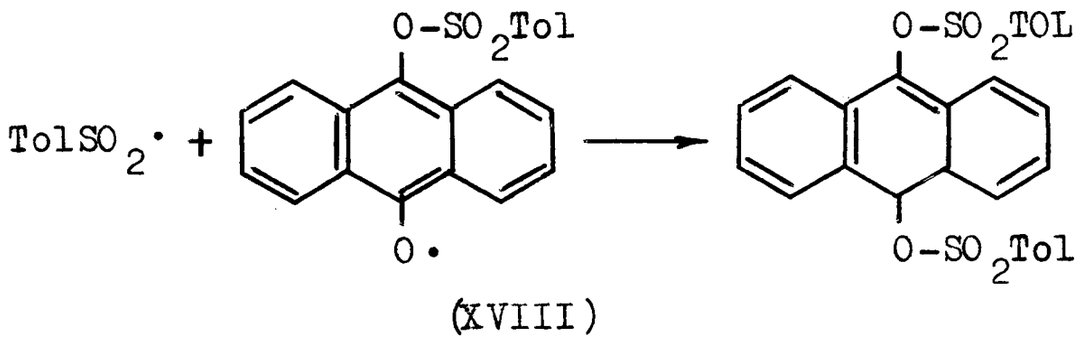
From examination of the results, it was found that quinones of higher redox potential are more reactiv towards p-tolylsulphonyl radicals than quinones of low redox potential. It may also be concluded that quinones with bulky groups vicinal to the oxygen atoms are also of low reactivity.

The influence of both effects can be better understood if the results were examined in groups(p.110, 111).

In group A the greater reactivity of p-benzoquinone(VIII) relatively to anthraquinone(IX) accords to the high redox potential of (VIII) and the small potential of (IX).The absence of (XVII) can not be ascribed to steric hindrance since product (XVI) is formed under similar conditions(p.115):



(XVI)

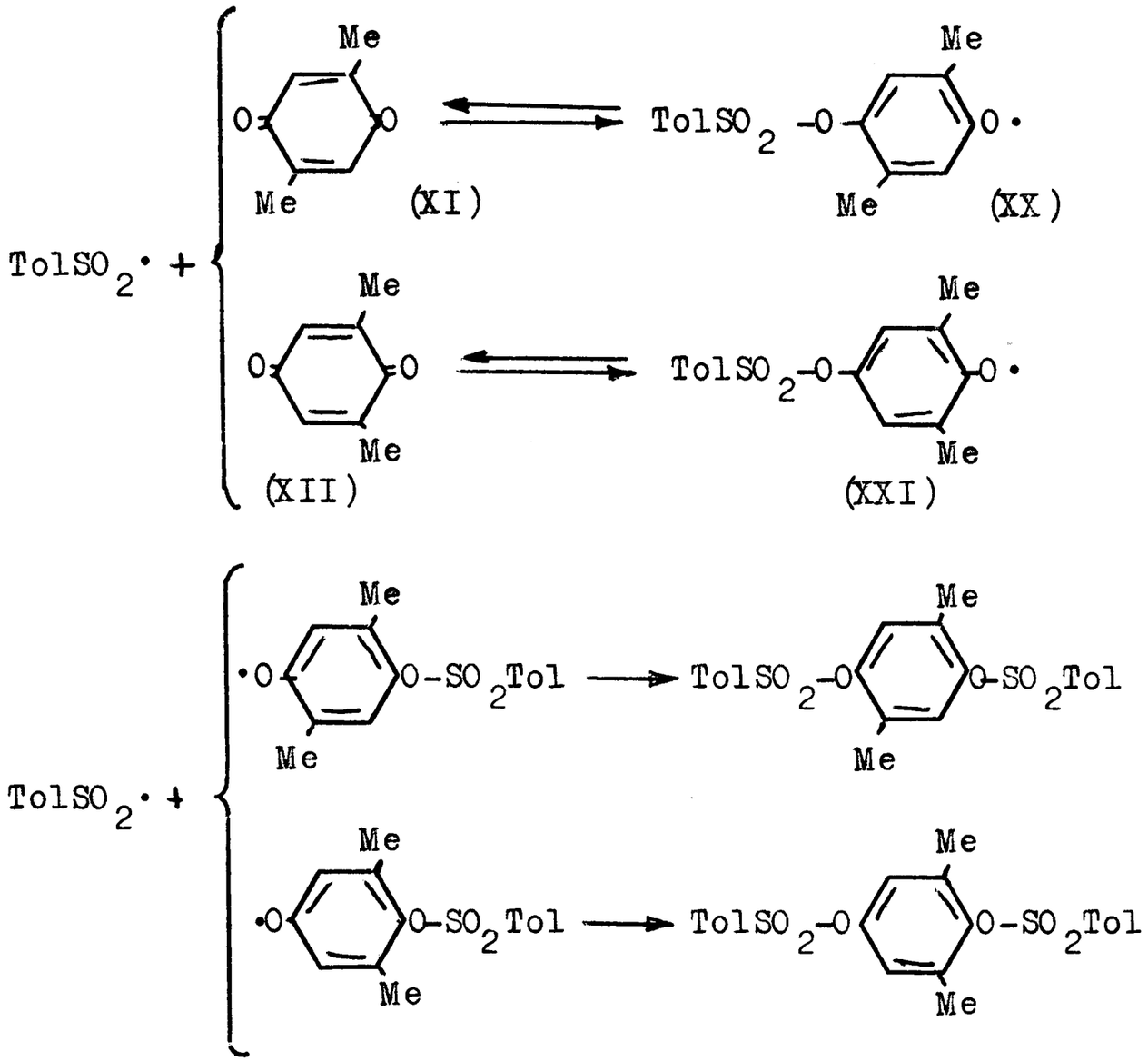


(XVII)

Attack on the radical (XVIII) should be sterically easier than on (XIX).

In group B the greater reactivity of (X) may be due to its greater redox potential.Steric effects should make the addition of the second tosyl group more difficult to (X) than to (IX).

The difference of reactivities of quinones (XI) and (XII) in group C may be explained on the basis of steric factors. If tolylsulphonyl radicals attack quinones (XI) and (XII) as shown next page:

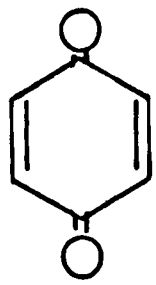
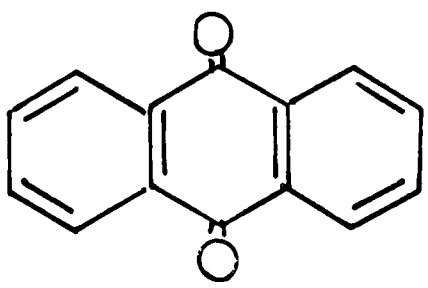


The attack by a second radical $TolSO_2\cdot$ on the phenoxy radicals (XX) and (XXI) would certainly be sterically more difficult in the case (XXI) than in (XX).

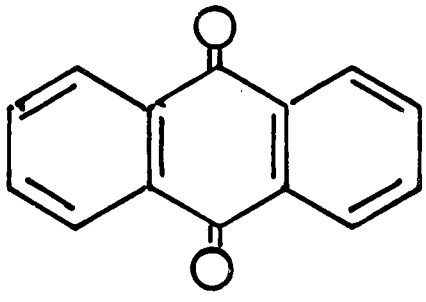
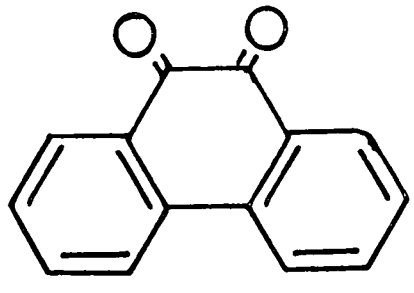
In goup D both effects(potential redox and steric hindrance) are present.

Chloranil(group E) is less reactive than toluquinone(XV) and p-xyloquinone(XI) which have both lower redox potential.Steric effects are probably present since both oxygen atoms in chloranil(XIV) are close to two chlorine atoms.

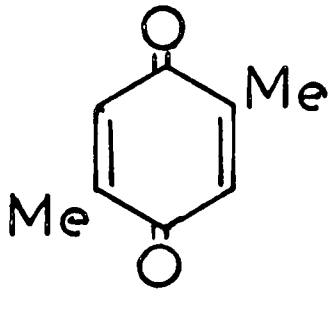
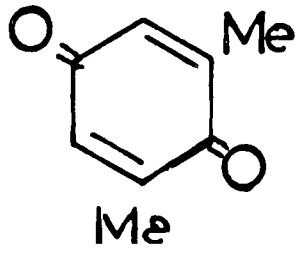
GROUP A

QUINONE	YIELD of di-ester	Redox potential of quinone(V)
 (VIII)	46.5	0.711
 (IX)	0.0	0.150

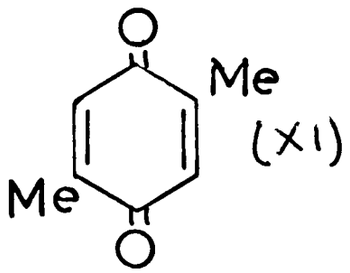
GROUP B

 (IX)	0.0	0.150
 (X)	2.4	0.471

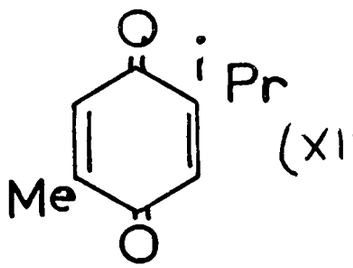
GROUP C

 (XI)	12.0	0.597
 (XII)	0.66	0.600

GROUP D

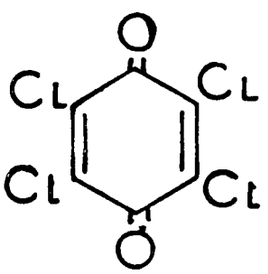


(XI) 12.0 0.597

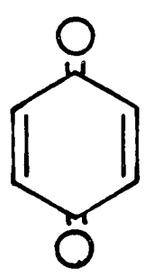


(XIII) 2.8 0.589

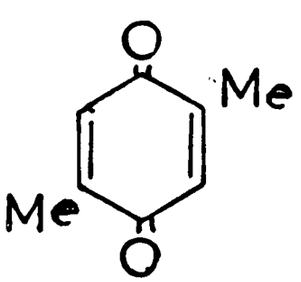
GROUP E



(XIV) 2.4 0.703



(XV) 2.8 0.653



(XI) 12.0 0.597

The unreactivity of duroquinone (tetramethyl-p-benzoquinone) may be due to its low redox potential and to the presence of two methyl groups shielding each oxygen atom.

The redox potentials used in page 107 were those of Aparicio and Waters[88] which have been measured in aqueous ethanol containing N-hydrochloric acid.

As shown by Kvalnes[159] these redox potentials are a good guide to the relative potentials in benzene.

In this discussion it is hoped that the relative magnitude of the potentials given at p.107 is not appreciably disturbed when carbon tetrachloride is substituted for benzene.

From the discussion on the previous pages it may be concluded that the highier the redox potentials of the quinones the more reactive they are towards free p-tolylsulphonyl radicals. It may also be concluded that shielding of the oxygen atoms of the quinone by methyl groups or by chlorine decreased the reactivity.

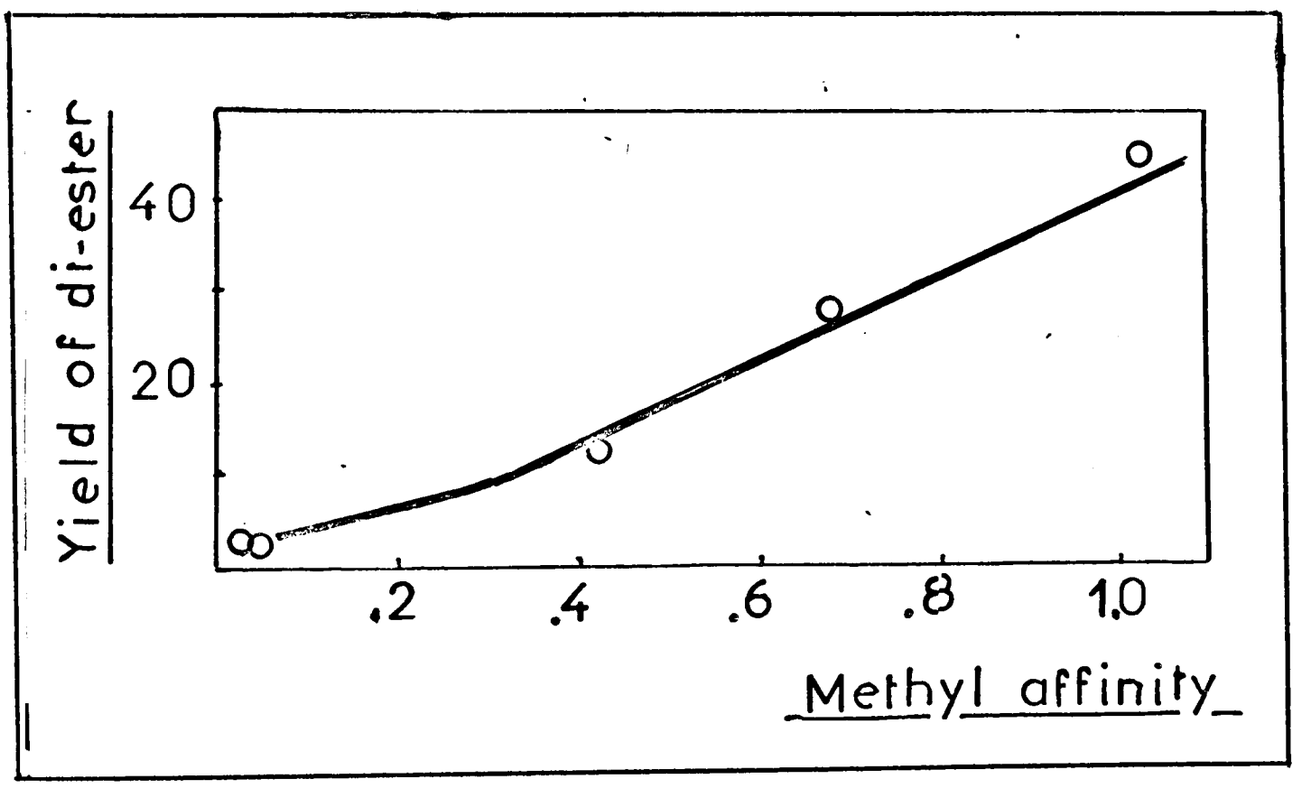
The reactivities of the various quinones towards these radicals were measured by the yields of di-esters, since these were the only products of the reaction.

1.2.8 - Relation between tthe yields of reaction and methyl affinities of quinones.

The relation between the methyl affinities as defined by Szwarc [96] and the yields of di-esters, $TolSO_2$-Q-O-SO_2TOL, is shown below:

Quinone	Di-ester	Methyl affinity
p-Benzoquinone	46.5%	1.00
Toluquinone	28.0%	0.68
Phenanthraquinone	2.4%	0.046
p-Xyloquinone	12.0%	0.41
Chloranil	2.4%	0.02

This is graphically illustrated as follows:



These results showed a reasonable agreement between these two sets of values. This is to be expected since Fueno and Furukawa [97] have shown that methyl radicals probably add first to the oxygen atoms of quinones.

The agreement between yields of di-esters and methyl affinities may be an indication that both reactions have the same nature, i.e., radical attack on the oxygen atoms of quinones.

1.3. Further indications of the free radical nature of reactions of p-toluenesulphonyl iodide.

1.3.1. Reaction of p-toluenesulphonyl iodide with aromatic hydrocarbons.

1.3.1.1. Reaction with anthracene.

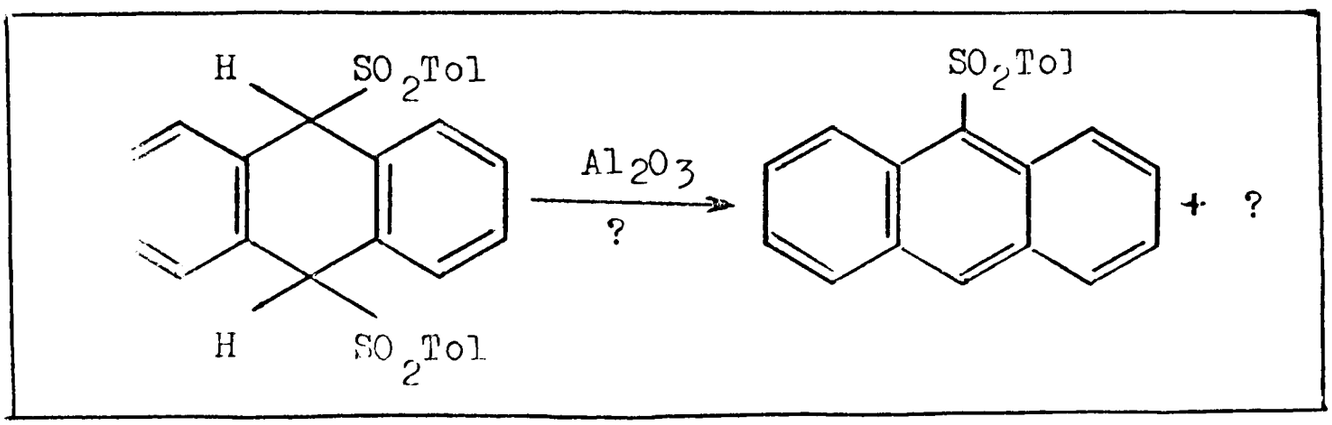
A - Reaction in the presence of copper bronze.

When p-toluenesulphonyl iodide was decomposed in benzene in the presence of copper bronze and anthracene, 9,10-di-p-tolylsulphonyl-9,10-dihydroanthracene (I) was obtained (22%).

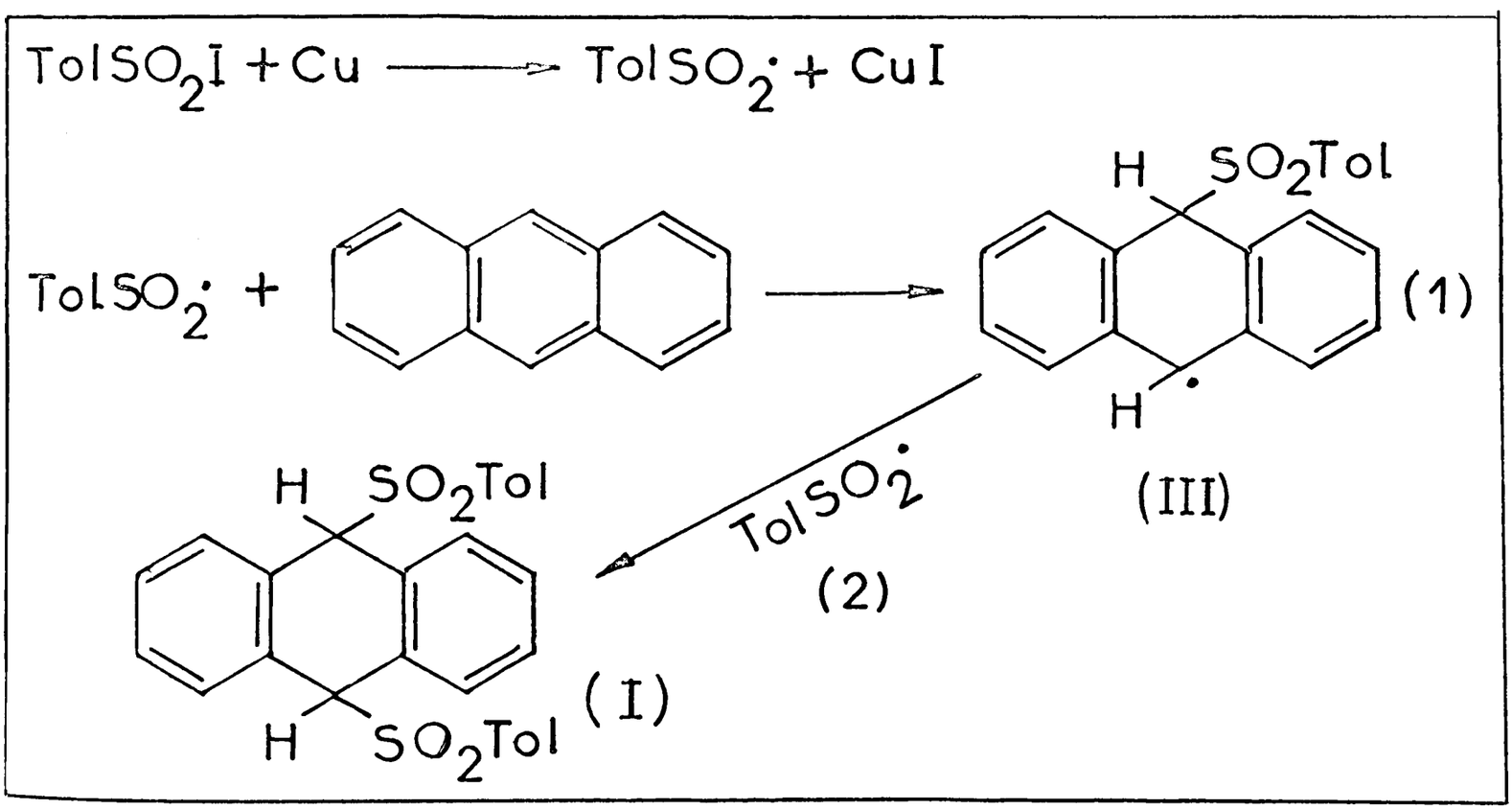
A further amount was obtained mixed with another compound but the mixture could not be separated by solvent extraction or chromatography.

Analysis of this mixture gave values close to that required for 9,10-di-p-tolylsulphonyl-9,10-dihydroanthracene. This indicated that either the mixture was largely (I) or a mixture of stereoisomers. When the chromatography of this mixture was attempted on alumina or silica gel, the substitution product 9-p-tolylsulphonylanthracene (II) was formed. This product was also formed when (I) was passed

through alumina:

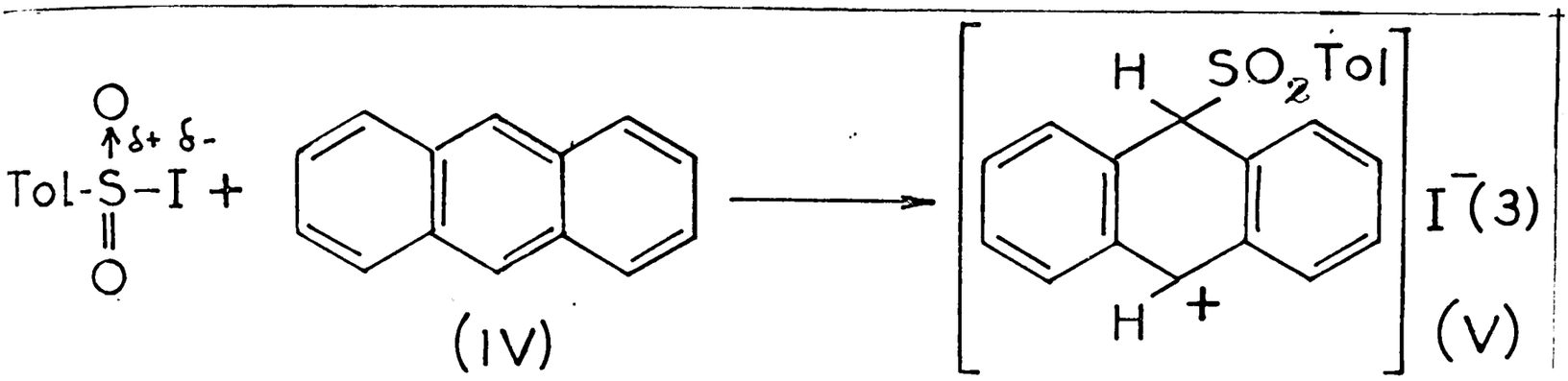


The formation of (I) may be explained by a radical addition process similar to many other reactions of free radicals with anthracene:

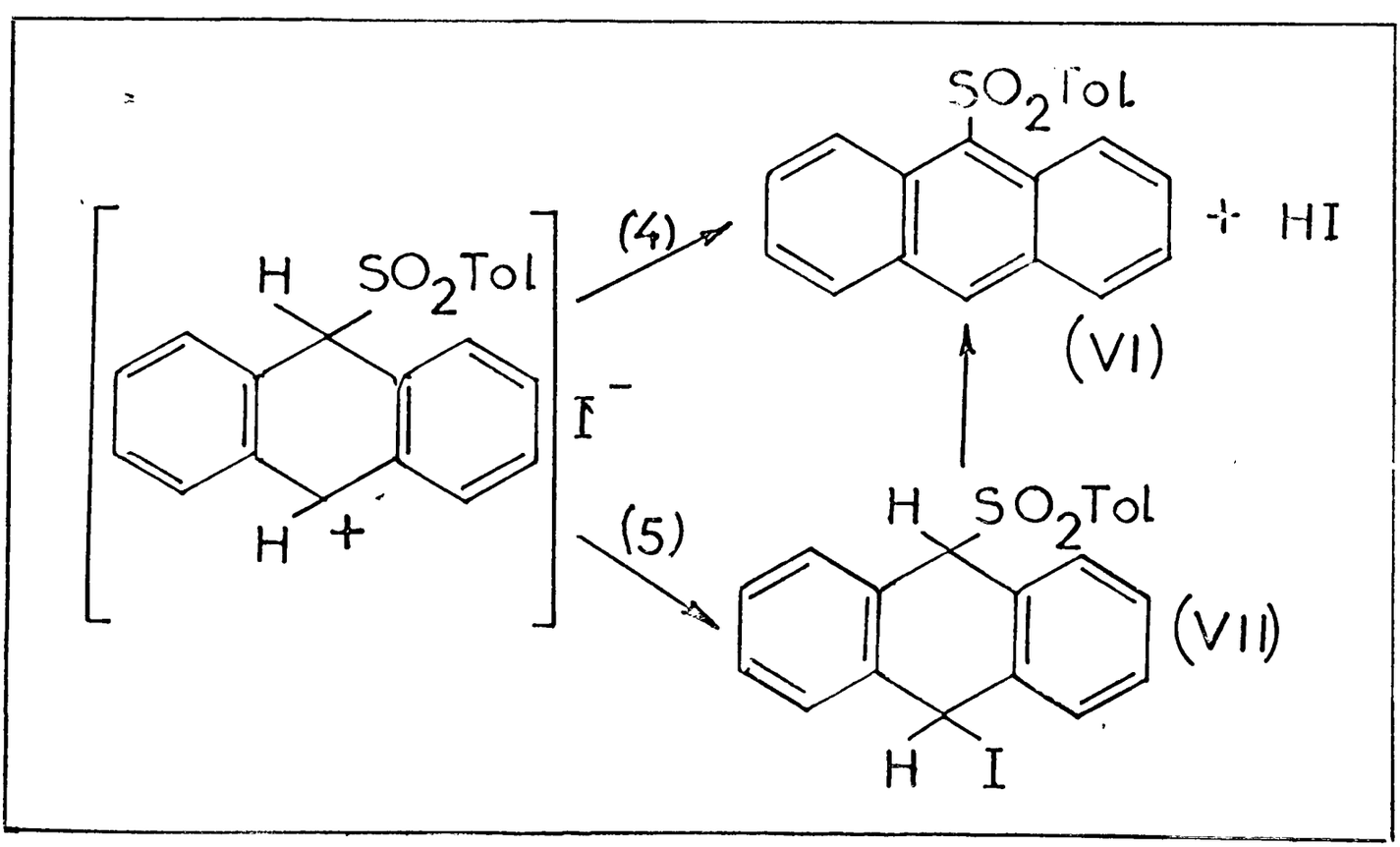


If the sulphonyl iodide is polarized as (IV) attack on the

meso position would give:



This intermediate carbonium ion (V) would probably react with iodide ion to give a substitution product (VI) or an adduct (VII):



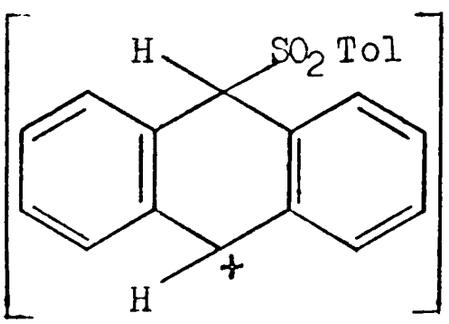
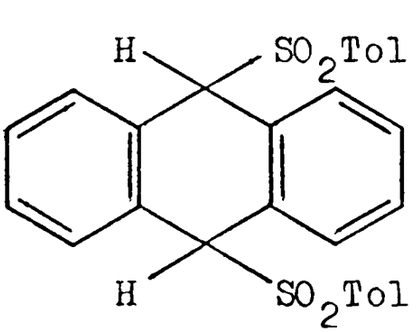
Adduct (VII) could lose hydrogen iodide to yield the substitution product (VI). These would be obtained if attack on the anthracene molecule was by the sulphonyl cation, $TolSO_2^+$, or by the sulphonyl iodide $TolSO_2^+I^-$. The non-occurrence of products (VI) or (VII) in the reaction of the sulphonyl iodide with anthracene is an indication that mechanism (3) is not involved.

However, the presence in solution of the sulphinate anion, $TolSO_2^-$, may explain the formation of the addition product (I)

(6) $TolSO_2I + Cu \longrightarrow TolSO\overset{\delta-}{O}\!-\!\overset{\delta+}{Cu} +$ Copper iodide

(7) $TolSO_2^{\delta-}Cu^{\delta+} \longleftrightarrow TolSO_2^- Cu^+$

(8) $TolSO_2^- \longleftrightarrow TolS^-(=O)_2$

(9) I^- [] $+ TolS^-(=O)_2 Cu^+ \longrightarrow$  $+ CuI$

(I)

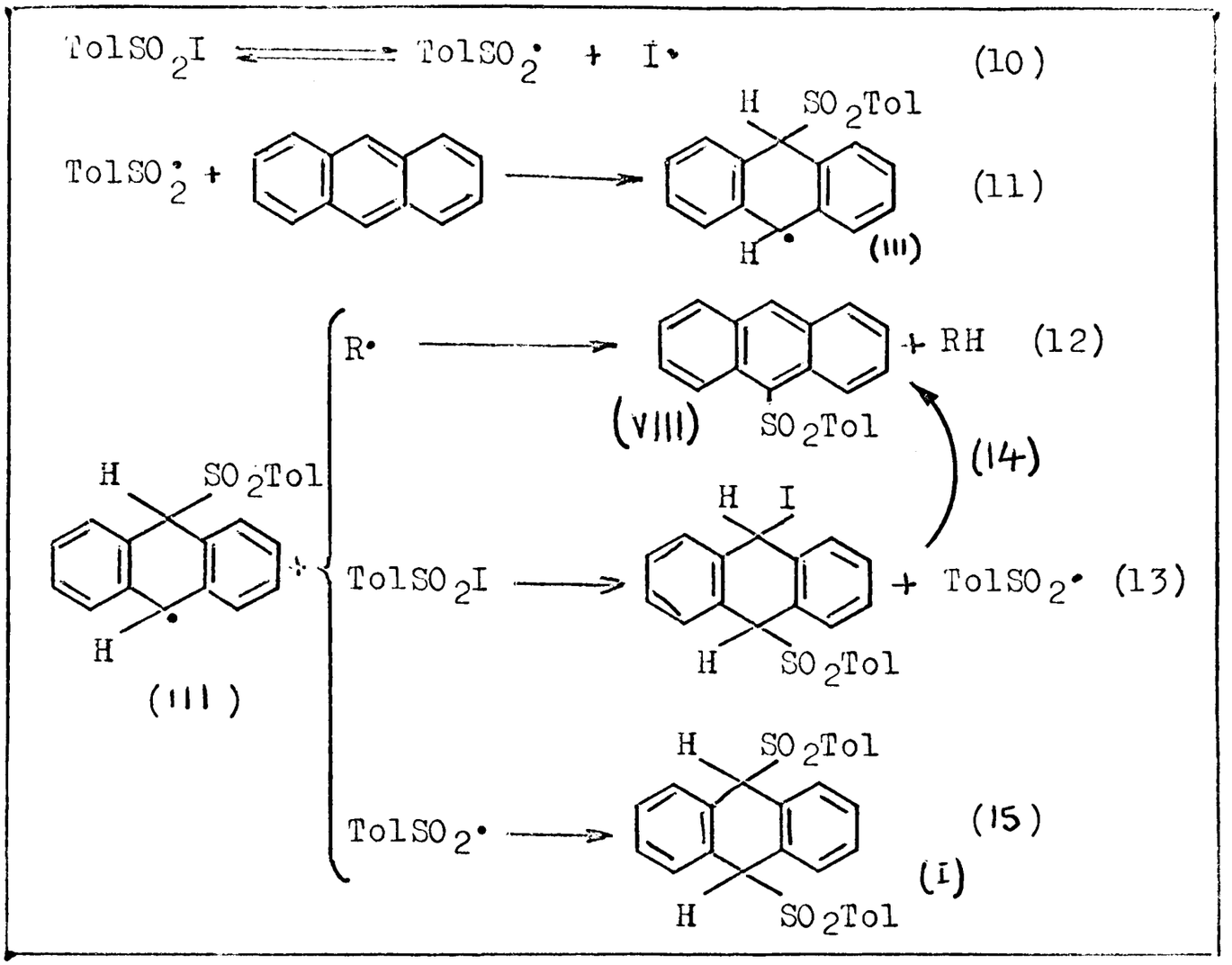
Thus the formation of (I) is not unequivocally diagnostic of a homolytic addition of $TolSO_2^{\bullet}$ radicals.

B - Reaction in the absence of copper bronze

When p-toluenesulphonyl iodide and anthracene were refluxed in benzene for eight hours, 9,10-di-p-tolylsulphonyl-9,10-dihydroanthracene (17%) and 9-p-tolylsulphonylanthracene (8.8%) were formed.

9-p-tolylsulphonyl anthracene (VIII) was not formed in the presence of copper bronze.

If the reaction of the sulphonyl iodide with anthracene is a radical reaction this fact may be explained as follows:



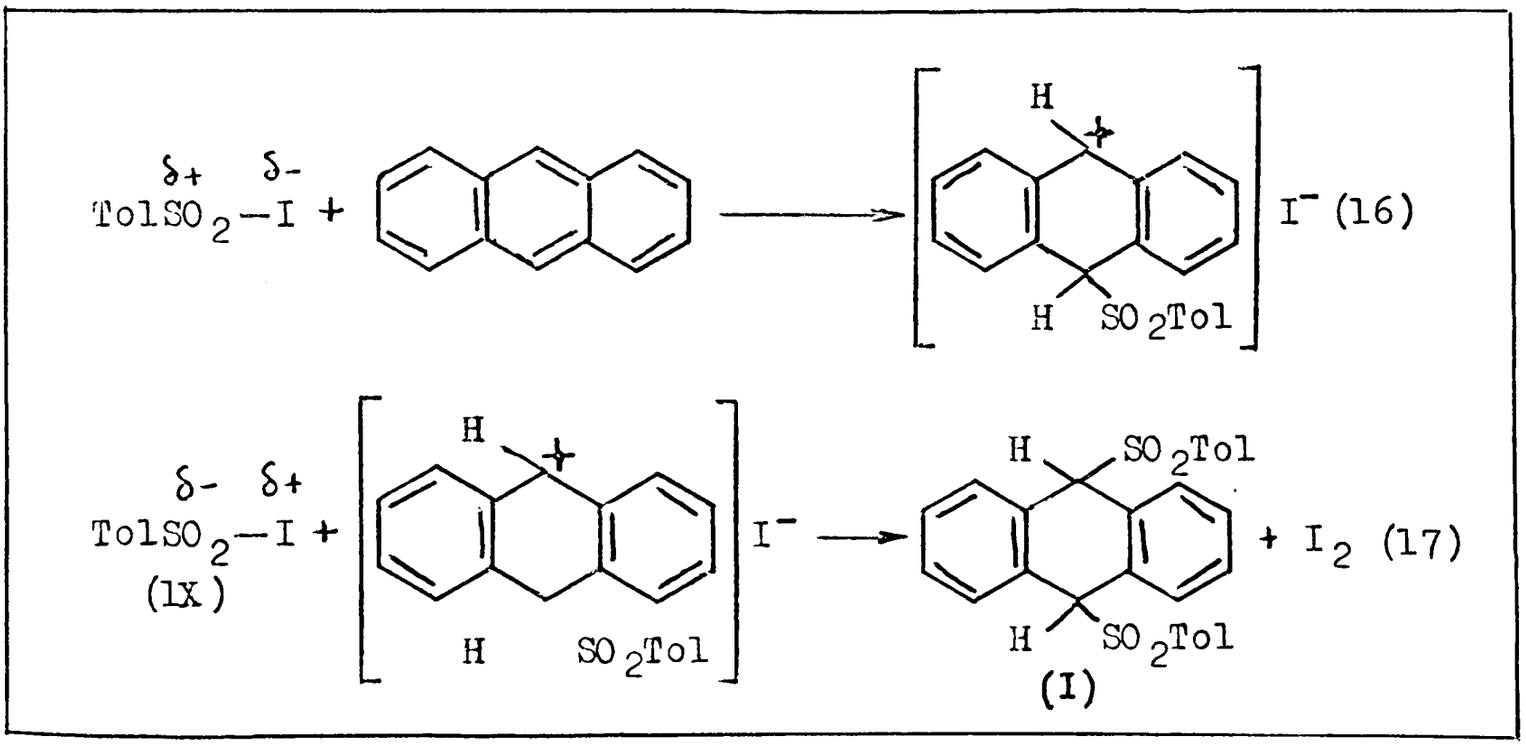
i.e., the sulphonyl iodide may decompose to small extent as process (10) and attack of the sulphonyl radical on anthracene (11) would yield intermediate (III). This intermediate, by reaction with any radical R· in solution could give 9-p-tolylsulphonylanthracene (VIII), (equation 12). Radical R· could be p-tolylsulphonyl, $TolSO_2$·, p-tolylsulphonyloxy, $TolSO_2$-O· or atomic iodine. In the

presence of copper bronze there is a competition between radical (III) and copper bronze for the radical R• .

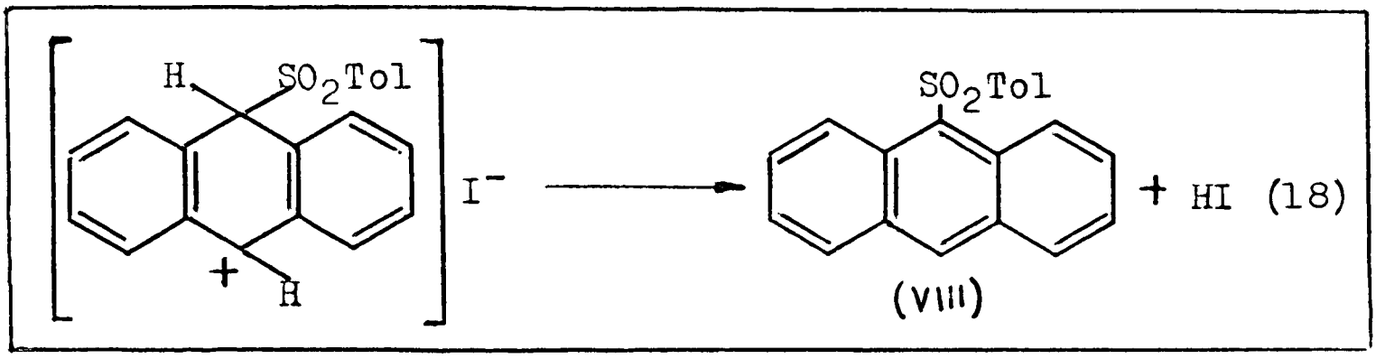
Formation of copper sulphonate in the decomposition of the sulphonyl iodide and sulphonic acid in the reaction of the sulphonyl iodide with cumene (p.127) is an indication that R• could be p-tolylsulphonyl oxy radical, $TolSO_2-O^{\bullet}$.

Reaction (13) could also be involved but it should also occur in the reaction using copper bronze.

If the reaction is an heterolytic process, the formation of the reaction products is more difficult to explain. In this case product (I) only could be formed if there was in solution anionic and cationic sulphonyl species:



Formation of 9-p-tolylsulphonyl antracene (VIII) by a heterolytic process may occur as shown below:



However if this process operates in the absence of copper bronze why does it not operate in the presence of the metal? It is plausible that copper or its salts could facilitate (but not inhibit) this heterolytic attack:

$$TolSO_2I + Cat. \longrightarrow [TolSO_2^+]\,[Cat.\bar{I}]$$

(in which Cat. could be the metal or its salts).

Some Friedel-Crafts reactions of sulphonyl chlorides were reported but these were substitution reactions and no addition product like (I) was obtained.[173,174] However, reactions of free radicals with anthracene usually give addition products across the meso positions.

The lack of formation of dianthryl dimers cannot be taken as a proof of non-radical reactions. In non-polar solvents like benzene, heterolytic decomposition of sulphonyl

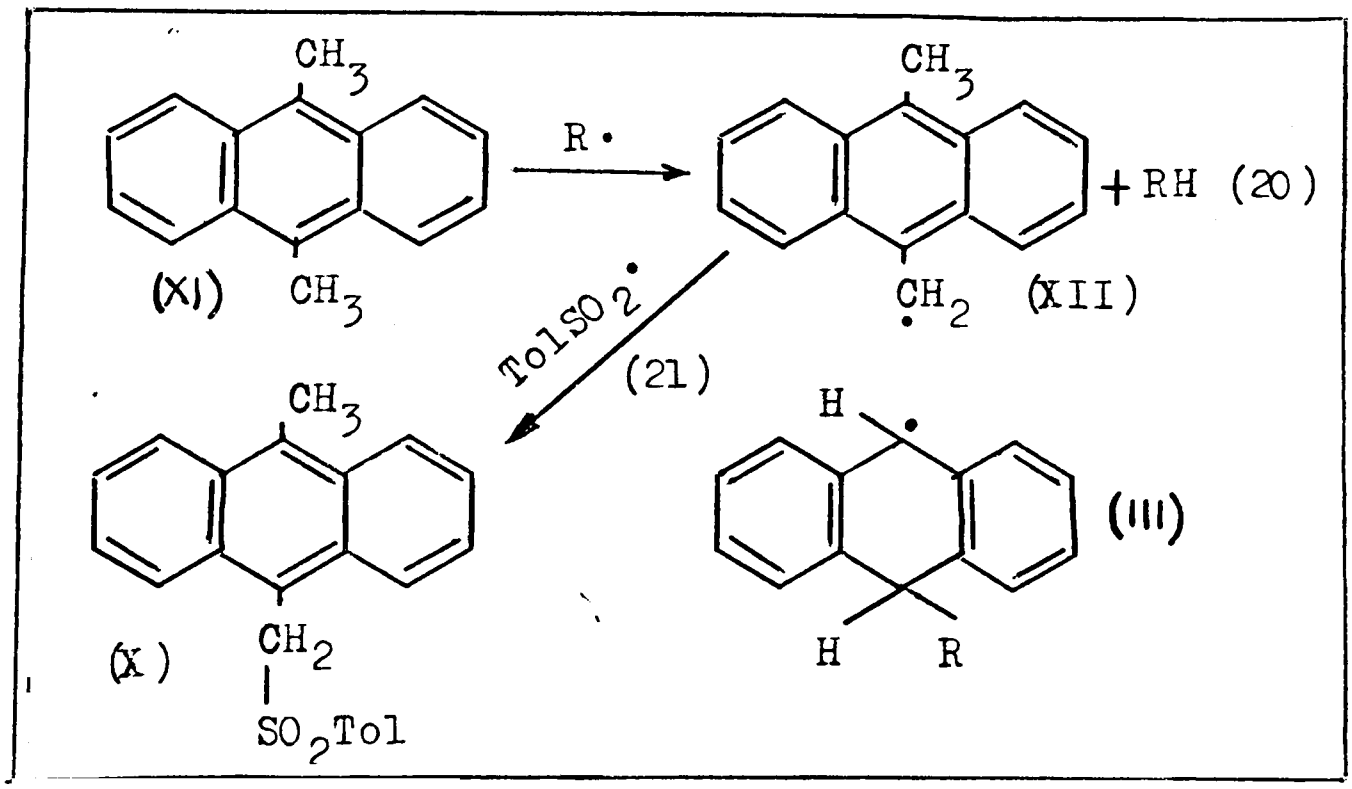
halides are very unlikely; sulphonyl cations are only formed under very special conditions , for example in the presence of silver perchlorate.[175]

1.3.1.2. Reaction with 9,10-dimethylanthracene.

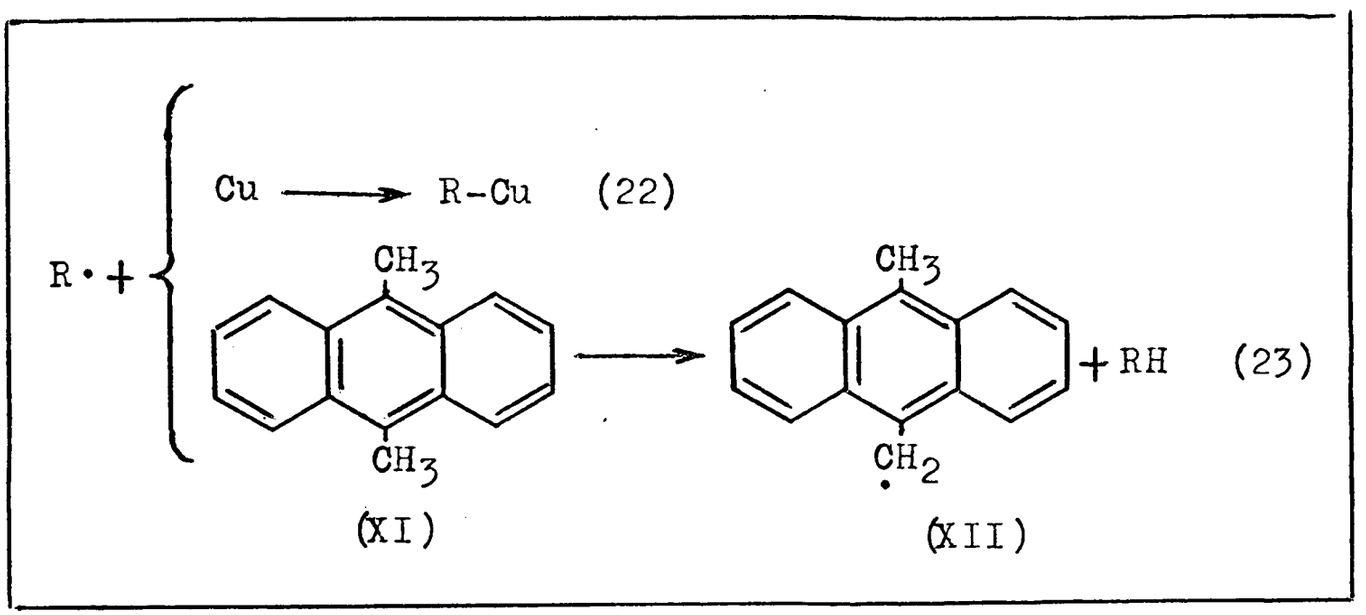
An excess of p-toluenesulphonyl iodide and 9,10-dimethyl-anthracene were refluxed in benzene for five hours in the presence of copper bronze.

p-Tolylsulphonyl-(10-methyl-9-anthryl) methane was formed (49%) and no other anthracene derivative was obtained.

The formation of this product is a strong indication of a radical reaction, since 9,10-di-methylanthracene reacts with acyl halides and acid anhydrides under Friedel-Crafts conditions[160] to give substitution products on the aromatic nucleus in the 2-position. This reaction also indicates the presence in solution of any radical which is able to abstract hydrogen from the side chain:



Hydrogen abstraction from the side chain of (XI) must be easier than from the radical (III) because this only occurred in the absence of copper bronze when no competition to R• existed. Hydrogen abstraction from the side chain of (XI) occurred even in the presence of copper bronze:

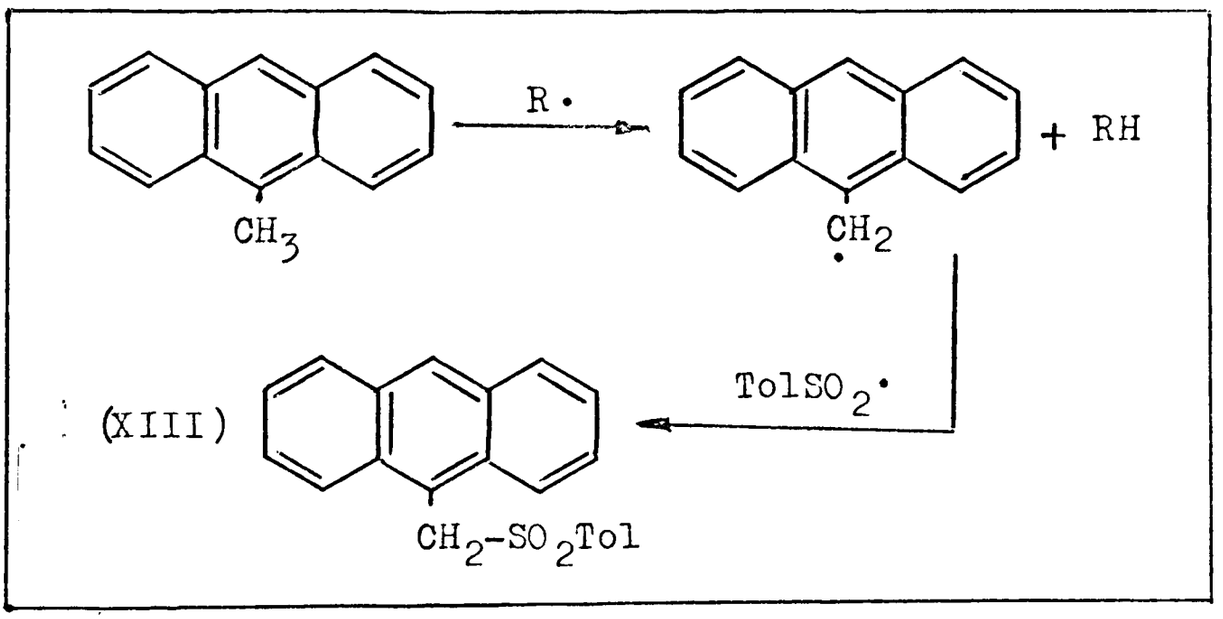


Reaction (23) is more favourable than reaction (22).

1.3.1.3. Reaction with 9-methylanthracene

9-Methylanthracene reacted with p-toluenesulphonyl iodide in the presence of copper bronze to yield p-tolylsulphonyl-9-anthrylmethane (35.8%), (XIII). A Friedel-Crafts attack by the sulphonyl cation on the 9-methylanthracene molecule should certainly give a substitution product on the 10 position [61].

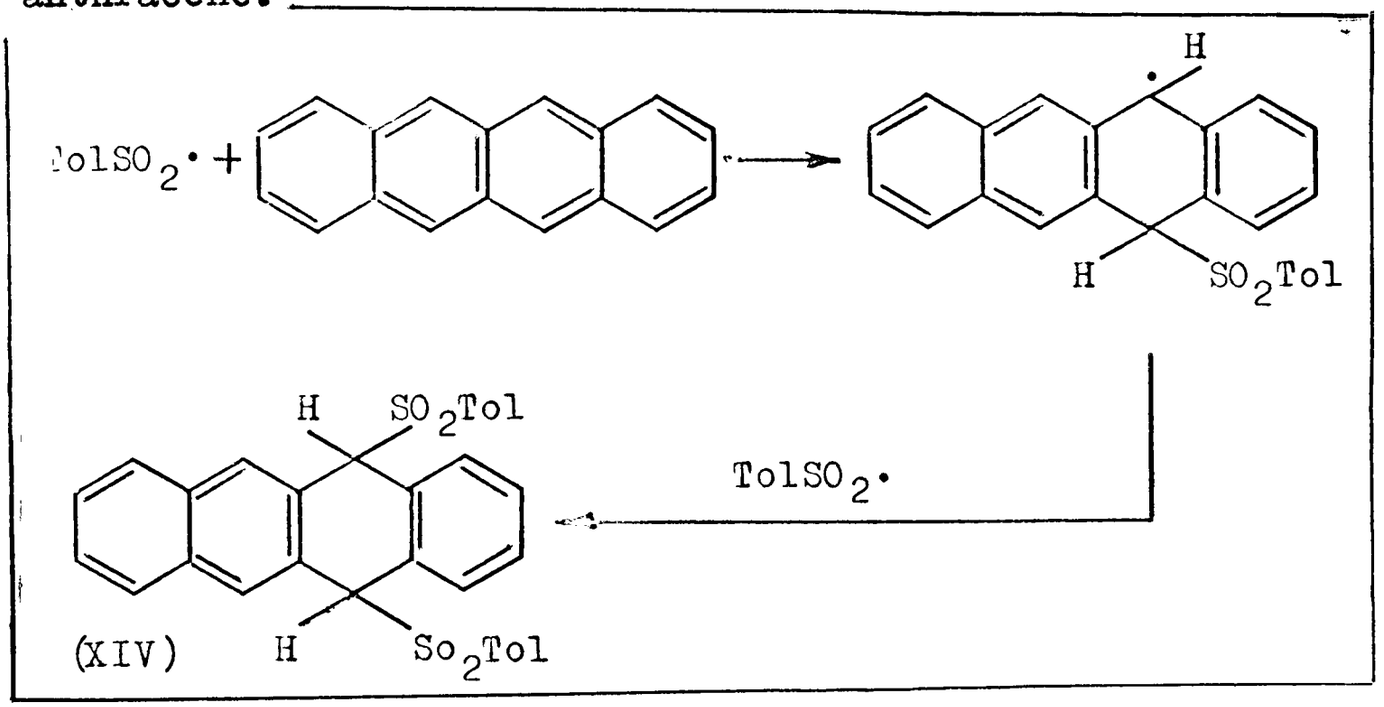
The mechanism proposed to explain the formation of product (XIII) is:



This is further proof that any free radical that can abstract hydrogen from the side chain could exist in solution.

1.3.1.4. Reaction with 2,3-benzanthracene.

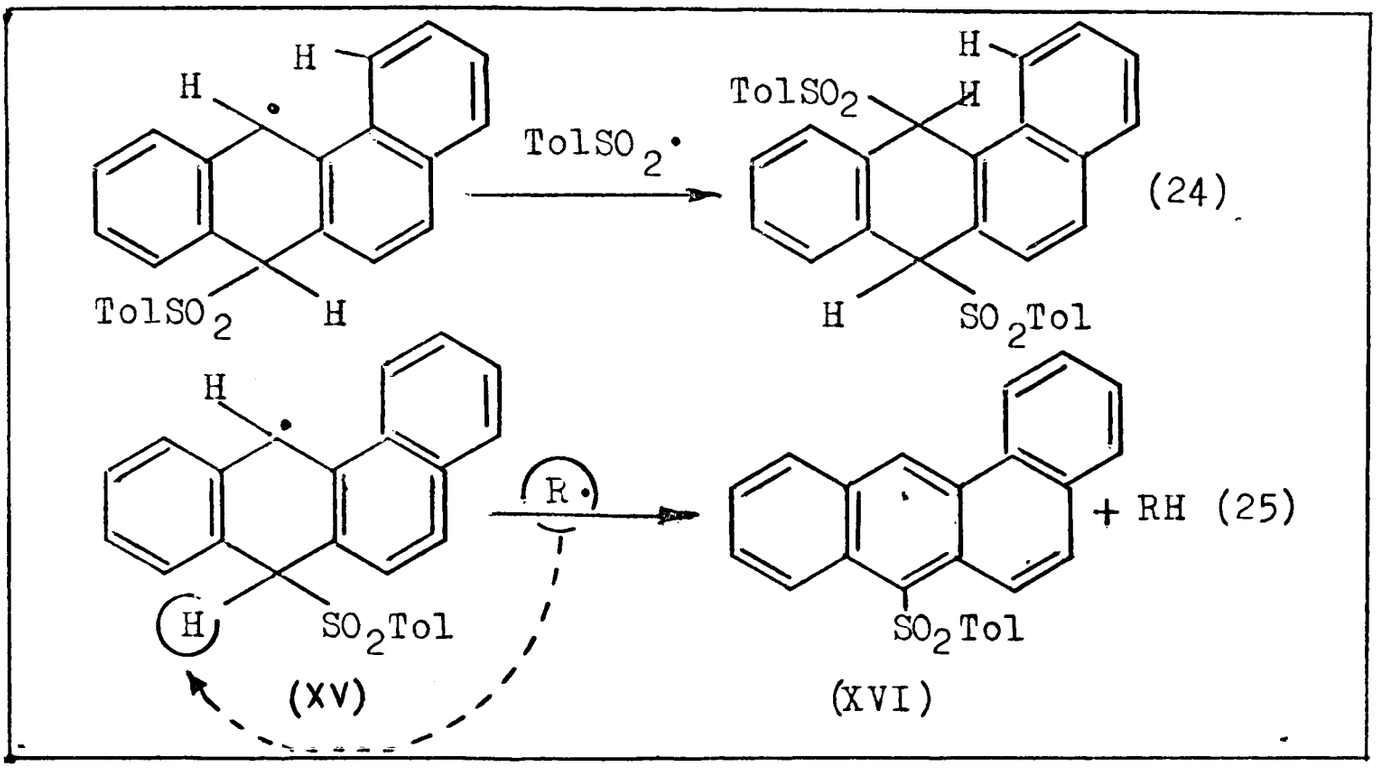
p-Toluenesulphonyl iodide, 2,3-benzanthracene and copper bronze were refluxed together in benzene for five hours. The only product of reaction was indicated by analysis, i.r. u.v. and n.m.r. to be very likely 9,10-di-p-tolylsulphonyl-9,10-dihydro-2,3-benzanthracene (XIV). Yield 61.4%. The mechanism suggested to explain the formation of this addition product is the same as for the reaction with anthracene:



1.3.1.5. Reaction with 1,2-benzanthracene

p-Toluenesulphonyl iodide was refluxed in boiling benzene in the presence of copper bronze and 1,2-benzanthracene, but no addition or substitution on the aromatic

hydrocarbon occurred. Steric hindrance could inhibit the addition reaction (24) but not the substitution reaction (25):



The experiment was then carried out in the absence of copper bronze. It was expected that under these different conditions no competition could then occur between radical (XV) and copper bronze for the radical R·, and (XVI) should be obtained. Again no products were isolated.

1.3.1.6. Reactions with phenanthrene and cumene

When these aromatic hydrocarbons were refluxed in benzene in the presence of p-toluenesulphonyl iodide and copper bronze, only products from the decomposition of the

sulphonyl iodide could be detected.

Since the 9,10-positions of phenanthrene are known to be inactive to radical attack but readily attacked by cationoid reagents[132], the participation of molecules $TolSO_2^+ I^-$ in reactions 1.3.1.1. → 1.3.1.4. is unlikely. This appears to favour the view that those reactions are of a free radical nature.

p-Toluenesulphonyl iodide was then decomposed in the presence of copper bronze in cumene solution. It was expected that some bicumyl could be formed by the process

$$PhCHMe_2 + R\cdot \longrightarrow Ph\dot{C}Me_2 + RH$$

$$2\ Ph\dot{C}Me_2 \longrightarrow PhC(Me_2)C(Me_2)Ph$$

but it could not be detected in the reaction mixture. However p-toluenesulphonic acid was obtained when the copper iodide formed in the reaction was extracted with water. This solution was light blue and contained a copper salt. Whether the sulphonic acid was formed in reaction (26) or by hydrolysis (27) of the copper sulphonate was not determined:

$$2\ TolSO_2^{\bullet} \longrightarrow TolSO_2\text{-}O^{\bullet} + TolSO^{\bullet}$$

$$TolSO_2\text{-}O^{\bullet} + PhC(H)Me_2 \longrightarrow TolSO_2\text{-}OH + Ph\dot{C}Me_2 \qquad (26)$$

or

$$(TolSO_3)_2Cu + 2H_2O \longrightarrow 2TolSO_3H + Cu(OH)_2 \qquad (27)$$

However it seems that the sulphonyloxy radical, $TolSO_2\text{-}O\cdot$, should be present in solution to form either sulphonic acid or its copper salt. Formation of sulphonic acid by reaction of the sulphonyl iodide with water is very unlikely because special precautions were always taken to keep all solutions dry.

1.3.1.7. Conclusion

p-Toluenesulphonyl iodide reacts with aromatic hydrocarbons yielding the following products:

Hydrocarbon	Products
Anthracene*	9,10-di-p-tolylsulphonyl- -9,10-dihydroanthracene (22%)
Anthracene**	9,10-di-p-tolylsulphonyl- -9,10-dihydroanthracene (17%) 9-p-tolylsulphonylanthracene (8.8%)
2,3-Benzanthracene*	9,10-di-p-tolylsulphonyl- -9,10-dihydro-2,3-benzanthracene (61.4%)

9-Methylanthracene*	p-tolylsulphonyl-9-anthrylmethane (35.8%)
9,10-Dimethylanthracene*	p-tolylsulphonyl-9-(10-methyl-anthryl)methane (49%)

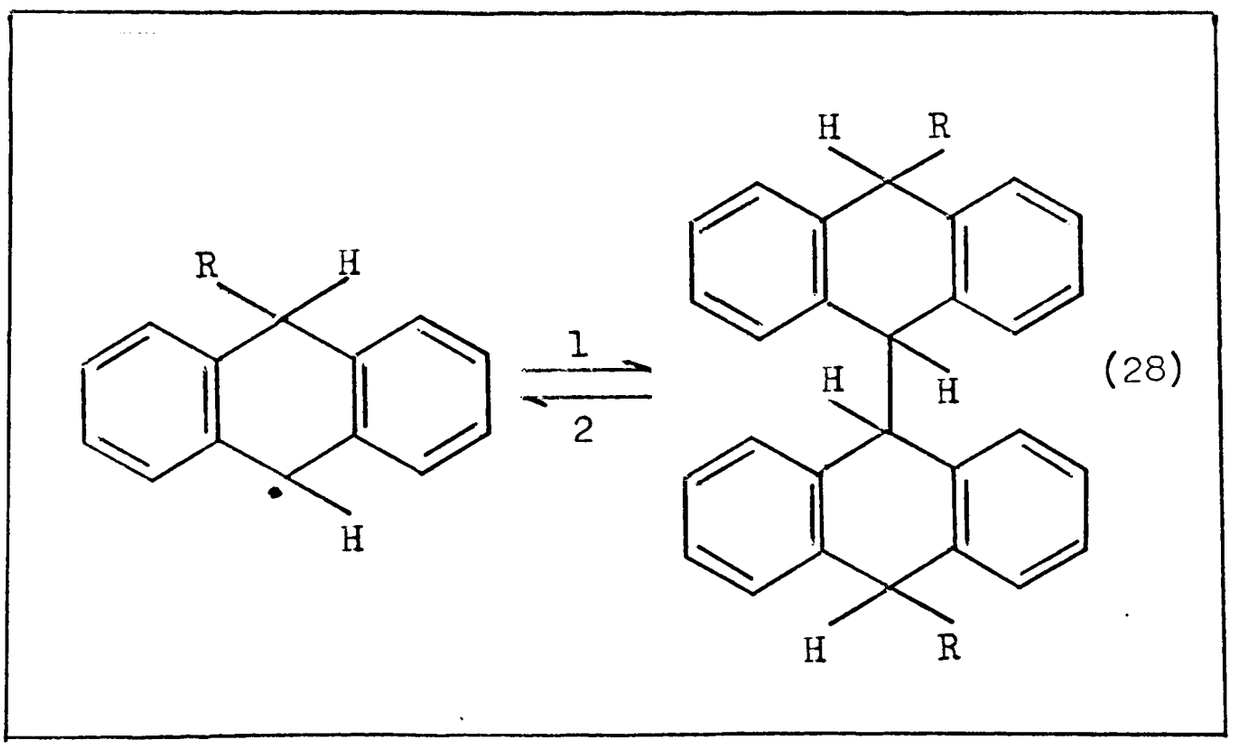
Notes

* Reaction in the presence of copper bronze.

** Reaction in the absence of copper bronze.

1,2-Benzanthracene, phenanthrene and cumene did not react.

No dianthryl product was found in the reaction mixtures, this however does not indicate the absence of free anthryl radicals, since the reversible reaction (28) was found to take place in other free radical reactions of anthracene:[122,134]



(28)

Reaction (1) is favoured by low temperatures.[122,134]

The reaction products of these reactions are better explained by assuming free radical mechanisms, shown previously (p.120). Reactions with 9-methyl- and 9,10-dimethylanthracene can only be explained by hydrogen abstraction on the side chain and are a good evidence for radical reactions.

The absence of cationoid species in these reactions is indicated by the failure to react with phenantrene, which is more readily attacked by cationoid reagents than by free radicals.[132]

The participation of anionic particles in the reaction mixture in the absence of copper bronze is unlikely.

1.3.2. Reaction of p-toluenesulphonyl iodide with acrylonitrile.

A - Reaction in the presence of copper bronze

p-Toluenesulphonyl iodide, a small excess of acrylonitrile and copper bronze were refluxed in carbon tetrachloride for three hours.

The addition product, 2-iodo-3-p-tolylsulphonylpropionitrile (XVII) was formed (62.5%) but no other product could be

isolated. The adduct (XVII) may be formed by a radical mechanism (28) or by an ionic mechanism (29):

(28) $TolSO_2I + Cu \longrightarrow TolSO_2\cdot$ + copper iodide

$TolSO_2\cdot + CH_2 = CH\text{-}CN \longrightarrow TolSO_2\text{-}CH_2\text{-}\dot{C}H\text{-}CN$

$TolSO_2\text{-}CH_2\text{-}\dot{C}H\text{-}CN + TolSO_2I \longrightarrow TolSO_2CH_2CHICN + TolSO_2\cdot$ (XVII)

The heterolytic addition would involve anionic species, $TolSO_2^-$, since the sulphonyl cation would be attacked at the α carbon atom:

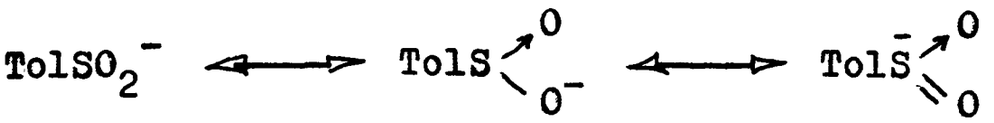
$$CH_2{=}CH\text{-}CN \xrightarrow{TolSO_2^+ I^-} \underset{\substack{\beta \quad \alpha \\ I \quad SO_2Tol}}{CH_2\text{-}CH\text{-}CN}$$

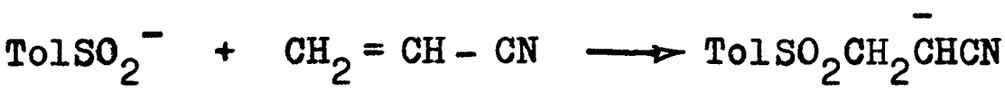
$$CH_2{=}CH\text{-}CN \xrightarrow{TolSO_2^- I^+} \underset{\substack{\beta \quad \alpha \\ TolSO_2 \quad I}}{CH_2\text{-}CH\text{-}CN}$$

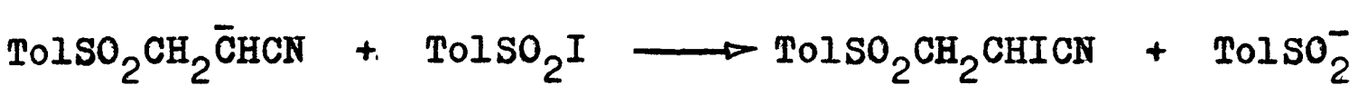
The presence of anionic species, $TolSO_2^-$, might be due to the presence of copper bronze and the heterolytic mechanism can then be:

(29) $TolSO_2I + 2Cu \longrightarrow TolS(=O)(O\text{-}Cu)$ + copper iodide

$TolSO_2Cu \rightleftharpoons TolSO_2^- + Cu^+$



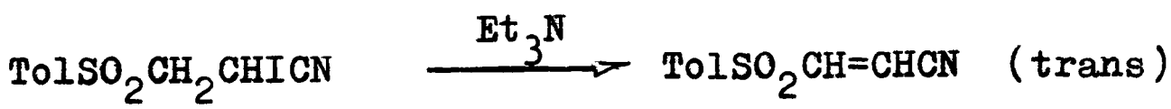




(XVII)

B - Reaction in the absence of copper bronze at room temperature

A solution of p-toluenesulphonyl iodide and acrylonitrole (small excess) in ether was left at room temperature for about twenty hours. No special precautions were taken to protect the solution from the light. The addition product (XVII) was separated from the reaction mixture (87%). This product was transformed into the ethylenic derivative by elimination of hydrogen iodide:



This reaction B showed that copper bronze was not necessary to initiate the reactiom. It also showed that participation of anionic species $TolSO_2^-Cu^+$ can be excluded.

The smaller yield of reaction A is probably due to:

a) Competition between copper bronze and radical (XVIII):

$$TolSO_2CH_2\dot{C}HCN \quad (XVIII) + TolSO_2I \longrightarrow \text{Adduct (XVII)} + TolSO_2\cdot$$

$$Cu + TolSO_2I \longrightarrow \text{Copper iodide} + TolSO_2\cdot$$

b) One of the steps in mechanism (28) is exothermic and reversible, and favoured by low temperatures.

C - Reaction in the presence of aluminium chloride

The heterolytic addition of p-toluenesulphonyl iodide and chloride, and benzenesulphonyl chloride was attempted. If the addition could be carried out, the sulphonyl group should be attached to the α-carbon atom.

In the first experiment p-toluenesulphonyl iodide and aluminium chloride were used. A small amount of addition product (XVII) was formed (7.5%). p-Toluenesulphonyl chloride was then used but no adduct could be detected in the reaction mixture. An improved method was attempted by using liquid benzene sulphonyl chloride and aluminium chloride in the absence of another solvent,[162] but no reaction occurred.

In all casex it was expected that the following reaction takes place:

$$RSO_2X + AlCl_3 \longrightarrow [RSO_2^+][AlCl_3X^-]$$

$$[RSO_2^+][AlCl_3X^-] + CH_2{=}CH{-}CN \longrightarrow$$

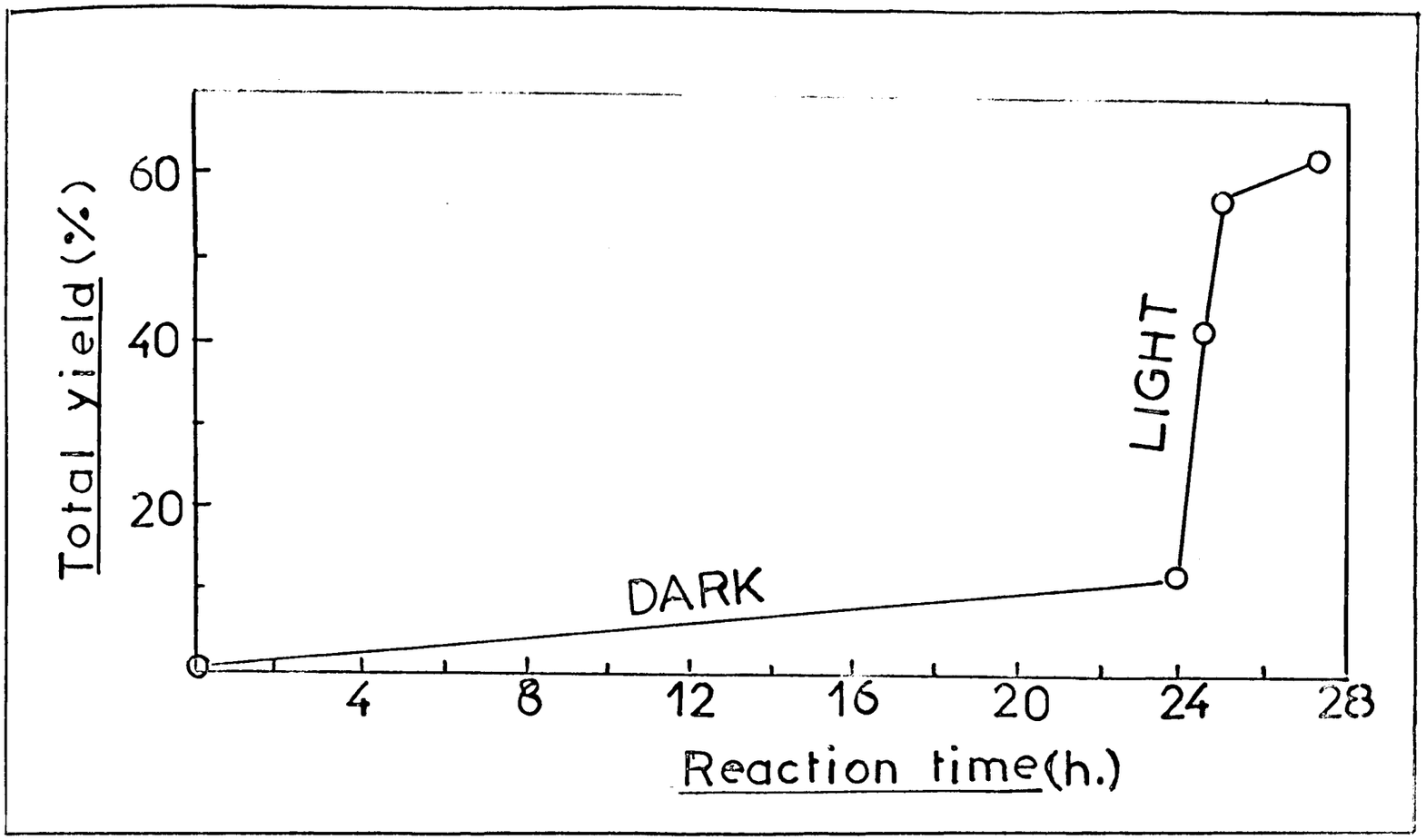
$$\longrightarrow CH_2X{-}\underset{\displaystyle SO_2R}{\underset{|}{CH}}{-}CN + AlCl_3$$

D - Reaction of p-toluenesulphonyl iodide with acrylonitrile in the absence of light.

When p-toluenesulphonyl iodide and acrylonitrile were dissolved in ether and left in the dark for twenty four hours, 11.8% of addition product was obtained, and separated by filtration. After leaving the filtrate in the light for half an hour a further yield was obtained. This was separated for further intervals of time; results are summarized below:

Total Reaction Time	Total Product Collected
24 h. (dark)	11.8%
24½ h. (½ h. in light)	41.8%
25 h. (1 h. in light)	57.8%
27½ h. (3½ h. in light)	63.0%

This is graphically illustrated as follows:



These results indicated the initiating process of the free radical addition of p-toluenesulphonyl iodide to acrylonitrile is very likely an homolytic decomposition by light:

$$TolSO_2I \xrightarrow{h\nu} TolSO_2\cdot + I\cdot$$

The formation of some addition product in the dark may be due to the presence of peroxides in the commercial acrylonitrile and in the ether. Initiation of the chain reaction in the absence of light could be carried out by either of the processes (30) or (31):

$$(30)\begin{cases} R\text{-}O\text{-}O\text{-}R \longrightarrow 2RO\cdot \\ R\text{-}O\cdot + TolSO_2I \longrightarrow ROI + TolSO_2\cdot \end{cases}$$

$$(31)\begin{cases} RO\cdot + CH_2{=}CH\text{-}CN \longrightarrow RO\text{-}CH_2\text{-}\dot{C}H\text{-}CN \\ RO\text{-}CH_2\text{-}\dot{C}H\text{-}CN + TolSO_2I \longrightarrow RO\text{-}CH_2CHICN + TolSO_2\cdot \end{cases}$$

E - Reaction in the absence of light in the presence of inhibitor

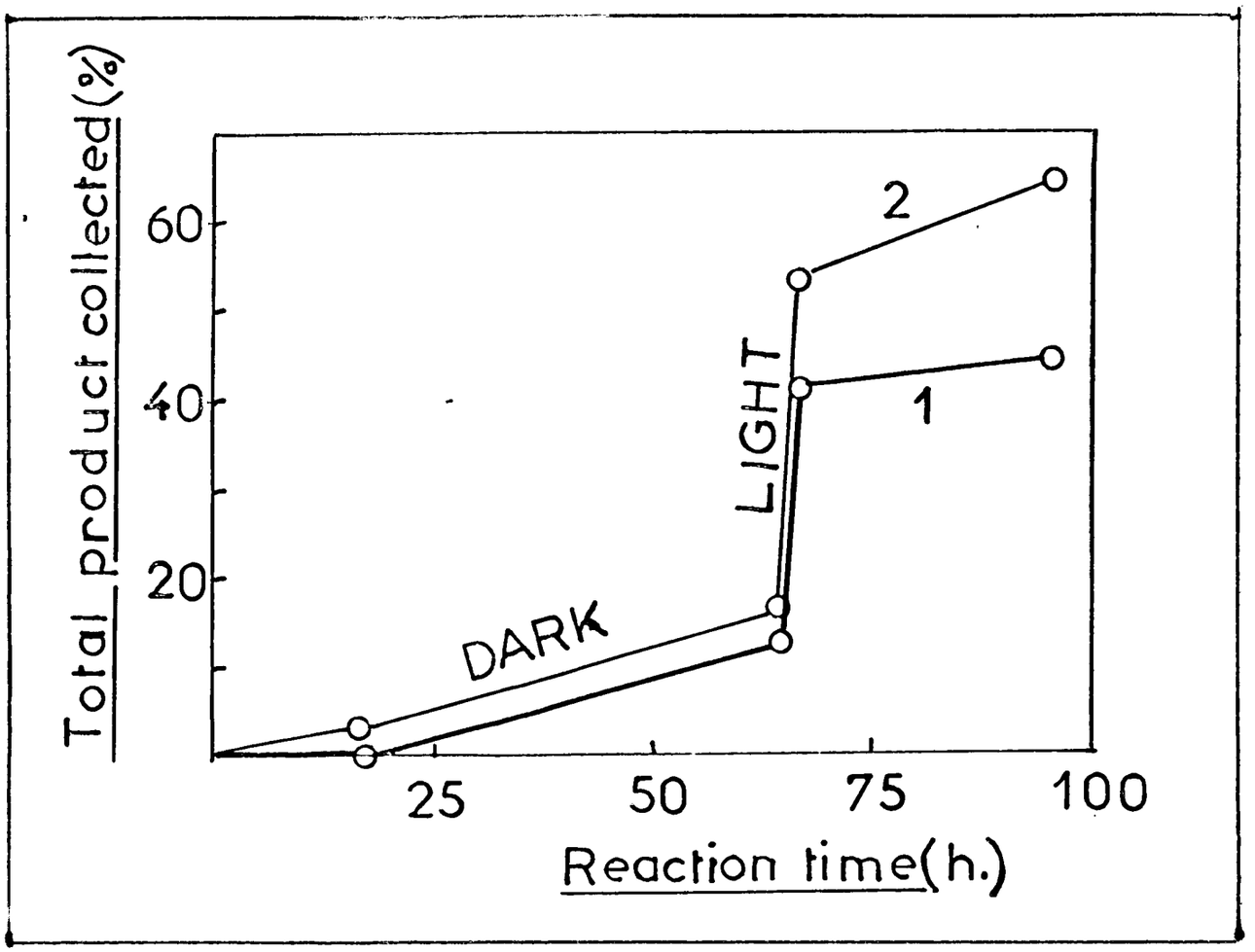
The complete removal of peroxides from olefins is always difficult. A useful way of eliminating the action of peroxides is by the addition of an inhibitor. An inhibitor may be a stable radical or an active molecule. If the inhibitor is a molecule it may be able to add on radicals or supply hydrogen atoms to the active reaction centre to destroy it. The new radical formed from the inhibitor must be too inactive to initiate new chains. The mechanism of inhibition is not general and in each type of reaction several inhibitors may behave differently.

The reaction of p-toluenesulphonyl iodide with acrylonitrile was repeated in ether (peroxide free) in the presence of hydroquinone (15% molar relatively to the sulphonyl iodide) in the dark. After twenty two hours at room temperature, no adduct was detected in the reaction mixture.

The reaction was also carried out in the presence of smaller quantities of hydroquinone. The results are summarized as follows:

Total Reaction time	Total product collected
Reaction 1 (6.8% hydroquinone)	
17 h. (dark)	0
65 h. (dark)	12.5%
72 h. (7 h. in light)	41.5%
96 h. (31 h. in light)	45.1%
Reaction 2 (3.4% hydroquinone)	
17 h. (dark)	3.4%
65 h. (dark)	16.8%
72 h. (7 h. in light)	54.3%
96 h. (31 h. in light)	65.6%

These results showed that reactions in the presence of hydroquinone are slower, even in the presence of light. This is graphically illustrated as follows:



F - Conclusion

p-Toluenesulphonyl iodide reacts with acrylonitrile to give the 1:1 addition product. Participation of cationic particles, $TolSO_2^+$, in the reaction was excluded because:

a) the sulphonyl group should be attached to the α-carbon atom

b) under Friedel Crafts conditions, sulphonyl cations did not react with acrylonitrile or α-methylstyrene.[32]

The participation of sulphonyl anions, $TolSO_2^-$, in the addition reaction is unlikely in the absence of copper bronze. Heterolytic fission of the sulphur-iodine bond in solvents of low polarity, e.g. carbon tetrachloride, would be difficult.

Light greatly accelerates the addition and hydroquinone acted as an inhibitor.

The action of hydroquinone may be due to one of the processes:

a) Supplying of hydrogen atoms to neutralise the action of peroxides present in the mixture (32) or to terminate chains (33):

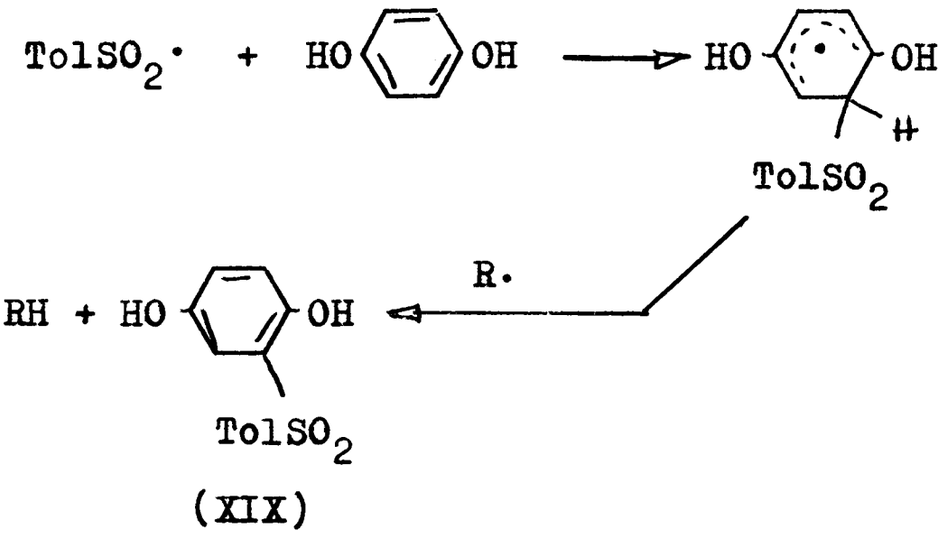
$$RO\cdot + HO\text{-}C_6H_4\text{-}OH \longrightarrow ROH + \underset{(XX)}{\cdot O\text{-}C_6H_4\text{-}OH} \qquad (32)$$

$$TolSO_2CH_2\dot{C}HCN + HOC_6H_4OH \longrightarrow TolSO_2CH_2CH_2CN + \cdot O\text{-}C_6H_4\text{-}OH \qquad (33)$$

b) Reaction with sulphonyl radicals

$$(34)\begin{cases} TolSO_2\cdot + HOC_6H_4OH \longrightarrow TolSO_2H + \cdot OC_6H_4OH \\ \cdot OC_6H_4OH + TolSO_2\cdot \longrightarrow TolSO_2H + O{=}C_6H_4{=}O \end{cases}$$

or

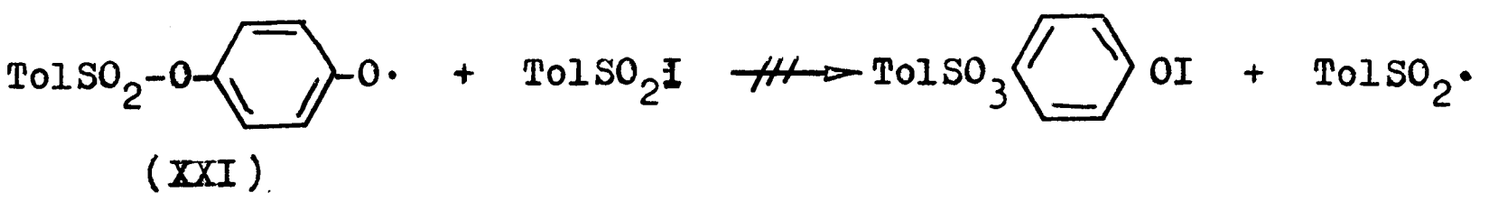


(35)

(XIX)

Product (XIX) was formed when p-toluenesulphonyl iodide and hydroquinone were refluxed in carbon tetrachloride, in the presence of copper bronze.

Inhibition by process a) should lead to semiquinone radicals (XX) which are too stable to start chains or to abstract iodine from the sulphonyl iodide. This was confirmed in the reaction of p-toluenesulphonyl iodide with p-benzoquinone in the absence of copper bronze (1.2.1.):



(XXI)

i.e. semiquinone type radical (XXI) was too stable to initiate a chain reaction by abstracting iodine fro m the sulphonyl iodide.

The process of addition of p-toluenesulphonyl iodide to olefins is very likely a free radical chain reaction initiated by light or traces of peroxides in the commercial olefin:

$$TolSO_2I \xrightarrow{h\nu} TolSO_2\cdot + I\cdot$$

$$TolSO_2\cdot + CH_2{=}CH{-}CN \longrightarrow TolSO_2CH_2\dot{C}HCN \quad (XXII)$$

$$TolSO_2CH_2\dot{C}HCN + TolSO_2I \longrightarrow TolSO_2CH_2CHI + TolSO_2\cdot \quad \text{etc.}$$

Attack on the terminal carbon atom of the double bond yielded the more stable radical (XXII), with the unpaired electron then delocalised over the α-carbon and the CN group.

p-Toluenesulphonyl iodide also reacts with styrene, α-methylstyrene, 1,1-diphenylethylene and butadiene by a similar attack on the terminal carbon atom. The experiments concerning these reactions are not present in this thesis because they will be submitted in a thesis in Oporto University, Portugal. Results are given as follows:

Olefin	Reaction product	Yield
α-Methylstyrene	$TolSO_2CH_2C(=CH_2)Ph$	59%
Styrene	$TolSO_2CH_2CHIPh$	93%
1,1-Diphenylethylene	$TolSO_2CH=CPh_2$	50%
Butadiene	$TolSO_2CH_2CH=CHCH_2I$	89-100%
Cyclohexene	$CH_2CH_2CH_2CH_2CHICH\text{-}SO_2Tol$	58%

2. Some attempted reactions with sulphinyl chlorides

2.1 - The decomposition of sulphinyl chlorides in the presence of copper bronze.

2.1.1 - Preparation of benzenesulphinyl chloride.

The first method used to prepare benzenesulphinyl chloride was that of Douglass and Poole[163] :

$$R\text{-}S\text{-}S\text{-}R + 3\ Cl_2 \longrightarrow 2\ R\text{-}SCl_3$$

$$R\text{-}SCl_3 + H_2O \longrightarrow RSOCl + 2\ HCl$$

This method was found to give bad results since it was very difficult to know when to stop the passage of chlorine gas into the solution of the dissulphide.Benzenesulphonyl chloride was thus obtained instead of the expected sulphinyl chloride.These authors corrected the method later,using liquid chlorine[164].

Benzenesulphinyl chloride was then prepared as described by Barnard[145] :

$$PhSO_2CL \xrightarrow{Na_2SO_3 / H_2O} PhSO_2H$$

$$PhSO_2H \xrightarrow{SOCl_2} PhSOCl$$

This method was length but gave the sulphinyl chloride with an infra-red spectrum identical with that described in literature[165] .The derivative sulphinamide was also prepared, m.p. 120-2º(lit.[166] 120º).

2.1.2 - The decomposition of benzenesulphinyl chloride

Benzenesulphinyl chloride and an equimolecular amount of copper bronze were refluxed together in carbon tetrachloride for three hours.

The reaction product was a liquid that could not be crystallised or distilled, but its i.r. spectrum was identical with that of phenyl benzenethiosulphonate[167]. This thiosulphonate has a low melting point, 37-38°, so the presence of some impurities in the reaction mixture would prevent crystallization.

2.1.3 - The decomposition of p-toluenesulphinyl chloride.

The sulphinyl chloride was prepared as described in Org.Synth.[168]:

$$TolSO_2Cl \xrightarrow{Zn} TolSO_2Na, 2H_2O$$

$$TolSO\ Na, 2H_2O \xrightarrow{SOCl_2} TolSOCl$$

A mixture of p-toluenesulphinyl chloride and copper bronze in carbon tetrachloride was stirred at room temperature for six hours. p-Tolyl-p-toluenethiosulphonate (36.5%) was obtained. This product can be considered to be the dimer of p-toluenesulpinyl radicals, as had been proposed by several authors[68,146,147]:

$$2\ TolSOCl + Cu \longrightarrow 2\ TolSO\cdot + CuCl_2$$

$$TolSO\cdot \longleftrightarrow TolS\cdot \longleftrightarrow TolS$$
$$\qquad\qquad\quad \downarrow O \qquad\qquad\quad \backslash O\cdot$$

$$TolS\cdot - TolS \longrightarrow \left[TolS\text{-}O\text{-}STol\right] \longrightarrow TolSO_2STol$$
$$\downarrow O \qquad \backslash O\cdot \qquad\quad \downarrow O$$

Alternatively an heterolytic reaction may occur:

$$TolSOCl + 2\ Cu \longrightarrow TolSO\overset{\delta-}{-}Cu\overset{\delta+}{-} - CuCl$$

$$TolSO\overset{\delta-}{-}Cu\overset{\delta+}{-} - TolS\overset{\delta+}{-}Cl\overset{\delta-}{} \longrightarrow \left[TolS\text{-}O\text{-}S\text{-}Tol\right] + CuCl$$
$$\qquad\qquad\qquad\quad \downarrow O \qquad\qquad\quad \downarrow O$$

$$TolSO_2STol$$

To investigate whether free radicals were present in the solution some reactions were attempted.

2.2 - The attempted addition of sulphinyl chlorides to olefins.

If free radicals were formed in solution it would be expected that a chain reaction could be set up by copper in a solution of the sulphinyl chloride in the presence of an olefin:

$$TolSOCl + Cu \longrightarrow TolSO\cdot + \text{Copper chloride}$$

$$TolSO\cdot + CH_2{=}CH\text{-}R \longrightarrow Tol\text{-}\underset{\overset{\|}{O}}{S}\text{-}CH_2\text{-}\dot{C}H\text{-}R$$

$$\underbrace{TolSO\text{-}CH_2\text{-}\dot{C}H\text{-}R}_{X\cdot} + TolSOCl \longrightarrow TolSO\text{-}CH_2\text{-}CHCl\text{-}R + TolSO\cdot$$

This chain reaction depends on three important points:

a) the formation of sulphinyl radicals,

b) the reactivity of these radicals,

c) the reactivity of radical X· towards the abstraction of chlorine from a molecule of sulphinyl chloride.

2.2.1 - Reactions of benzenesulphinyl chloride with cyclohexene and α-methylstyrene.

Benzenesulphinyl chloride, cyclohexene and copper bronze in carbon tetrachloride were refluxed together for five hours. The reaction mixture was worked up to yield a brown oily liquid that showed no sulphoxide absorption band in the i.r. spectrum. A similar negative result was obtained when α-methylstyrene was used in place of cyclohexene.

2.2.2 - Reactions with p-toluenesulphinyl chloride.

A mixture of p-toluenesulphinyl chloride, cyclohexene and carbon tetrachloride was stirred for four hours at room temperature.

As the dimer ,p-tolyl-p-toluenethiosulphonate,was obtained under similar conditions in the absence of an olefin(2.1.3), no heating was used in this experiment.The only product obtained was the dimer(44%).

As copper bronze was used in excess relatively to the sulphinyl chloride the experiment was repeated with only traces of metal to initiate the reaction,which was carried out at about 80°.In this case a liquid residue was obtained. The analysis of this residue by i.r. spectroscopy and thin layer chromatography showed it to contain p-tolyl-p-toluenethiosulphonate.The i.r. spectrum showed no sulphoxide band and was similar to that of the thiosulphonate.

Styrene and ethyl cinnamate produced similar results.

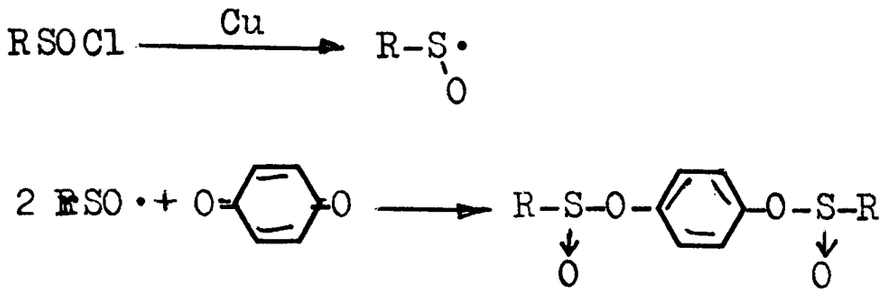
2.2.3 - The attempted addition of β-naphthalenesulphinyl chloride to styrene.

Naphthalenesulphinyl chloride was used because it should give solid products.

A solution of naphthalenesulphinyl chloride and styrene in benzene was irradiated by a mercury arc lamp at 70-80°,for six hours.The solution was then evaporated *in vacuo* to a brown oil that showed no sulphoxide absorption band when examined by i.r. spectroscopy.

2.3 - Reaction of p-toluenesulphinyl chloride with p-benzoquinone.

It would be expected that sulphinyl radicals should add to the oxygen atoms of p-benzoquinone to give a di-sulphinate:

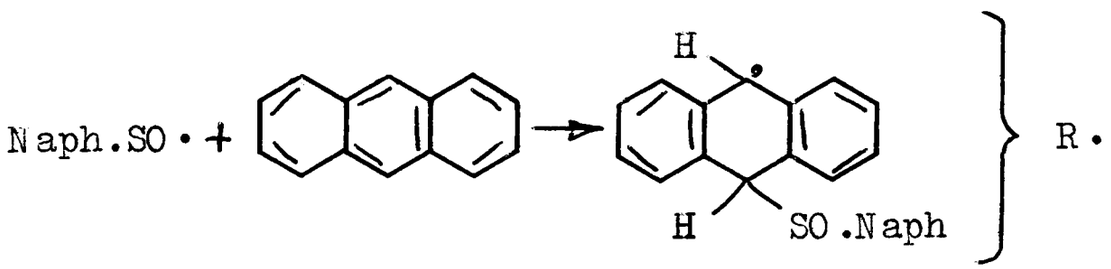


As arylsulphinates decompose easily when heated, the reaction was first attempted at room temperature.

A mixture of p-toluenesulphinyl chloride, p-benzoquinone, copper bronze and carbon tetrachloride was stirred for three hours, then left for two days. The only product of reaction was the dimer (38.5%). The reaction was also carried out at 80°, by refluxing the mixture of reactants in carbon tetrachloride for two hours. The dimer, tolyl toluenethiosulphonate, (40.7%) and a small yellow oil were the only isolated products of the reaction. The liquid was not identified but the i.r. spectrum indicate it to be probably a decomposition product of the dimer.

2.4 - Attempted reaction of β-naphthalenesulphinyl chloride with anthracene.

It was hoped to trap sulphinyl radicals with anthracene:



Radical R· could dimerise, or react with another sulphinyl radical. The reaction was carried out by heating under reflux a mixture of naphthalenesulphinyl chloride, anthracene, copper bronze and benzene.

The only isolated product of reaction was a white solid that was thought to be the dimer naphthyl naphthalenethiosulphonate, because it had the reported melting point[177] and its i.r. spectrum showed two strong $-SO_2-$ bands at 1140 and 1325 cm^{-1}. However analysis gave C-81.1, H-4.66 and S-7.39%.

Req. for the dimer: C-68.6, H-4.03 and S-18.3%

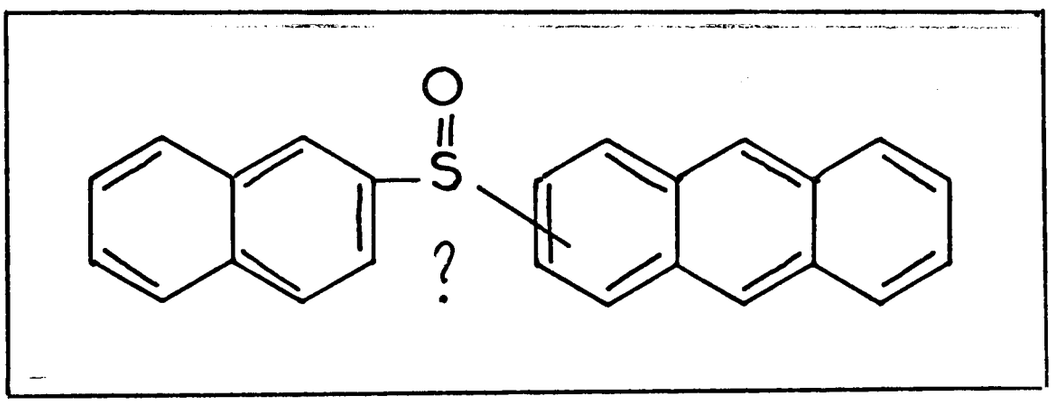
Req. for naphthyl anthryl sulphoxide:

C-81.67, H-4.58 and S-9.09

Req. for naphthyl anthryl sulphone:

C-78.2, H-4.38 and S-8.72%

Analysis of this compound by thin layer chromatogrophy showed the compound to be pure. The n.m.r. spectrum (p.277) indicated it to be probably an anthracene derivative, substituted by a naphthyl sulphonyl or sulphinyl group in 1 or 2-position:



The light absorption maxima in chloroform, at 2550 Å(ε',3575), 3245 Å(ε',117.5), 3400 Å(ε',144), 3580 Å(ε',206) and 3770 Å(ε',212) were calculated from concentrations in g./100 ml.

The i.r. spectrum in nujol showed the following bands:

Aromatic:

C=CH skeletal in-plane vibrations-1580(m), 1620(m) and 1500(m) cm^{-1}.

C-H out-of-plane deformations:

Four adjacent hydrogen atoms-730*(s), 755**(s) cm^{-1}

One isolated hydrogen atom-895*(s) cm^{-1}.

Region 1225-950 cm^{-1}:

1,2-Substitution-1070 (m)*, 1115 (s)** cm^{-1}

960 (s)** cm^{-1}

Sulphur groups:

$-SO_2-$ stretching-1145 (s) and 1330 (s) cm^{-1}

Other bands:

660 (s)*, 780 (w)*, 880 (s)**, 1240 (w)*, 1270 (m)** and 1350 (m)** cm^{-1}

Notes:

* - Corresponding bands present in 9-tolylsulphonyl-anthracene.

* * - Corresponding bands in β-naphthylsulphinylchloride.

2.5 - Attempted addition of 2,4-dinitrobenzenesulphinyl radicals to benzoquinone.

2.5.1 - The production of sulphinyl radicals.

The method reported by Topping and Kharasch[147] was used to generate sulphinyl radicals. They prepared sulphenyl nitrates by reaction of sulphenyl chlorides with silver nitrate at low temperature.

$$R\text{-}S\text{-}Cl + AgO\text{-}NO_2 \longrightarrow R\text{-}S\text{-}O\text{-}NO_2 + AgCl$$

Some of these sulphenyl nitrates were reasonable stable but in certain solvents such water and ethanol they decompose to thiosulphonate and nitrogen dioxide:

$$2\ R\text{-}S\text{-}O\text{-}NO_2 \longrightarrow R\text{-}SO_2\text{-}S\text{-}R + 2\ NO_2$$

The Kharasch interpretation of this decomposition was by supposing the formation of free radicals:

$$R\text{-}S\text{-}O\text{-}NO_2 \longrightarrow R\text{-}S\text{-}O\cdot + NO_2$$

When R-2,4-di-nitrophenyl, the solid sulphenyl nitrate is stable at room temperature for a few days. It is stable when dissolved in benzene and carbon tetrachloride but it decomposes in ethanol, water, ethylene or methylene chlorides to give the thiosulphonate.

2.5.2 - The decomposition of 2,4-di-nitrobenzenesulphenyl NITRATE in the presence of p-benzoquinone.

The sulphenyl nitrate was prepared in acetonitrile solution. This solution was concentrated at room temperature by passing dry air through the solution. The sulphenyl nitrate was then decomposed in ethanol in the presence of p-benzoquinone, at

room temperature. 2,4-Di-nitrophenyl-2,4-di-nitrobenzene-thiosulphonate (44%) was the only isolated product of the reaction.

2.6 - Conclusion

When the production of sulphinyl radicals by reaction of sulphinyl chlorides with copper bronze was attempted, the corresponding thiosulphonate was obtained with an average yield of about 40%.

No addition of sulphinyl chlorides to reactive olefins, for example styrene and α-methylstyrene, ocurred.

No reaction occured with p-benzoquinone and anthracene gave a product which was not identified .

From these results one of the two conclusions may be formulated:

a) No sulphinyl radicals were formed, or

b) if they were produced, they were particles of very low energy and the only reactions they underwent was dimerization to thiosulphonate .

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EXPERIMENTAL SECTION

1. Some Reactions of Sulphonyl Radicals

1.1 - Decomposition of p-toluenesulphonyl iodide.

1.1.1 - Decomposition in the presence of copper bronze

The reaction was carried out in a 500 ml. flask fitted with a mechanical stirrer, a reflux condenser and a calcium chloride guard tube.

p-Toluenesulphonyl iodide (18.0 g. 0.064 mole) was dissolved in slightly warm dry carbon tetrachloride (200 ml.) and the solution was placed in the flask. To this solution, copper bronze (4.1 g. 0.064 g.atom) was added and the mixture was stirred and refluxed for six and a half hours on a water bath. The hot reaction mixture was filtered by suction and a grey solid (A) was separated. (14.37 g., 118% of copper iodide). The solid (A) was extracted with hot organic solvents (benzene, chloroform and ethanol). From the benzene extracts, after distillation of the solvent, no product could be obtained. Chloroform and methanol extracted small amounts of grey solid. When this solid was heated in a flame a green colour was obtained.

The infra red (i.r.) spectrum of this solid showed very broad absorption bands and it had similarities with those of salts of p-toluenesulphonic and sulphinic acids.

A Lassaigne test on the solid (A) separated from the reaction mixture showed the presence of iodine and traces of

sulphur. Copper was also present (flame test). This solid (A) was extracted with distilled water and a pale blue solution was obtained (B).

The ultra violet (u.v.) spectrum of this aqueous solution showed an absorption maximum at 222 mμ.

p-Toluene sulphonic acid, p-toluene sulphinic acid and their salts have absorption maxima near 222-223 mμ:

Solute	Solvent	Absorption maxima
$p\text{-TolSO}_3H$	EtOH	222 mμ
$(p\text{-TolSO}_2)_2O$	EtOH	222 mμ
$p\text{-TolSO}_3H$	H_2O	222 mμ
$p\text{-TolSO}_2Na$	H_2O	223 mμ

A test for sulphinic acids was carried out on the blue aqueous solution (B). That is, an acidic solution of ferric chloride was added to the solution (B). No precipitate of ferric sulphinate was seen and so the test was negative. We think that the excessive weight of (A) may be due to the presence of copper p-toluene sulphonate. The hot carbon tetrachloride filtrate of the reaction mixture was left in a refrigerator overnight. In the morning small white crystals were seen in the mixture. These crystals were separated by filtration and dried. 4.47 g. (69%) of crystals, m.p. 99-100° were obtained (C).

This product was characterised as p-toluene sulphonic anhydride by comparison with an authentic specimen [152], m.p. 98-102°C (lit.[152] 128-129.5°) (cp.above).

The low melting points of these samples (synthetic and that isolated) did not indicate that the products were very impure. It was shown by L.Field[152] that small quantities of p-toluenesulphonic acid in the anhydride decrease considerably the melting point of the anhydride.

The anhydride was analysed as follows:

Found: C = 51.46% H = 4.78% S = 19.62%

Required for

$C_{14}H_{14}S_2O_5$: C = 51.50% H = 4.32% S = 19.65%

The i.r. spectra of p-toluenesulphonic anhydride (C) and that of the synthetic sample were identical. The mixed melting point was 98-102°.

The characterization of this product was completed by dissolving 2.0 g. of the solid (C) in 50 ml. of benzene and adding 3 ml. of aniline. The mixture was shaken for some minutes and left. After 5-10 minutes very small white crystals separated (1.46 g., 90%). These crystals were very soluble in water and their i.r. spectrum was identical with that of phenylammonium p-toluenesulphonate, which was prepared by reaction of p-toluenesulphonic acid with aniline (see p.282) The carbon tetrachloride filtrate of (C) was concentrated to about 50 ml. and then left in the refrigerator for one day.

No more sulphonic anhydride was obtained. The solution was then distilled under reduced pressure (water pump) and the solvent was removed leaving a yellow liquid. The yellow liquid was cooled and scratched and a solid was obtained.

This solid was triturated in the presence of ~~a~~ petroleum ether (20 ml.) separated by filtration and recrystallised from petroleum ether.

p-Tolyl-p-toluenethiosulphonate was obtained. 1.79 g. (57.5%), m.p. 75-76° mixed and alone, (lit.[48] 76°). This product was characterized by comparison of m.p. and i.r. spectrum with an authentic specimen prepared as described by Karrer[48]. After the distillation of the petroleum ether used in trituration of the p-tolyl-p-toluenethiosulphonate, a small quantity of a yellow oil was obtained as residue. No conclusion could be adduced from the i.r. spectrum of this oil. The oil was kept for several weeks in the refrigerator but no solid products crystallised. This oil was examined by thin layer chromatography and a spot with a large Rf was seen. A similar spot was obtained when p-tolyl-p-toluene-thiosulphonate was heated at about 150-200°. We think that this oil was formed by decomposition of the thiosulphonate.

1.1.2 - Decomposition in solution in the presence of copper bronze and in the absence of oxygen.

The carbon tetrachloride used in this experiment was an "Analar, B.D.H." product. The solvent was refluxed with

phosphorus pentoxide, decanted, and distilled through a 50 cm. fractionation column. The distillate was received directly into the reaction flask. The distillation apparatus had previously been flushed through with nitrogen for about half an hour.

The decomposition was carried out in a three neck flask fitted with a reflux condenser, a mechanical stirrer and a gas lead. Nitrogen was passed through the whole system for about half an hour. In this experiment p-toluenesulphonyl iodide (17.0 g., 0.0605 mole) was dissolved in pure carbon tetrachloride (200 ml.) in the presence of copper bronze (5.0 g., 0.079 g.atom). The mixture was refluxed and stirred for four hours; nitrogen was passed slowly through the system during the whole time for the reaction. The reaction mixture was treated in the same manner as the previous reaction, and similar results were obtained. Results of the experiments of the decomposition of p-toluene-sulphonyl iodide in solution in the presence of metals are given in the following table:

Decomposition of p-toluenesulphonyl iodide in boiling solvents

Run no.	Solvent	Metal	Reaction time (hours)	$(TolSO_2)_2O$ %	$TolSO_2STol$ %	obs.
1	CCl_4	Cu	6½	69	57.5	-
2	CCl_4	Cu	7	65	60.5	1
3	CCl_4	Cu	7	69.5	-	-
4	CCl_4	Cu	4	69.5	72 =	2
5	C_6H_6	Ag	4½	45	-	3

Obs: 1 - carbon tetrachloride was purified as described by McNamara (58)

2 - carbon tetrachloride B.D.H. (Analar) was dried over phosphorus pentoxide and fractionated. The reaction was carried out in the absence of oxygen.

3 - p-toluenesulphonic anhydride was estimated from the amount of phenylammonium p-toluenesulphonate isolated.

Yields were calculated on the basis of the equation:

$$6\ TolSO_2I + 6Cu \longrightarrow 2(TolSO_2)_2O + TolSO_2STol + 6Cu\ I$$

The next experiment was performed to see if the solubility of p-toluenesulphonic acid in benzene was great enough to give an observable amount of phenylammonium p-tolu-

enesulphonate:

- To 50 ml. of dry benzene excess of p-toluenesulphonic acid was added. The mixture was stirred and filtered. To the benzene filtrate 3 ml. of aniline were added. The solution was left several days, but no solid separated.

This proves that all the phenylammonium salt which separated in previous experiments was formed from reaction of sulphonic anhydride with aniline and not from the acid.

1.1.3. Stability of the dimer p-tolyldisulphone in the conditions of the previous experiments.

p-Tolyldisulphone (p. 282) (4.0 g., 0.019 mole) was dissolved in boiling carbon tetrachloride (100 ml.) Copper bronze (2.0 g., 0.0315 g.atom) was added to the solution and the mixture was refluxed for seven hours. The reaction mixture was filtered hot; a metallic solid separated (A). The carbon tetrachloride filtrate was left overnight in the refrigerator. The mixture was then filtered; 0.30 g. of unreacted p-tolyldisulphone had separated. The filtrate from this solid was distilled but no residue was obtained.

The solid (A) was extracted several times with hot benzene and the combined extracts were distilled; 3.3 g. of p-tolyl disulphone was obtained as residue. The total amount of disulphone recovered from the reaction mixture

was 3.6 g. (90%), and was identified by analysis of m.p., mixed m.p. and i.r. spectrum. No p-toluenesulphonic anhydride could be detected in the i.r. spectrum of the unreacted disulphone. No reaction occurred between copper bronze and the dimer, p-tolyldisulphone.

1.1.4. Decomposition under ultra-violet radiation

p-Toluenesulphonyl iodide (17.0 g., 0.0604 mole) was dissolved in benzene (250 ml.). The solution was placed in a 500 ml. Pyrex round bottom flask, fitted with a reflux condenser with a calcium chloride guard tube. The solution was irradiated during seven hours with a "Hanovia" ultra-violet lamp (type 67/36, 1KW) which was placed 5-7 cm. from the bottom of the flask. The solution was initially yellow but gradually changed to brown during the reaction. This solution was left some hours in the refrigerator but no solid separated. Then the solution was extracted with a 10% aqueous solution of sodium thiosulphate to remove iodine and unreacted sulphonyl iodide. The mixture was separated into two layers. The aqueous layer was discarded. The organic layer was dried (sodium sulphate) and separated into two parts:

-Part A: the solution was distilled under reduced pressure and a small amount of white solid was obtained. This solid was washed with cold benzene; p-tolyldisulphone (0.2 g., 5.3%)

was obtained, m.p. = 218-219°. This product was identified by comparison of i.r. spectra and melting points with an authentic specimen of p-tolyldisulphone.
The benzene filtrate of this solid was seen to contain p-toluenesulphonic anhydride (a white precipitate was formed when treated with aniline).

-Part B: to this solution 3 ml. of aniline were added. The solution was shaken for one or two minutes and left for 10-15 minutes. The white solid which crystallized was filtered off and washed with cold benzene. After drying, phenylammonium p-toluenesulphonate (0.9 g.) was obtained, m.p.=221-5° This weight corresponds to 23% of p-toluenesulphonic anhydride. The phenylammonium derivative was characterised by comparison of i.r. spectra and mixed m.p. with an authentic specimen. No attempt was made to isolate p-tolyl-p-toluenethiosulphonate. This experiment proved that the formation of p-toluenesulphonic anhydride is not dependent on the presence of copper bronze or of silver.

1.1.5 - The reaction of p-toluenesulphonyl iodide with sodium p-toluenesulphinate.

A mixture of p-toluenesulphonyl iodide (9.0 g., 0.032 mole) and sodium p-toluenesulphinate dihydrate (10.7 g., 0.050 mole) in ether (250 ml.) was stirred for ten hours in the absence of light.

A solid (A), (9.5 g.) which was completely soluble in water separated and was collected; the aqueous solution of (A) gave a positive test for sulphinic acid (ferric chloride in hydrochloric acid). The solution was neutral (B.D.H. wide range testing paper), showing the absence of free sulphonic acid.

The ether of the filtrate was removed leaving a yellow-brown solid (7.5 g.). The infrared spectrum of this residue was identical with that of p-toluenesulphonyl iodide. No absorption bands of p-toluenesulphonic anhydride were found in the spectrum.

The experiment was repeated with carbon tetrachloride as solvent.

p-Toluenesulphonyl iodide (3.0 g., 0.0107 mole) and sodium p-toluenesulphinate dihydrate (3.0 g., 0.0141 mole) in carbon tetrachloride (60 ml.) were refluxed together for three hours. The reaction mixture was filtered hot and a brown solid (B) was collected (3.2 g.). This solid was partially soluble in water. The solution was tested for iodine (starch solution), iodide ion (silver nitrate solution) and sulphinic acids with positive results.

The solid (B) was extracted with 50 ml of benzene and residue (C) was collected. The filtrate was treated with 3 ml. of aniline, but no precipitate of phenyl ammonium p-

toluenesulphonate was obtained, showing the absence of p-toluenesulphonic anhydride in (B). The solid (C) was extracted several times with water to remove sodium sulphinate. These extracts were neutral, and the insoluble residue (0.10 g.) was identified as p-toluenesulphonyl iodide by comparison with an authentic specimen (m.p., mixed m.p. and i.r. spectrum).

The carbon tetrachloride filtrate was kept at 0° for twelve hours. p-Tolyldisulphone (0.12 g.) separated, m.p.=217-220°, identified by comparison with an authentic specimen (m.p., mixed m.p. and i.r. spectrum). No p-toluenesulphonic anhydride was found.

1.1.6 - Decomposition in the presence of free radicals

A - Decomposition in the presence of 2-cyanomethyl-2-propyl radicals.

Azo-bis(2-cyanomethyl-2-propyl) (9.0 g., 0.055 mole) and p-toluenesulphonyl iodide (15.0 g., 0.053 mole) were dissolved in benzene (250 ml.). This solution was placed in a 500 ml. round bottom flask fitted with a reflux condenser (with a calcium chloride guard tube). The solution was refluxed for six hours.

The reaction mixture was yellow and no solid separated when the solution was cooled. 50 ml. of this solution were treated with 2 ml. of aniline. 0.5 g. of phenylammonium p-toluenesulphonate were separated by filtration (37.4% of total

theoretical p-toluenesulphonic anhydride). The remainder of the solution was distilled and all the products with bp $\leq 82^{o}$ were removed. The residue was a brown solution. To this solution 250 ml. of petroleum ether were added and the mixture cooled. The mixture then consisted of a solution and an orange solid. This orange solid (A) was separated by filtration and treated with carbon tetrachloride. 1.18 g. of an insoluble white solid (B) were obtained. This solid was characterized as p-tolyldisulphone using the usual techniques (mixed m.p. and infrared spectra). The yield of (B) calculated on the total 250 ml. of benzene solution was 17.8% The carbon tetrachloride solution from (B) was distilled under reduced pressure. A small amount of a brown oil (a very complex mixture) was obtained. The petroleum ether filtrate from (A) was distilled and all the products with bp $\leq 81^{o}C$ were removed. The residue was a brown-yellow liquid. This liquid was distilled under reduced pressure yielding the following fractions:

- Solvent traces
- Slightly brown-red liquid, bp=62^{o}/15 mm, (4.0 g.)
- High b.p. residue

The liquid b.p.-62^{o}/15 mm was identified as 2-iodo-2-methyl-propionitrile, $Me_2C(CN)I$, by comparison of its b.p. and infra red spectrum with those of an authentic specimen (p.283)

The total yield was 35%. This product was hydrolised to

the corresponding amide, $Me_2CICONH_2$, by reaction with sulphuric acid and water, as described by Stevens and Coffield (~~119~~ 153). The melting point of this derivative was 181-182°C (lit.[153] 183-4°C). The high boiling point residue of the distillation flask was not characterized.

The decomposition was repeated in carbon tetrachloride solution, using 15.0 g.(0.0915 mole) of azo compound, 18.0 g. (0.064 mole) of sulphonyl iodide and 250 ml of solvent. The solution was refluxed for nine hours. The reaction mixture was then left in the refrigerator overnight; 3.83 g.of white crystals (B) had separated. The infrared spectrum of these crystals showed absorption bands corresponding to the p-toluenesulphonic anhydride and p-tolyldisulphone. No nitrile, CN, absorption band could be detected in this spectrum. The analysis of the mixture by thin layer chromatography indicated that two products had been formed with Rf values identical with those of p-tolyldisulphone and p-toluene-sulphonic anhydride.

1.0 g. of this mixture was dissolved in 50 ml. of cold benzene and filtered. The filtrate was treated with 2 ml. of aniline and 0.39 g. of phenylammonium p-toluenesulphonate were collected by filtration. (Total yield of p-toluene sulphonic anhydride 26.7%). The remainder of the solid

was thought to be p-tolyldisulphone (3.04% yield).

The carbon tetrachloride filtrate of (B) was distilled, leaving a brown-red residue. It was treated with 200 ml. of petroleum ether (40-60°) and then cooled. This procedure left a brown oily residue in the bottom of the flask and long white crystals suspended in the petroleum ether layer. The crystals and solution were separated from the brown residue (D).

The white crystals were removed by filtration (C) yielding 2.53 g. (29.1%) m.p.=154-158° (lit.[179] 163-4°). This was characterized as the dimer, tetramethylsuccinonitrile, $Me_2C(CN)C(CN)Me_2$, by comparison with an authentic specimen (p.296).

The brown oily residue (D) was extracted with petroleum ether and the combined extracts were added to solution (C). This solution (C) was distilled and the products with b.p. $\leq 80°$ were removed. The residue was a light brown liquid. It was distilled under reduced pressure; 4.0 g. of slightly brown-red liquid, b.p. = 61-62°/15 mm were obtained. This liquid was characterized as 2-iodo-2-methyl-propionitrile, $Me_2C(CN)I$, by comparison of b.p. and i.r. spectrum with an authentic specimen. The yield was 32% The residue from the distillation (9 g.) was added to the dark brown residue (D) (5 g.) and this combined residue (14 g.) was dissolved in 140 ml. of benzene.

50 ml. of this solution were chromatographed on 400 g. of deactivated alumina. The following solvents were passed through the column:

Benzene	800 ml.
Benzene/ethyl acetate (10 ÷ 1)	450 ml.
" " " (5 ÷ 1)	350 ml.
" " " (2 ÷ 1)	300 ml.
" " " (1 ÷ 1)	600 ml.
Ethyl acetate	400 ml.
Ethyl acetate/methanol (10 ÷ 1)	450 ml.
" " " (5 ÷ 1)	500 ml.
" " " (2 ÷ 1)	300 ml.
" " " (1 ÷ 1)	500 ml.
Methanol	500 ml.

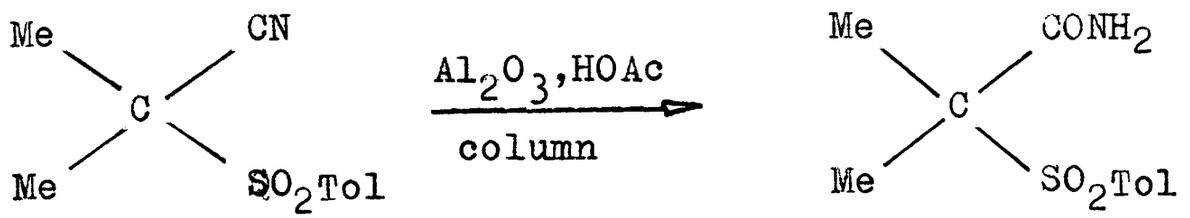
50 ml. fractions have been collected (99 fractions).

The only products from the column were dark brown oils, that could not be characterized, and 0.68 g. of a solid, m.p. = 181-183°C (fractions 92-94).

The infrared spectrum of this solid showed strong $-SO_2-$ and -CO- absorption bands, but the nitrile -CN absorption band was absent. The analysis of the solid gave the result:

Found: C=60.97% H = 6.17% S = 13.45% N = 6.12%

It is likely that this product may be formed by the reaction:



since the required percentages of this amide are:-

C= 55.5% H=6.25% S= 13.3% N=5.83%

but we have no other evidence to prove this.

B-The decomposition in the presence of 1-cyanomethylcyclohexyl radicals.

Azobis(1-cyanomethylcyclohexyl) (15.6 g., 0.064 mole) (p.295) and p-toluenesulphonyl iodide (18.0 g., 0.064 mole) were dissolved in benzene (250 ml.). The solution was refluxed for fortythree hours. The solution was then cooled and filtered; 0.1 g. of solid were separated. The i.r. spectrum of this solid was complex and showed no -CN or SO_2- bands.

The filtrate was concentrated by distillation to about 100 ml. and cooled. p-Tolyldisulphone (0.45 g., 4.55%) was separated by filtration and identified by using m.p., mixed m.p. and i.r. spectra. The filtrate was separated into two parts:

-Part (i) (25ml.): This solution was treated with 2 ml. of aniline and left. By filtration phenylammonium p-toluene-sulphonate (0.75 g.) was separated (total yield of p-toluene-sulphonic anhydride is 54%).

-Part (ii) (75 ml.): This solution was distilled. A brown oil was obtained as residue. This oil was treated with 100 ml. of hot petroleum ether and decanted from the residual dark brown oil (not characterized). The petroleum ether extract was cooled and 1.0 g. of white solid separated (F). The analysis of (F) by thin layer chromatography and infrared spectroscopy indicated that it was a mixture of p-toluene-sulphonic anhydride and the dimer, 1,1 -bis(1-cyanomethyl-cyclohexyl). The solid was washed with hot carbon tetra-chloride (50 ml.), yielding as an insoluble solid 0.5 g. (3.66%) of 1,1 -bis(1-cyanomethylcyclohexyl), m.p. = 190-215°, characterized by comparison of i.r. spectra and mixed m.p. with an authentic specimen (p.283).

The petroleum ether filtrate from (F) was distilled, thereby removing all fractions with b.p. $\leqslant 80^{\circ}C$.
As residue, a brown red liquid was obtained. This liquid was distilled under reduced pressure yielding 2.0 g. (13.3%) of a slightly orange liquid b.p. = 50-53°/0.05-0.1 mm. This liquid was analysed:

Found: I = 52.80% N = 6.02%

Required for

$C_6H_{10}(CN)I$: I = 54.0% N = 5.95%

Its i.r. spectrum and boiling point are similar to those of an authentic specimen (p.283) of 1-iodo-1-cyanomethylcyclohexane. The residue of the distillation was a dark brown oil that was not investigated further.

C-Results

The results of the decomposition of p-toluenesulphonyl iodide in solution in the presence of free radicals are given in the following table:

The decomposition of p-toluene sulphonyl iodide in solution in the absence of copper bronze

No.	Solvent	Reaction time	$(TolSO_2)O$	$(TolSO_2)_2$	Radical (Rad)	Radical dimer	Rad-I	Obs
1	C_6H_6	7 hr.	23%	5.3%	-	-	-	u.v.Radiation
2	C_6H_6	6 hr.	37.4%	17.8%	$Me_2\dot{C}CN$	?	35.0%	-
3	CCl_4	9 hr.	26.7%	3.04%	$Me_2\dot{C}CN$	29.1%	32%	-
4	C_6H_6	43 hr.	54%	4.55%	$(C_6H_{10}CN)\cdot$	3.66%	13.3%	-

1.2 - The reaction of p-toluenesulphonyl iodide with quinones.

These experiments were carried out in a 500 ml.flask, fitted with a mechanical stirrer,a reflux condenser and a calcium chloride guard tube.Heating was by means of a water bath.

1.2.1 - Reaction with p-benzoquinone

p-Toluenesulphonyl iodide(15.3 g.,0.0546 mole), p-benzoquinone(2.95 g.,0.0272 mole) and copper bronze (3.45 g.,0.0545 g. atom) in carbon tetrachloride(250 ml.) were refluxed together for seven hours.The reaction mixture was filtered hot and the grey residue(A) was washed with chloroform(2×50 ml.).No products could be detected in the washings.The carbon tetrachloride filtrate was left at 0° for twelve hours and small white crystals(6.4 g.,m.p.145-6°) separated.

2.0 g. of these crystals were washed with benzene(20 ml.), the mixture was filtered and white crystals(1.66 g.,m.p.153-8°) were collected(C).The i.r. spectrum of this solid indicated the absence of p-toluenesulphonic anhydride.

To the benzene filtrate 2 ml. of aniline were added.A white insoluble solid(0.86 g.) was collected and identified as phenylammonium p-toluenesulphonate by comparison with an authentic specimen(i.r. and mixed m.p.).This indicated the yield of p-toluenesulphonic anhydride was 12.3%.

The carbon tetrachloride filtrate was treated with 10% aqueous sodium hydroxide solution to extract any phenolic

products.The mixture was separated into two layers:

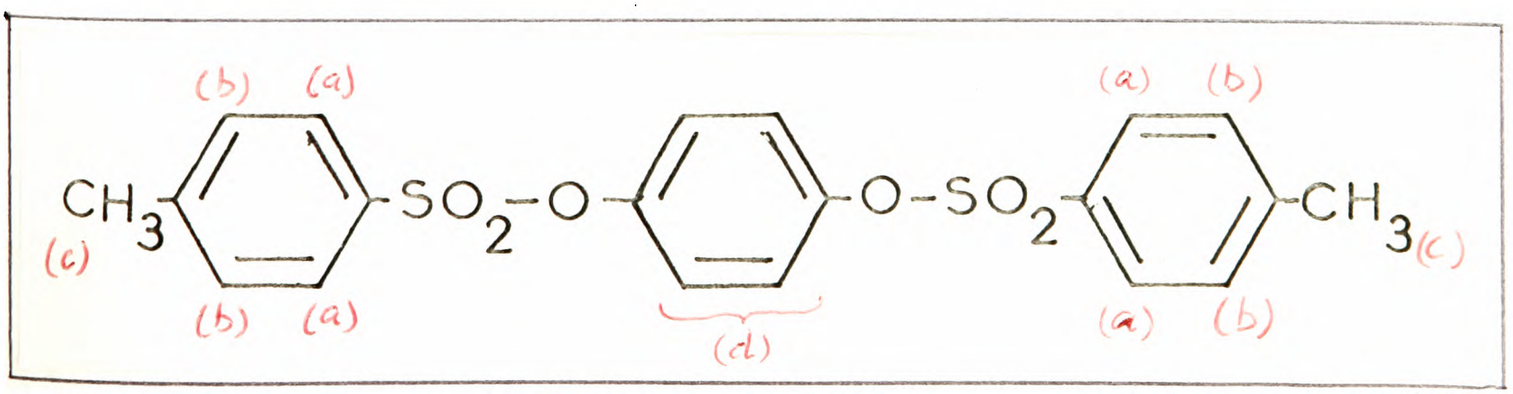
-The aqueous layer was acidified with hydrochloric acid: no insoluble solid was obtained.

-The organic layer was washed with a 10% solution of sodium dithionite and sodium hydroxide(3 × 100 ml.) to remove unreacted quinone.The organic layer was separated and washed with water(2 × 100 ml.) and dried(sodium sulphate). The solvent was removed under reduced pressure leaving a solid residue.This solid was washed with benzene(20 ml.) leaving 0.40 g. of white solid (D),m.p.153-8°.

The benzene filtrate was evaporated:the i.r. spectrum and mixed m.p.(74-5°) showed the residue to be p-tolyl-p-toluenethiosulphonate(lit.[48] m.p. 76°).

Solid (D) and (C) were identical(mixed m.p. and i.r. spectra).1.0 g. of solid (C) was recrystallised twice from benzene;small crystals,0.71 g.,m.p.152-3°.This product was identified as hydroquinone-di-p-toluenesulphonate by comparison with an authentic specimen(i.r. and mixed m.p.) which had been synthetised by reaction of the sulphonyl chloride with hydroquinone in the presence of sodium hydroxide(p.288).

The n.m.r. spectrum of the synthetic compound in deuterated chloroform(p.175) showed the following:



Proton	τ(p.p.m.)	J(c/sec.)	Relative intensity	Obs.
a	2.30	8.6	4	Doublet
b	2.70	8.6	4	Doublet
c	7.55	-	6	Singlet
d	3.08	-	4	Singlet

The positions of the lines of the A_2B_2 quartet and of the methyl group accord with the literature values.[155- nº 336,602]

The shift of the aromatic protons (d) relative to unsubstituted benzene protons is 0.35 P.P.M. The magnitude of this shift is close to that[156] established for hydroxyl groups (0.37 P.P.M.).

The i.r. spectrum of hydroquinone-di-p-toluenesulphonate determined in chloroform (p.176) and in nujol (p.177) exhibited the following characteristics:

Aromatic

C=CH skeletal in-plane vibrations-1595(m) and 1500(m) cm^{-1}

C-H out-of-plan deformations:

Two adjacent hydrogen atoms-820(s) or 840(s) cm^{-1}

Region 1225-950 cm^{-1}:

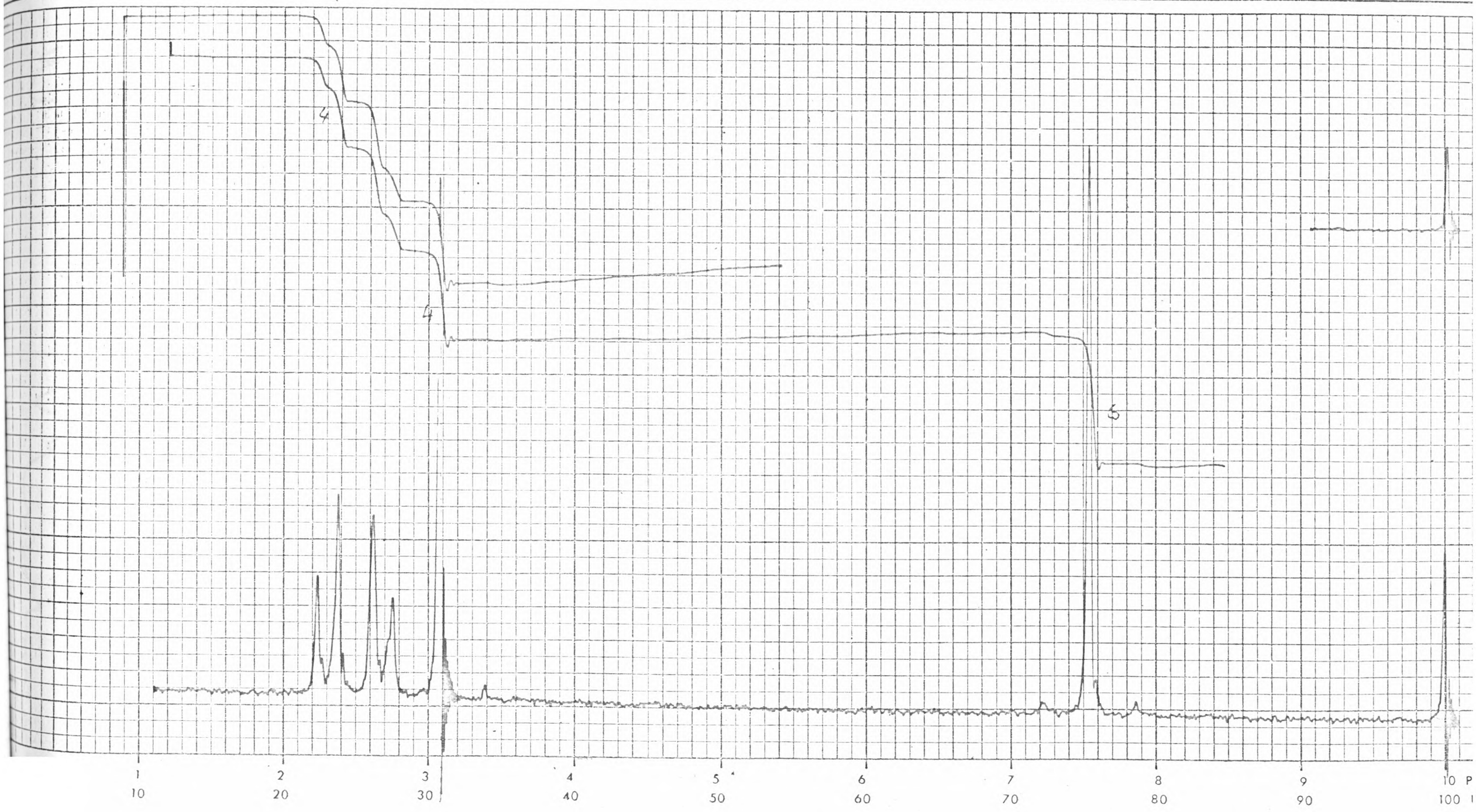
1,4-Substitution-1090(m), 1015(w) and 1040(w) cm^{-1}

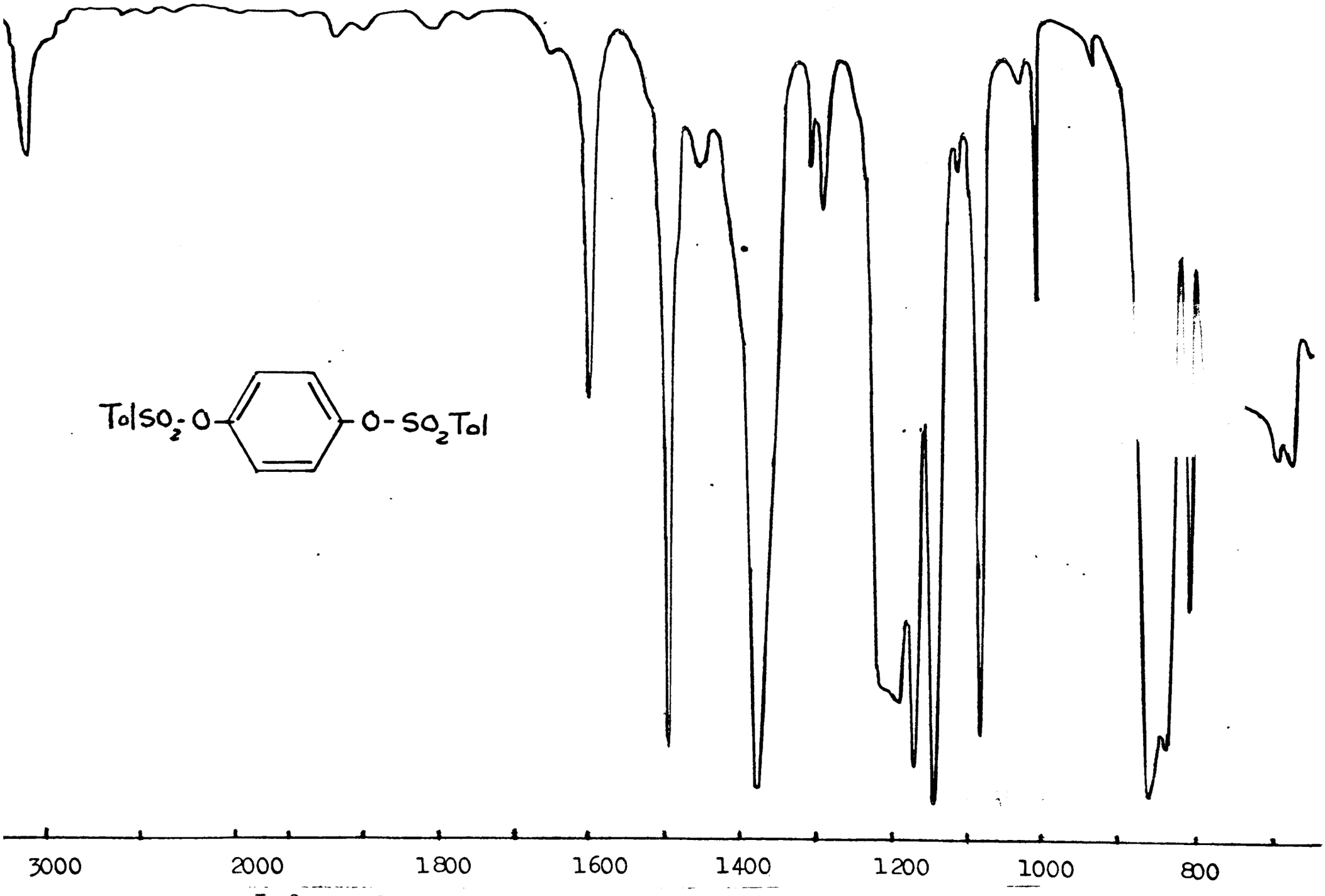
Sulphur groups

$-SO_2-O-$ stretching-1155(s) and 1380(s) cm^{-1}

The spectrum showed two strong bands at 1180 and 1200 cm^{-1}. The total yield of hydroquinone-di-p-toluenesulphonate was 46.5%. No other products were found. When the reaction was carried out in the presence of 2 ml. of water, no di-ester was formed.

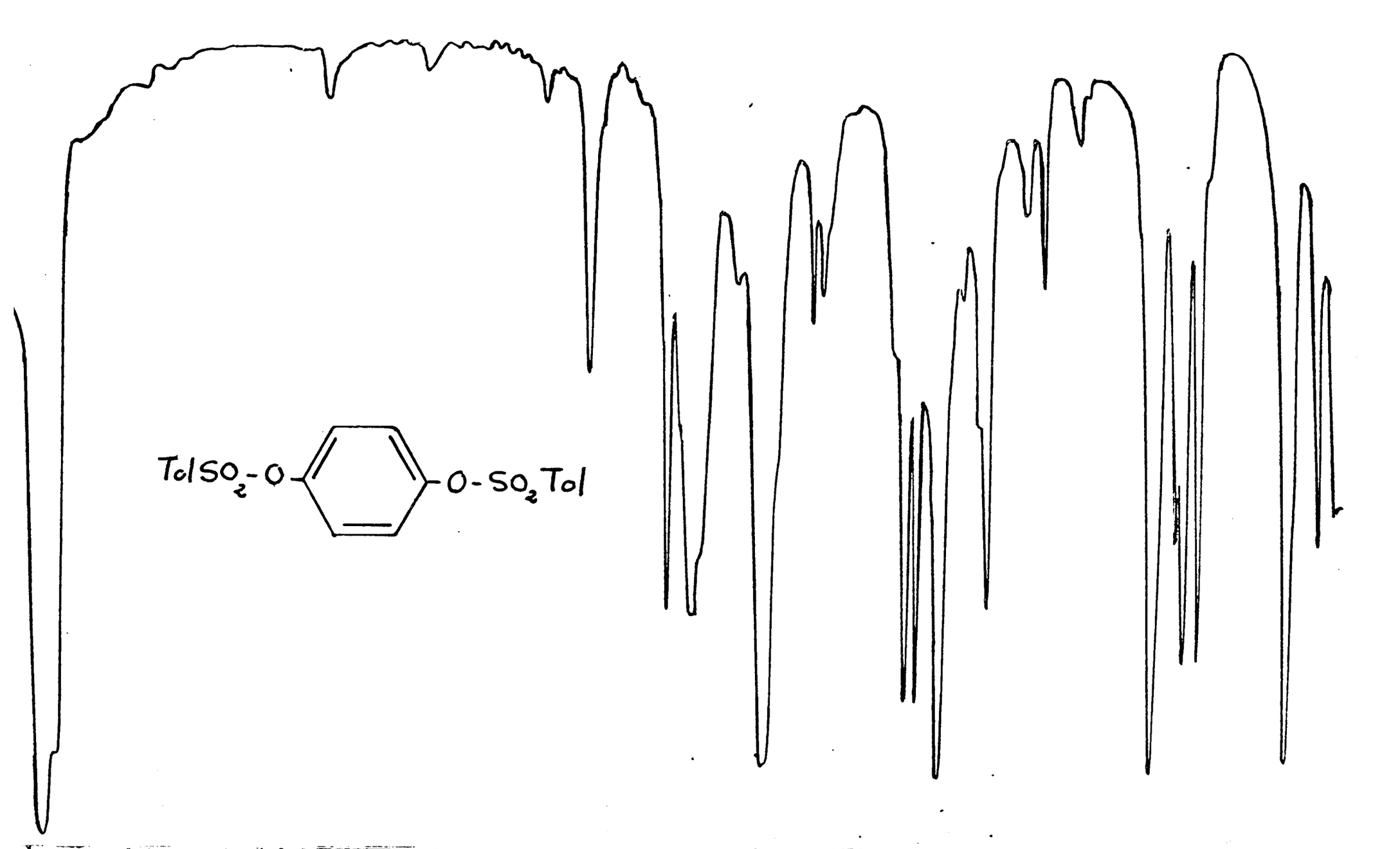
DATE 1966	DEC. SHIFT	REF. STD	R.F. FIELD	R.F. GAIN	REMARKS	SENSITIVITY NORM: 1 INT: 4	SWEEP RATE ____ UNITS PER MIN	TIME CONST. ____ SECS 0.15 M SECS	SCALE FACTO 6 C/S PER UNIT
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Infra red spectrum of hydroquinone-di-p-toluenesulphonate

(Chloroform solution)



Infra red spetrum of hydroquinone-di-p-toluenesulphonate

(Nujol film)

1.2.2 - Reaction with hydroquinone.

p-Toluenesulphonyl iodide(5.0 g.,0.0177 mole),hydroquinone(2.0 g.,0.0183 mole) and copper bronze(1.5 g.,0.0236 mole) in benzene(100 ml.) were refluxed together for four hours.The hot reaction mixture was filtered from a grey solid (A).

The benzene filtrate was left overnight in a conical flask and small white crystals separated and were collected, 0.34 g.,m.p. 155-80° ,(B).The filtrate was separated into two parts:

-To part (i) was added aniline(2 ml.).The mixture was left one hour but no precipitate of phenylammonium sulphonate was obtained.We may conclude that no sulphonic anhydride was formed in the reaction.

-Part (ii) was distilled under reduced pressure.Some drops of a brown-rsd liquid were obtained,which after standing some hours,changed to a dark brown oily solid soluble in 1-2 ml. of carbon tetrachloride.

The expected di-ester is not soluble in carbon tetrachloride.

The grey solid (A) whihh had separated from the reaction mixture was then examined.This contained some white crystals of the same size and shape as the crystals of hydroquinone used as starting material.

Since the expected di-ester is very soluble in cold chloroform,extraction of (A) with this solvent was attempted. The combined chloroform extracts were distilled leaving a small amount of dark green solid.This was shown to contain

copper salts(flame test),as well as hydroquinone and a sulphone(i.r. analysis).The i.r. spectrum was similar to that of product (B) .These spectra were rather different of the spectrum of the expected di-p-toluenesulphonate ester(p.177). Exctraction of the solid (A) by refluxing with 100 ml. of benzene was then attempted.The boilling mixture was filtered, cooled(6-8°) and the separated solid collected by filtration. The filtrate was then used for further extractions with the following results:

Extraction nº	Solid separated from the cold benzene
1	0.50 g.
2	0.43 g.
3	0.20 g.
4	0.06 g.
From the reaction mixture,(B)	0.34 g.
	1.53 g.,m.p.160-70

The cold benzene filtrate of this solid was distilled,but no solid could be obtained as residue.

The i.r. spectra of the extracted solids were similar to the spectrum of 2-p-tolylsulphonylhydroquinone.However bands at 760,840,1100,1220 and 1245 cm^{-1} in the spectra of different extracts varied in intensity relative to the other bands.These bands are present in the infra red spectrum of hydroquinone.These solids were combined and washed with ether (100 ml.).0.60 g. of white crystals,m.p.203-8° remained.Its i.r. spectrum showed complete absence of hydroquinone absorption bands.

This product was identified as p-tolylsulphonyl-hydro-

quinone by comparison of i.r. spectra and mixed m.p. (209-11°) with an authentic specimen (p. 288), lit.[176] m.p. 211-2°. No hydroquinone-di-p-toluenesulphonate, $TolSO_3C_6H_4OSO_2Tol$, could be detected in the infra red spectra of the solid products obtained in this experiment.

1.2.3 - Reaction with P-benzoquinone in the absence of copper bronze.

p-Toluenesulphonyl iodide (14.5 g., 0.0515 mole) and p-benzoquinone (3.0 g., 0.0278 mole) were dissolved in hot carbon tetrachloride (200 ml.) and the solution was heated under reflux for seven hours. The reaction mixture was then kept in a refrigerator for two days when yellow crystals (A) were precipitated (11.0 g., 76%, m.p. 84-6°) and identified as unreacted sulphonyl iodide by comparison of i.r. spectra and mixed m.p. with an authentic specimen. Absorption bands of p-benzoquinone and hydroquinone-di-p-toluenesulphonate were absent.

The carbon tetrachloride filtrate of (A) was examined by i.r. spectroscopy and gave no di-ester bands. Then it was washed with a 10% solution of potassium iodide and sodium dithionite (2×100 ml.) to remove unreacted sulphonyl iodide and quinone. The organic layer was separated, washed with water (100 ml.) and dried (magnesium sulphate). The aqueous layer was extracted with chloroform and the chloroform extract was dried (magnesium sulphate) and added to the extracted carbon tetrachloride layer. The solvent was removed by distillation under reduced pressure to give a yellow solid

(0.4 g.,m.p.113-4°) which was identified as p-benzoquinone by comparation with an authentic specimen(i.r. and mixed m.p.).

It was concluded that p-toluenesulphonyl iodide do not react with p-benzoquinone unless copper bronze is present.

1.2.4. - Blank tests.

1.2.4.1 - Effect of washing the reaction mixture with an alkaline sodium dithionite solution.

A mixture of p-toluenesulphonyl iodide(13.0 g.,0.046 mole), copper bronze(1.5 g.,0.033 g. atom) and carbon tetrachloride (150 ml.) was refluxed for seven hours.The hot reaction mixture was filtered and the filtrate was cooled.Most of the p-toluenesulphonic anhydride formed separated and was removed by filtration.To the carbon tetrachloride filtrate p-benzoquinone (3.0 g.,0.276 mole) was added.

The quinone solution was then washed with a 10% alkaline sodium dithionite solution(3× 100 ml.),water(100 ml.) and then dried over sodium sulphate.The solvent was then removed in vacuo leaving a pale yellow solid.This solid was suspended in 25 ml. of warm petroleum ether,cooled and collected.p-Tolyl--p-toluenethiosulphonate(0.81 g.)was obtained,m.p. 60-5°, mixed m.p.65-6°.No hydroquinone-di-P-toluenesulphonate was detected in this solid by i.r. spectrascopy and thin layer chromatography.

The mother liquor was evaporated under reduced pressure yielding a trace of the yellow oil formed in the decomposition of the sulphonyl iodide alone(p.86).

1.2.4.2 - Reaction between p-toluenesulphonic anhydride and p-benzoquinone.

p-Toluenesulphonic anhydride(6.52 g.,0.02 mole),and p-benzoquinone(2.16 g.,0.02 mole) in carbon tetrachloride (250 ml.) were heated under reflux for six hours.The reaction mixture was filtered hot but nosolid was obtained.The solution was allowed to cool to room temperature and p-toluenesulphonic anhydride separated and was collected(4.96 g.,76%),m.p.99-101°(A) characterized by comparison of i.r. spectra.

This anhydride was free of hydroquinone-di-p-toluenesulphonate.

The cold benzene filtrate from (A) was stored at 0° for twelve hours;sulphonic anhydride with traces of quinone separated and was collected(0.53 g.,B).The filtrate from (B) was then extracted with 10% alkaline sodium dithionite solution (3×100ml.),washed with water(2×100ml.) and dried(sodium sulphate).Removal of the solvent in vacuo gave p-toluenesulphonic anhydride(0.82 g.).The analysis of this solid by i.r. spectroscopy and thin layer chromatography indicated the absence of hydroquinone-di-p-toluenesulphonate.

The total sulphonic anhydride recovered from the reaction mixture was about 6.3 g.(96%)

1.2.4.3 - Reaction of p-toluenesulphonic anhydride with p-benzoquinone in the presence of a mixture of copper and copper iodide.

A mixture of p-toluenesulphonic anhydride(4.0 g.,0.0123 mole),p-benzoquinone(2.0 g.,0.0185 mole),copper bronze(6.0 g.

,0.095 g.atom),copper iodide(separated in previous experiments)(6.0 g.) and carbon tetrachloride(200 ml.) was refluxed for seven hours.The hot reaction suspension was filtered hot and the filtrate was kept at 0° overnight.Sulphonic anhydride (3.6 g.,90%) separated,m.p.100-2° .Examination of the i.r. spectrum of the anhydride showed no hydroquinone-di-p-toluenesulphonate absorption bands.

The yellow mother liquor was washed with 10% alkaline sodium dithionite(3×100 ml.) and water(2×100 ml.) and then dried(sodium sulphate).The dry solution was evaporated in vacuo and the residue(a trace of yellow oil) was treated with 2-3 ml. of petroleum ether.No solid product was obtained.

1.2.5 - Reaction with toluquinone(methyl-p-benzoquinone)

p-Toluenesulphonyl iodide(18.5 g.,0.0657 mole),toluquinone (4.0 g.,0.032 mole)(p.284) and copper bronze(4.15 g.,0.0657 g.atom) were refluxed in carbon tetrachloride(250 ml.) for seven hours.The grey suspension was filtered hot(A) and the filtrate was cooled and kept twelve hours at 0° .Filtration of the mixture gave slightly yellow crystals(6.41 g.,m.p.144-9°) (B),and a yellow solution (C).

(B) was analysed by using i.r. spectroscopy and thin layer cromatography and it was concluded to be a mixture of p-toluenesulphonic anhydride and a second product.

2.0 g. of (B) were dissolved in benzene(25 ml.) and by adding aniline(2 ml.) phenylammonium p-toluenesulphonate (0.39 g.,m.p.196-202°) crystallized.This corresponds to 22% conversion to sulphonic anhydride in the main reaction.

The remainder of solid (B),4.41 g.,was recrystallized from ethanol and then from carbon tetrachloride to give colourless crystals,2.95 g.,m.p.148-53°,(D).

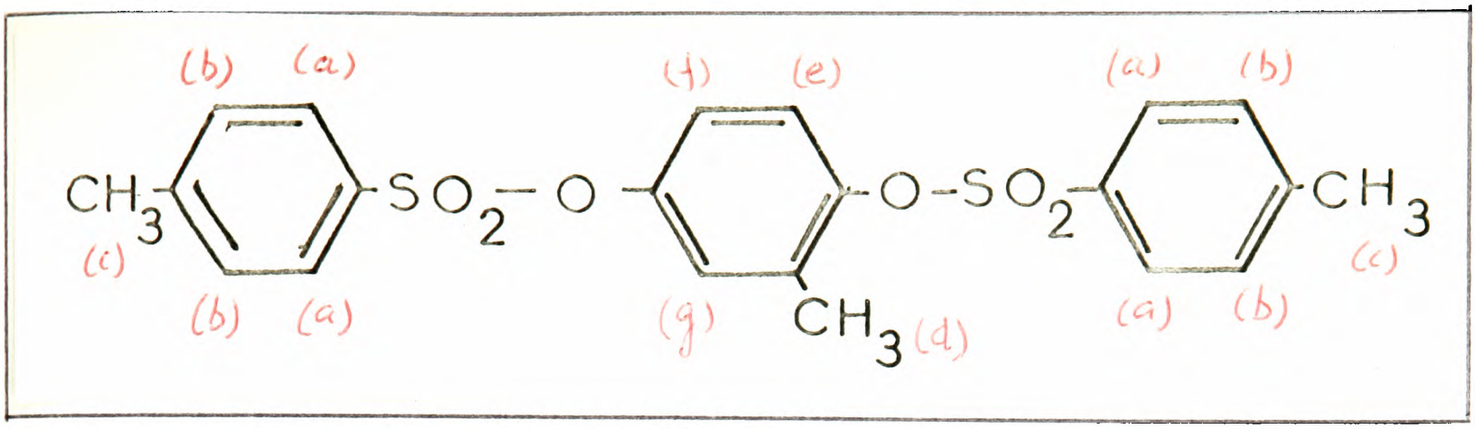
The carbon tetrachloride filtrate (C) was extracted with a 10% solution of sodium hydroxide(50 ml.) and the aqueous layer was acidified with hydrochloric acid but no solid material was deposited.The organic layer was then washed with water and then with 10% alkaline sodium dithionite solution (2×100 ml.) in order to remove unreacted quinone.

The organic layer was washed with water(2×100 ml.) and dried(sodium sulphate).The dry solution was concentrated under reduced pressure to 25 ml. and the solution was cooled in an ice bath yielding colourless crystals(1.17 g.,m.p.148-50°). These crystals were recrystallized from carbon tetrachloride 0.98 g.,m.p.151-4°,(E).

The i.r. spectra of solids (D) and (E) were identical and showed no p-toluenesulphonic anhydride absorption bands. The mother liquor of (E) was distilled under reduced pressure and a trace of brown uncrystallizable oil of unknown composition was obtained.

Extraction of the grey solid (A) with chloroform gave only a trace of a copper salt.

The only product isolated,(C) and (D),was identified as methylhydroquinone-di-P-toluenesulphonate,by comparison with an authentic specimen which was prepared from methyl hydroquinone and p-toluenesulphonyl chloride(p.288), m.p.152-4°.The n.m.r. spetrum of this in deuterated chloroform showed the following characteristics(p.186):



Proton	τ(P.P.M.)	J(c/sec.)	Relative intensity	Obs.
a	2.26	8.6	4	Doublet
b	2.67	8.6	4	Doublet
c	7.52	-	6	Singlet
d	7.97	-	3	Singlet
e,f,g	2.94-3.40	-	3	Complex

The i.r. spectrum in nujol showed (p.187):

Aromatic

C=CH skeletal in-plane vibrations-1600(m) and 1500(m) cm^{-1}

C-H out-of-plane deformations:

Two adjacent hydrogens-820(m) cm^{-1}

One isolated hydrogen-865(s) cm^{-1}

1,2,4-Substitution-840(m) cm^{-1}

Region 1225-950 cm^{-1}:

1,4-Substitution-1090(m),1020(w) and 1040(w) cm^{-1}

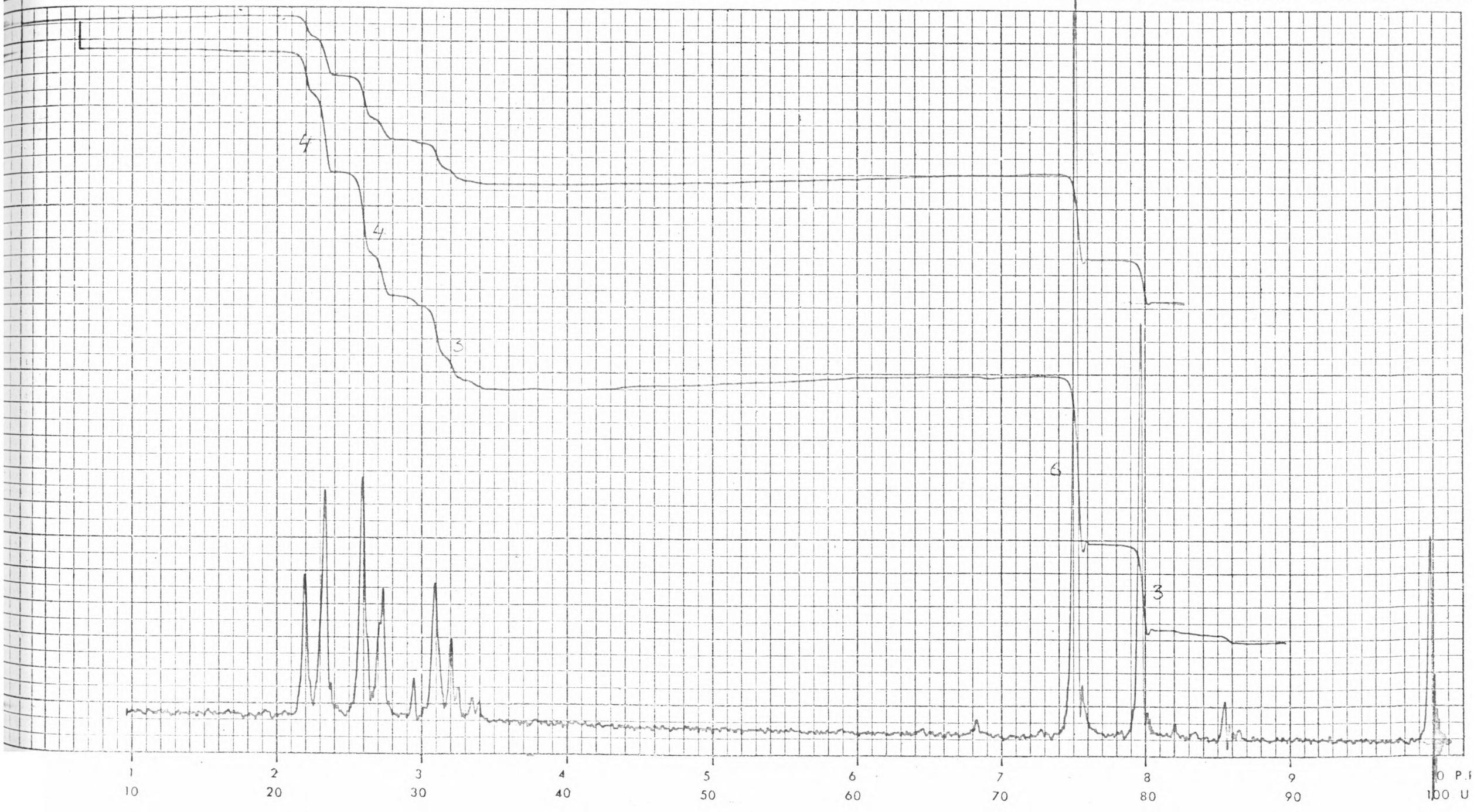
1,2,4-Substitution-960(m) cm^{-1}

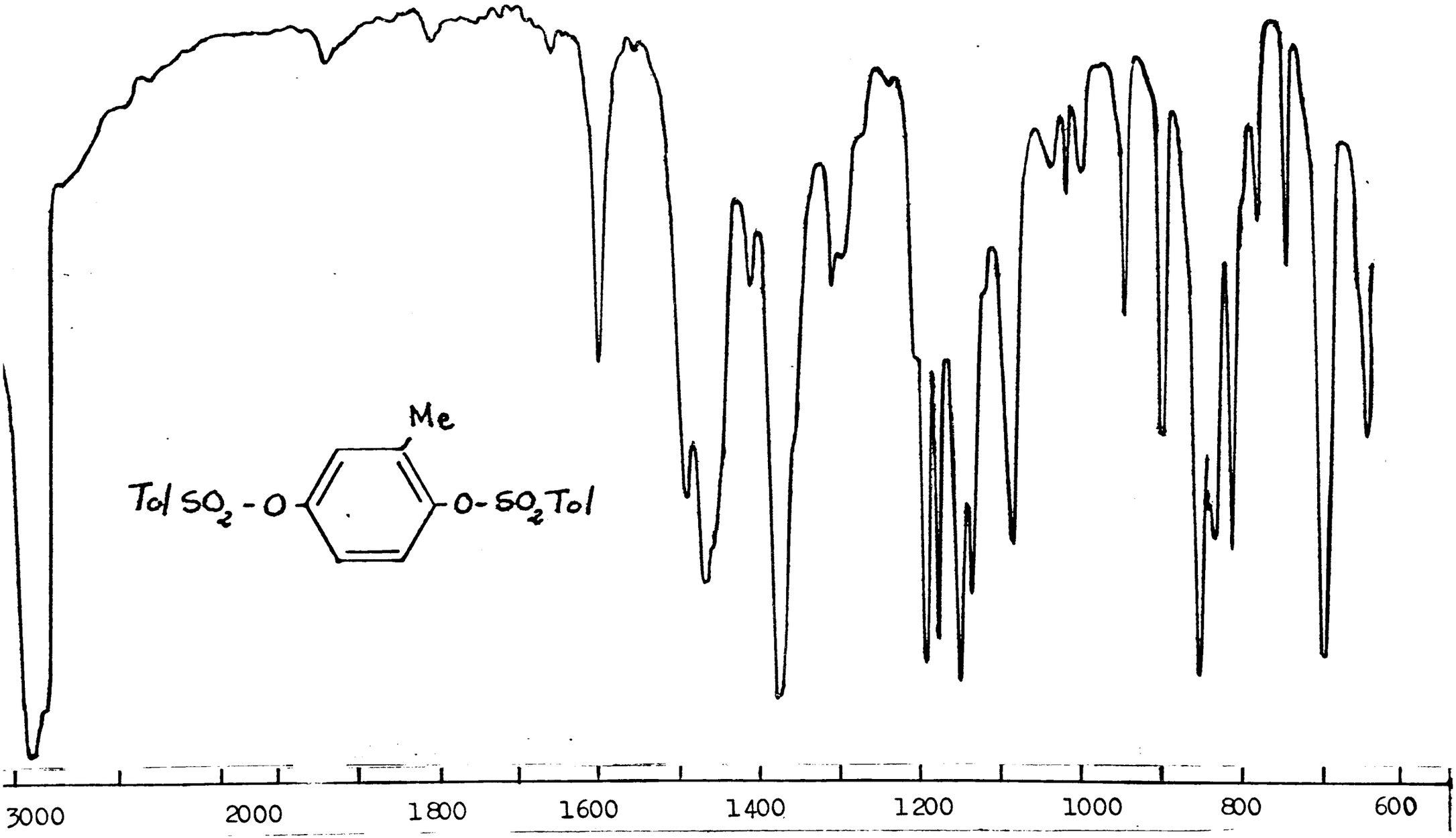
Sulphur bands

$-SO_2-O-$ stretching-1155(s) and 1380(s) cm^{-1}

The total yield of di-ester was 28%.

DATE: 1 MAR 1966	DEC. SHIFT	REF. STD.	R.F. FIELD	R.F. GAIN	REMARKS	SENSITIVITY NORM: 1 INT: 2.4	SWEEP RATE ____ UNITS ____ PER MIN	TIME CONST. ____ SECS 0.1S M SECS.	SCALE FACTOR 6 C/S PER UNIT
____	____	____	____	____					





Infra red spectrum of methylhydroquinone-di-p-toluenesulphonate

(Nujol film)

1.2.6- Reaction with chloranil (tetrachloro-p-benzoquinone)

A mixture of p-toluenesulphonyl iodide (14.5 g., 0.0515 mole), chloranil (6.32 g., 0.0258 mole) and copper bronze (3.25 g., 0.0515 g.atom) in carbon tetrachloride (250 ml.) was refluxed for eight hours. Filtration of the hot suspension gave a grey solid and a violet filtrate. Extraction of the solid with hot chloroform and hot carbon tetracloride gave a trace of yellow solid the i.r. spectrum of which was identical of that of chloranil.

The violet filtrate was washed with 10% sodium dithionite (3 × 100ml.) and water (2 × 100ml.). The organic layer was dried over sodium sulphate, then, concentrated in vacuo to a pale yellow solid (0.40 g.) which was suspended in ethanol (5ml.). Filtration yielded a colourless solid (0.35 g.), m.p. 200-12°. A Lassaigne test on the solid indicated it contained sulphur and chlorine.

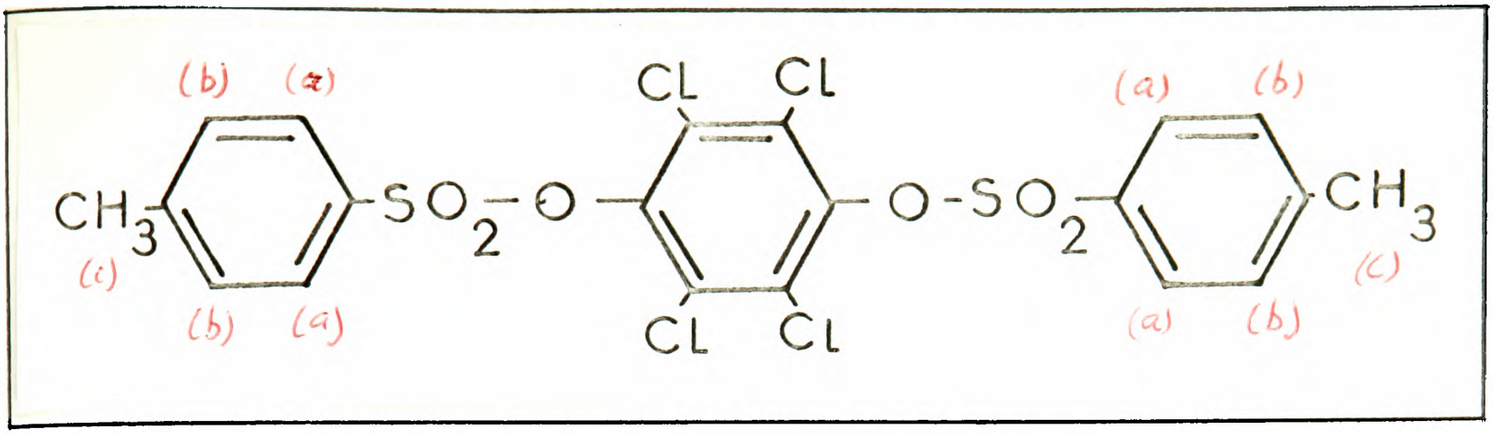
Recrystallization of the solid (0.20 g.) from ethanol gave colourless small crystals, (0.18 g.), m.p. 227-8° of tetrachlorohydroquinone-di-p-toluenesulphonate, the i.r. spectrum of which was identhical with that of the material of m.p. 200-12°.

Analysis gave: C-43.89; H-2.64; Cl-24.80; S-11.12%

Req.for $C_{20}H_{14}Cl_4O_6S_2$:

C-43.18; H-2.54; Cl-25.49; S-11.54%

The n.m.r. spectrum of this compoud in deuterated chloroform (p.190) showed:



Proton	τ(P.P.M.)	J(c/sec.)	Relative intensity	Obs.
a	2.04	8.6	4	Doublet
b	2.58	8.6	4	Doublet
c	7.47	-	6	Singlet

The i.r. spectrum of the compound in nujol is showm on p.191

Aromatic

C=CH skeletal in-plane deformations:1605(m) and 1500(w) cm^{-1}

C-H out-of-plane vibrations:

Two adjacent hydrogen atoms-820 cm^{-1}(m)

Region 1225-950 cm^{-1}:

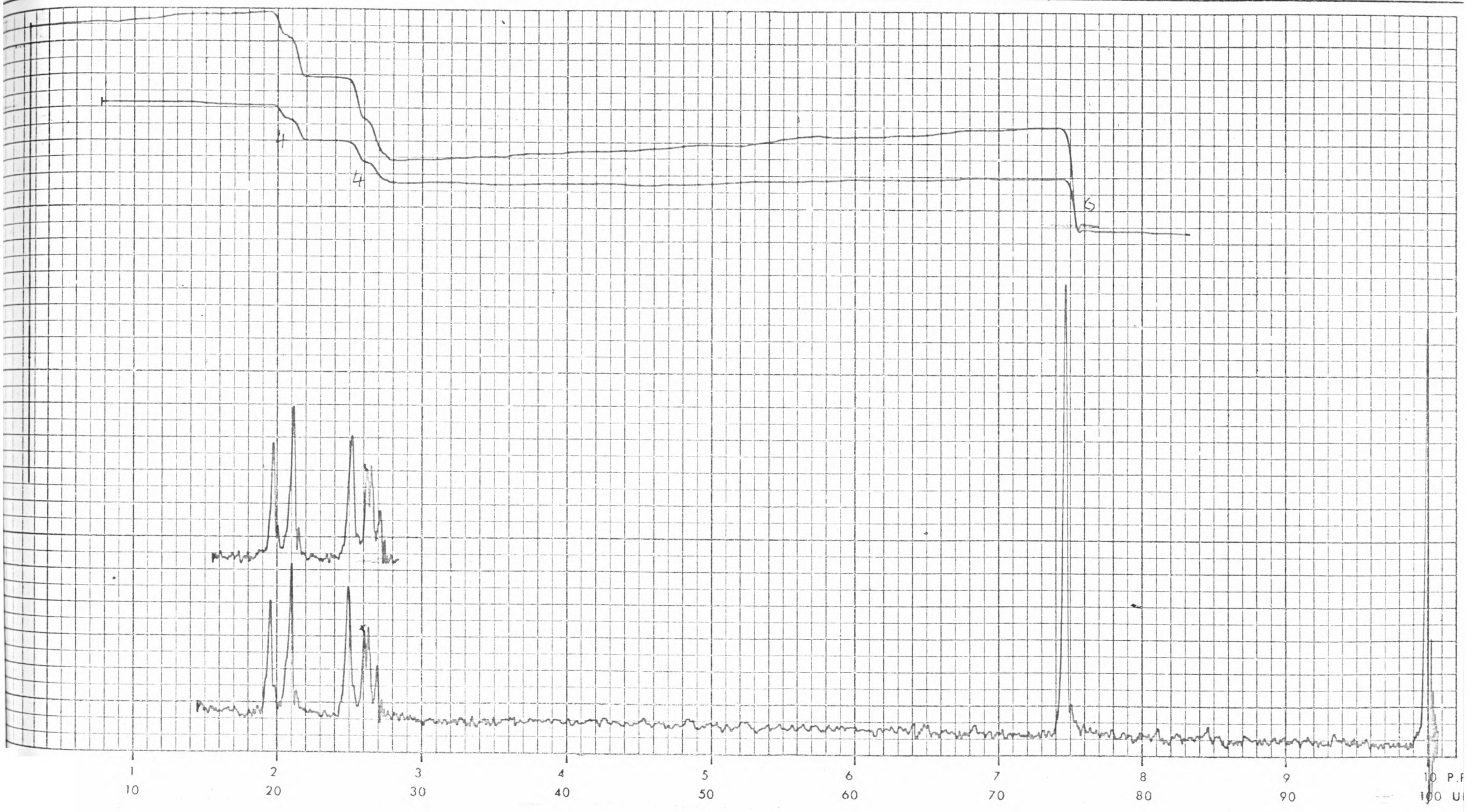
1,4 Substitution-1090(m),1020(w) and 1040(w) cm^{-1}

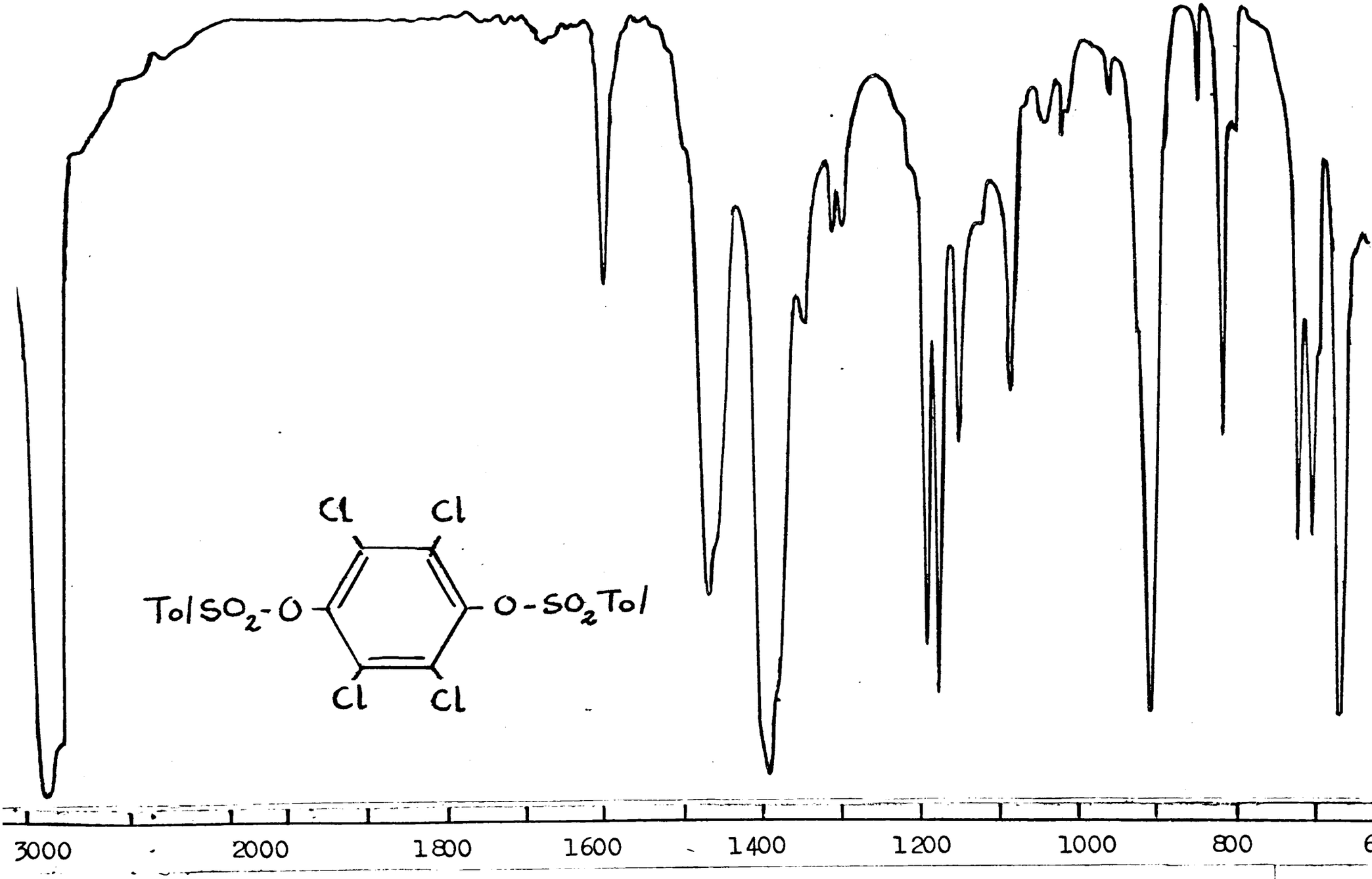
Sulphur bands

$-SO_2-O-$ stretching-1160 and 1380 cm^{-1} (s)

The two bands characteristic of the other di-esters at 1180 and 1200 cm^{-1} were also present.

DATE	DEC. SHIFT	REF. STD.	R.F. FIELD	R.F. GAIN	REMARKS	SENSITIVITY	SWEEP RATE	TIME CONST.	SCALE FACTOR
APR 1966					x up · as before ·	NORM: 2 INT: 4, 8	82 UNITS PER MIN	SECS .015 M SECS	6 C/S PER UNIT





Infra red spectrum of tetrachlorohydroquinone-di-p-toluenesulphonate

(Nujol film)

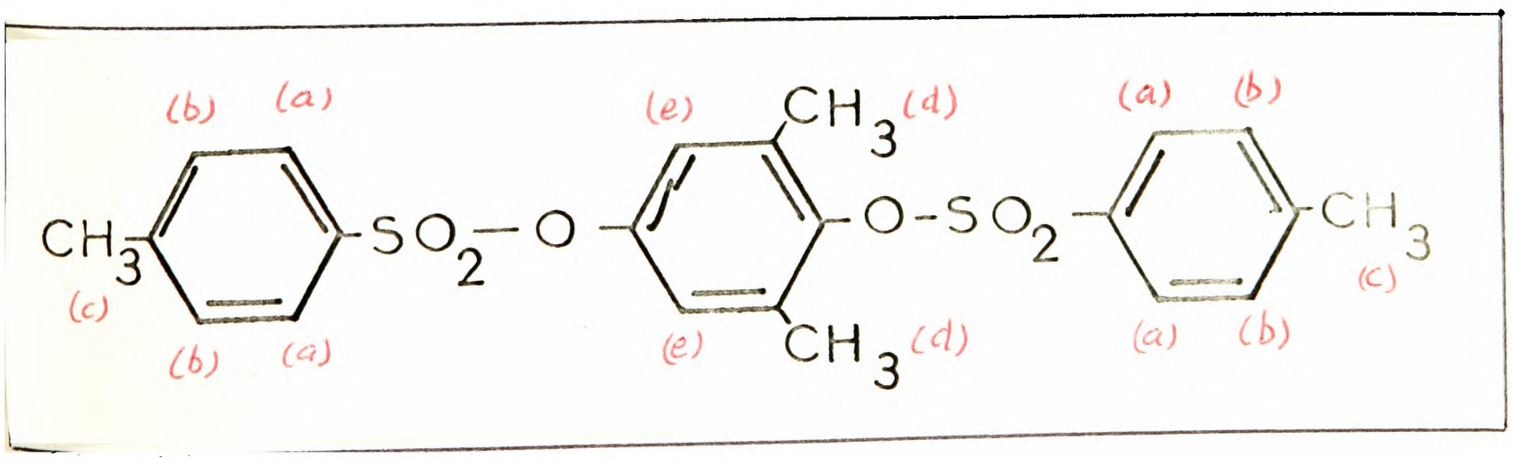
1.2.7 - Reaction with m-xyloquinone (2,6-dimethyl-p-benzoquinone)

A mixture of p-toluenesulphonyl iodide (19.0 g., 0.0675 mole), m-xyloquinone (4.6 g., 0.0337 mole) (p. 285), copper bronze (4.4 g., 0.0674 g.atom) and carbon tetrachloride (250 ml.) was boiled under reflux for eight hours. The hot suspension was filtered to remove a grey solid and the filtrate was stored overnight at 0°.

p-Toluenesulphonic anhydride (4.17 g., 48.5%) separated as colourless small crystals (m.p. 99-100°), and was collected. The i.r. spectrum of the anhydride was identical with that of an authentic specimen.

The filtrate was washed with 10% alkaline sodium dithionite solution (3 × 100 ml.) and water (2 × 100 ml.). The organic layer was dried (sodium sulphate) and concentrated in vacuo to 20 ml. 2,6-Dimethylhydroquinone-di-p-toluenesulphonate separated as colourless crystals (0.11 g., 0.66%, m.p. 160-2°) and was compared with an authentic specimen (i.r. and mixed m.p.) prepared as described at p. 288.

The n.m.r. spectrum of the synthetic product is shown at p. 194, and it is consistent with th following structure:



Proton	τ(P.P.M.)	Relative intensity	Obs.
a	2.34		
b	2.63	8.3	A_2B_2 quartet
c	7.55	6	Singlet
d	7.93	6	Singlet
e	3.30	2	Singlet

The tolyl A_2B_2 quartet was complex, showing other interactions.

The i.r. spectrum of this di-ester in nujol showed the following characteristics (p. 195):

Aromatic

C=CH skeletal in-plane vibrations-1595(m) and 1500(?) cm^{-1}
C-H out-of-plane deformations:

Two adjacent hydrogen atoms-810(s) cm^{-1}

One isolated hydrogen atom-890(s) cm^{-1}

1,2,3,5-Substitution-850(s) cm^{-1} ?

Region 1225-950 cm^{-1}:

1,4-Substitution-1090(s) and 1020(m) cm^{-1}

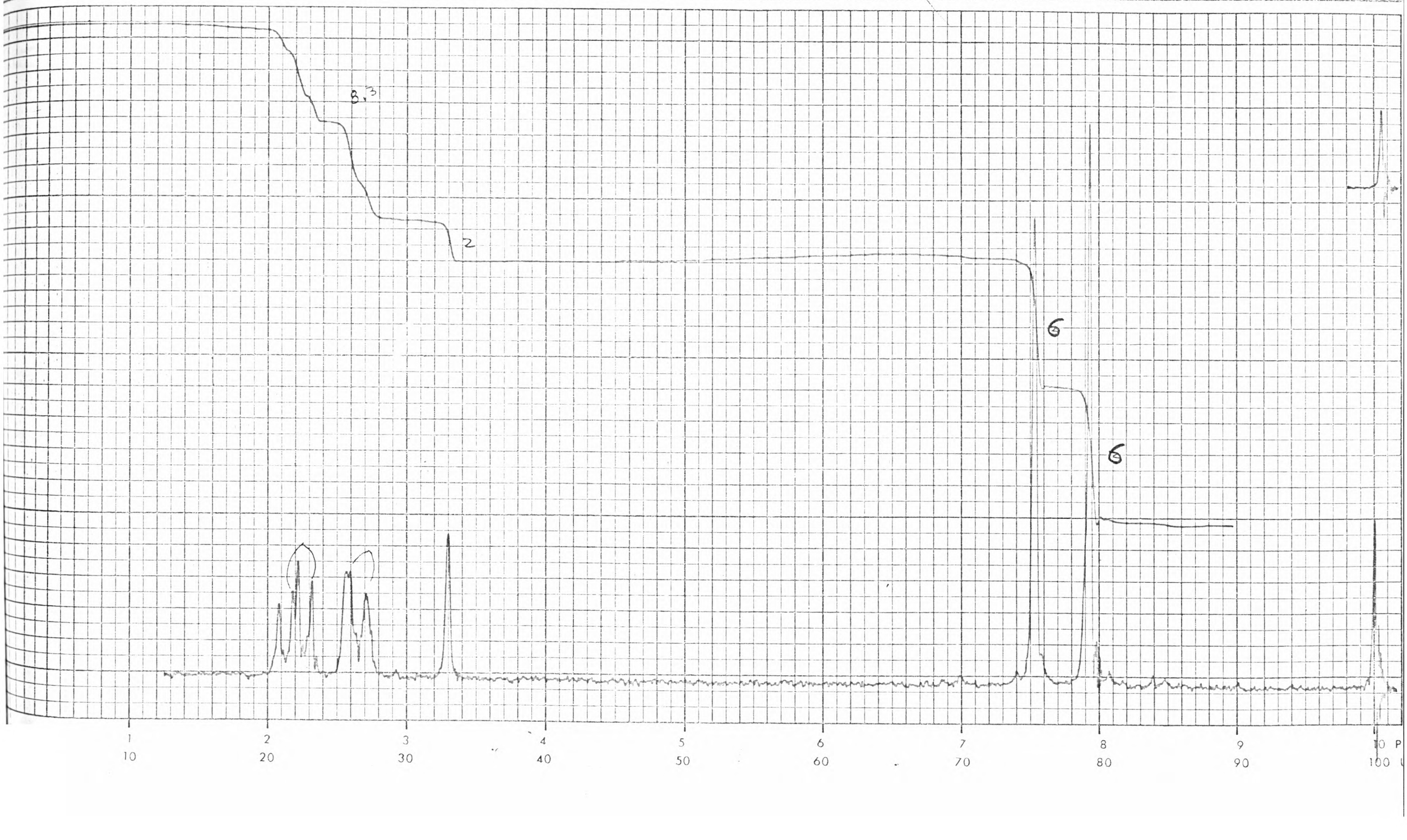
Sulphur bands

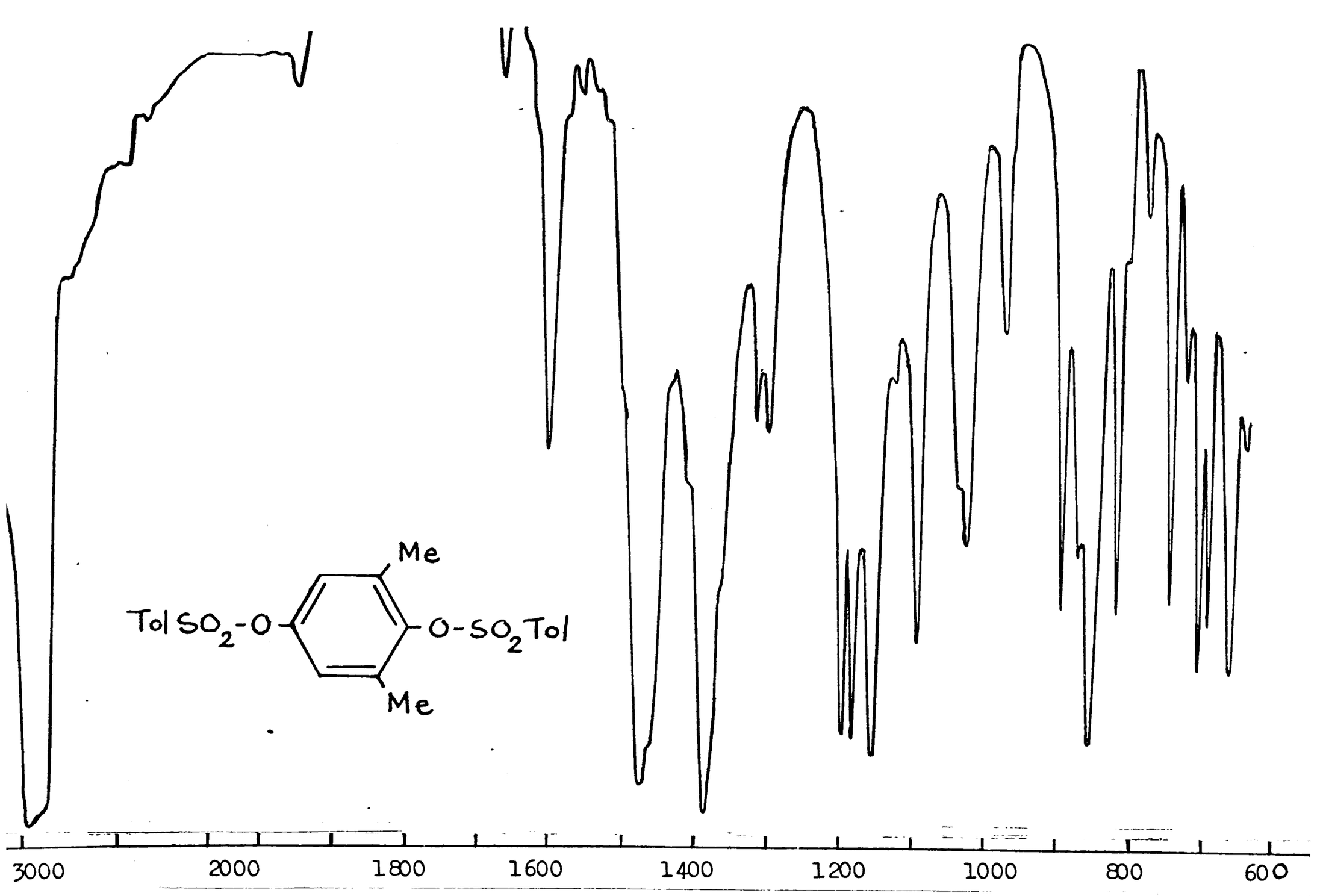
$-SO_2-O-$ stretching-1145(s) and 1380(s) cm^{-1}

The two bands (1180 and 1200 cm^{-1}) that appeared in all other di-esters were also present.

The mother liquor of crystals m.p.160-2° was concentrated to 1-2 ml. of brown oil which on treatment with hot petroleum ether gave a brown oil and a clear solution. The petroleum ether, on cooling, yielded colourless crystals (0.08 g.) of p-tolyl-p-toluenethiosulphonate, m.p. 75° alone and when mixed with an authentic specimen.

DATE 1956	DEC. SHIFT	PER. STD.	R.F. FIELD	R.F. GAIN	REMARKS	SENSITIVITY NORM: 1 INT: 4	SWEEP RATE ____ UNITS PER INCH	TIME CONST. ____ SECS 0.15 M. SECS	SCALE FACTO 6 C/S PER UNIT
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Infra red spectrum of 2,6-dimethylhydroquinone-di-p-toluenesulphonate

(Nujol film)

No further solids were obtained by treatment of the brown oil with organic solvents.

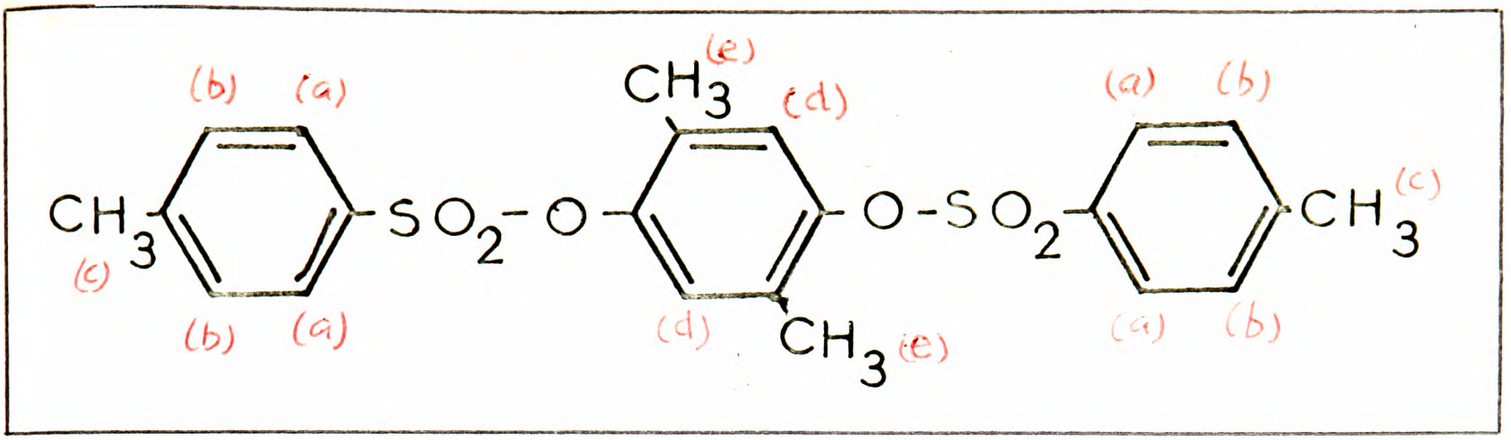
1.2.8 - Reaction with p-xyloquinone (2,5-dimethyl-p-benzoquinone)

Amixture of p-toluenesulphonyl iodide (17.0 g.,0.0604 mole), p-xyloquinone (4.1 g.,0.0302 mole) (p. 284), copper bronze (3.84 g., 0.0604 g.atom) and carbon tetrachloride (250 ml.) was refluxed for seven hours. The solid was removed by filtration and the filtrate was stored overnight at 0 . Filtration of this gave a filtrate (A) and colourless crystals (6.34 g.) shown by i.r. spectroscopy and thin layer chromatography to be a mixture of p-toluenesulphonic anhydride and a second compound.

Extraction of the mixture with benzene (2×20 ml.) removed the sulphonic anhydride and left an insoluble residue (1.62 g.,12%), m.p. 184-90° . Recrystallization of this from benzene gave 2,5-dimethylhydroquinone-di-p-toluenesulphonate as colourless crystals (1.46 g.), m.p. 192-4°, identical with an authentic specimen prepared as described at p. 288 .

Filtrate (A) was washed with 10% alkaline sodium dithionite (3×100 ml.) and water (2×100 ml.). THe organic layer was dried (sodium sulphate) and then concentrated to yield a trace of material which was shown by i.r. spectroscopy to be essencially p-tolyl-p-toluenethiosulphonate. No di-ester bands were detected in the i.r. spectrum of this solid.

The n.m.r. spectrum (p. 198 ϕ of the compound in deuterated chloroform confirmed the structure:



Proton	τ (P.P.M.)	J (c/sec.)	Relative intensity	Obs.
a	2.27	8.6	4	Doublet
b	2.65	8.6	4	Doublet
c	7.51	-	6	Singlet
d	3.08	-	2	Singlet
e	8.05	-	6	Singlet

The i.r. spectrum of the product in nujol showed the following:

Aromatic

C=CH skeletal in-plane vibrations-1600 (m) and 1505 (m) cm^{-1}

C-H out-of-plane deformations:

Two adjacent hydrogen atoms-820 (s) cm^{-1}

One isolated hydrogen atom-870 (s) cm^{-1}

1,2,4,5-Substitution-900 (s) cm^{-1}

Region 1225-950 cm^{-1}:

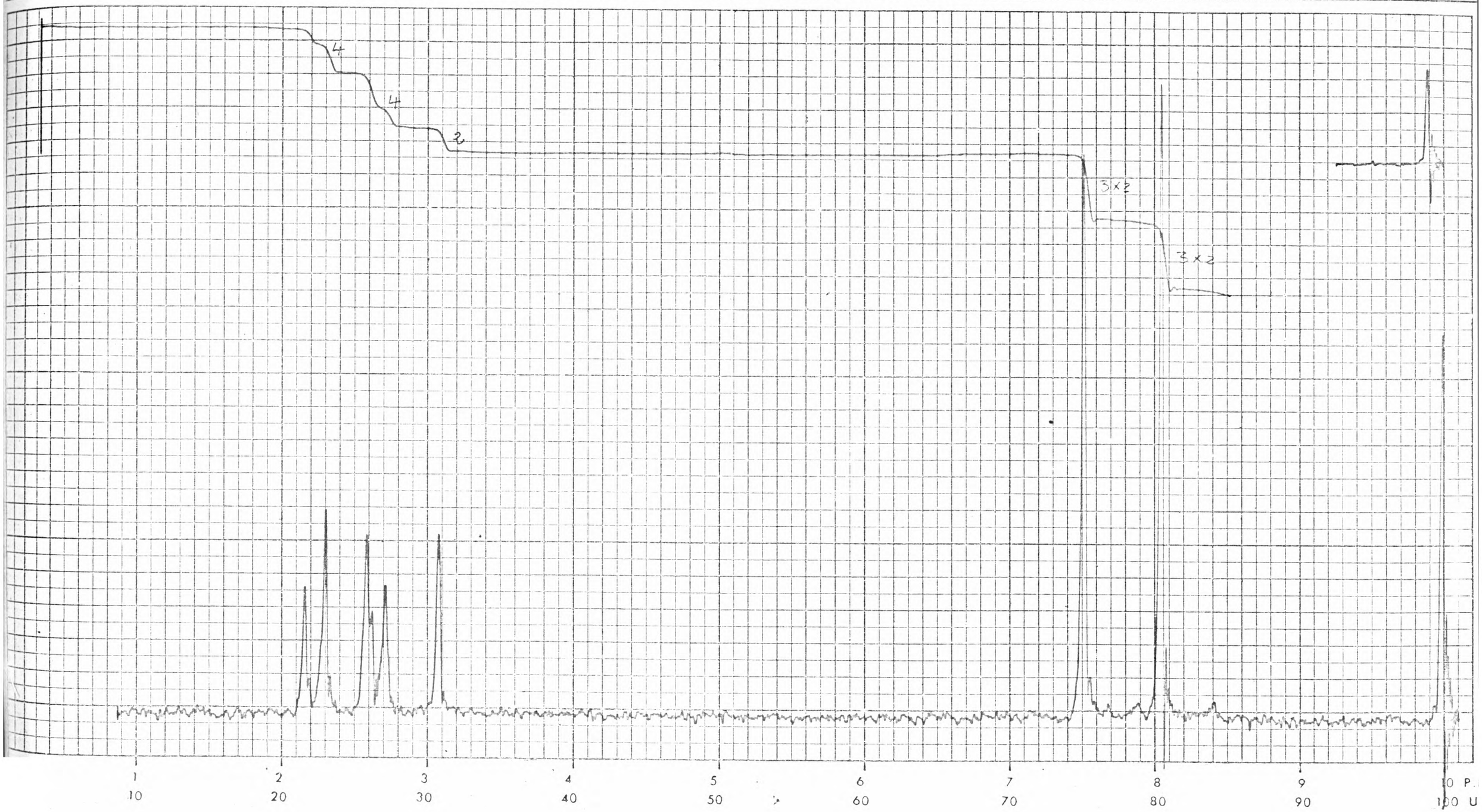
1,4-Substitution-1090 (s), 1020 (w) and 1040 (w) cm^{-1}

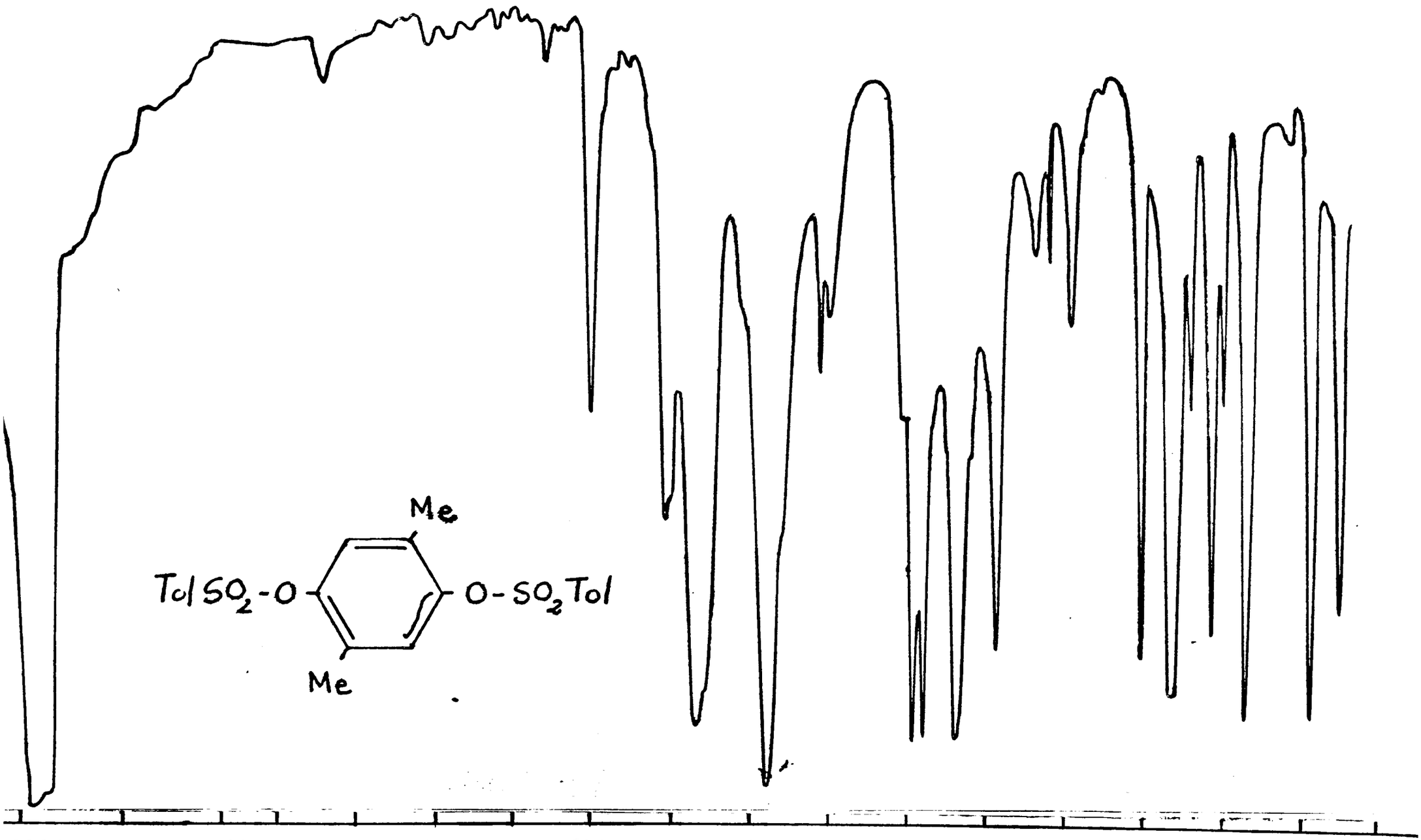
Sulphur bands

$-SO_2-O-$ stretching-1145 (s) and 1380 (s) cm^{-1}

Bands at 1180 and 1200 cm^{-1} were also present.

DATE	DEC. SHIFT	REF. STD.	R.F. FIELD	R.F. GAIN	REMARKS	SENSITIVITY	SWEEP RATE	TIME CONST.	SCALE FACTO
6 APR 1966			1	1/2		NORM: 2 INT: 4	____ UNITS PER MIN	0.1 SECS 0.15 M SECS	6 C/S PER UNIT





Infra red spectrum of 2,5-dimethylhydroquinone-di-p-toluenesulphonate

(Nujol film)

1.2.9 - Reaction with thymoquinone (2-methyl-5-isopropyl-p-benzoquinone).

A mixture of p-toluenesulphonyl iodide (17.7 g., 0.063 mole), thymoquinone (5.0 g., 0.0306 mole) (p.285), copper bronze (4.0 g., 0.063 g.atom) and carbon tetrachloride (250 ml.) was refluxed for seven hours.

The hot reaction mixture was filtered to remove copper salts and the filtrate was stored at 0 overnight. p-Toluene-sulphonic anhydride (5.37 g., 47%) separated, m.p. 98-101°, identified by comparison of i.r. spectra and mixed m.p. with an autentic specimen. The carbon tetrachloride filtrate was extracted with 10% sodium hydroxide solution (100 ml.). The aqueous layer was washed with 10% alkaline sodium dithionite (2× 100 ml.), water (100 ml.) and dried (sodium sulphate).

The solvent was removed under reduced pressure and a solid residue (0.51 g.) was obtained. This solid was washed with ether (15 ml.) and collected (0.40 g., m.p. 150-60°).

The washings were evaporated giving a trace of uncharacterised oil. The solid of m.p. 150-60° was recrystallized several times from a mixture of ether and benzene (3:1); m.p. 160-2°.

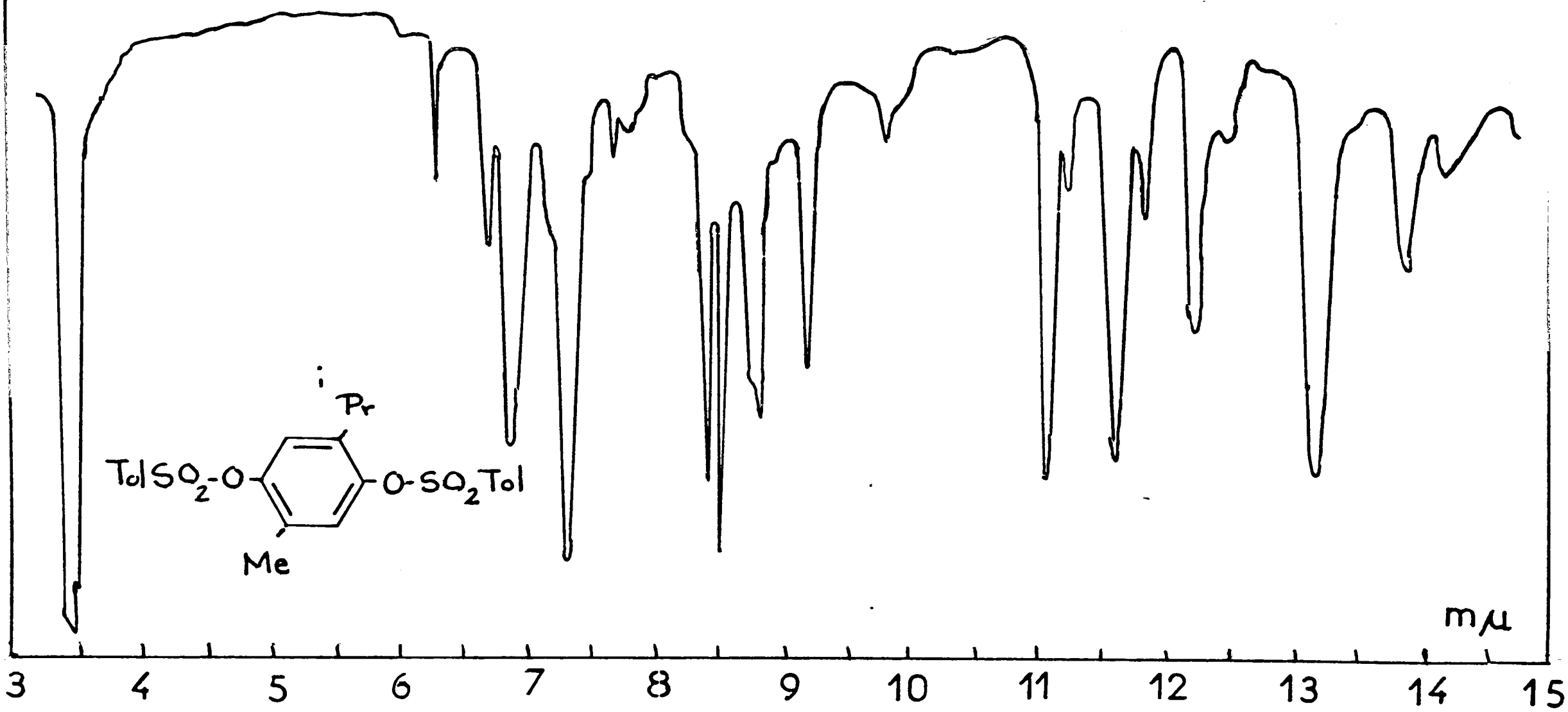
Analysis gave:

C-59.82% , H-5.25% , S-11.88%

$C_{24}H_{22}O_6S_2$ (2-methyl-5-isopropylhydroquinone-di-p-toluene-sulphonate) requires:

C-60.75% , H-5.52% , S-13.49%

The i.r. spectrum of the compound in nujol (p.201) was similar with that of 2,5-dimethyl-hydroquinone-di-p-toluene-sulphonate (p.199) and bands can be ascribed to:



Infra red spectrum of 2-methyl-5-isopropyl--hydroquinone-di-p-toluenesulfonate.
(Nujol film)

Aromatic

C=CH skeletal in-plane vibrations-1595(w) and 1500(m) cm^{-1}

C-H out-of-plane deformations:

Two adjacent hydrogen atoms-840(m) cm^{-1}

One isolated hydrogen atom-860(s) cm^{-1}

1,2,4,5-Substitution-900(s) cm^{-1} ?

Region 1225-950 cm^{-1}:

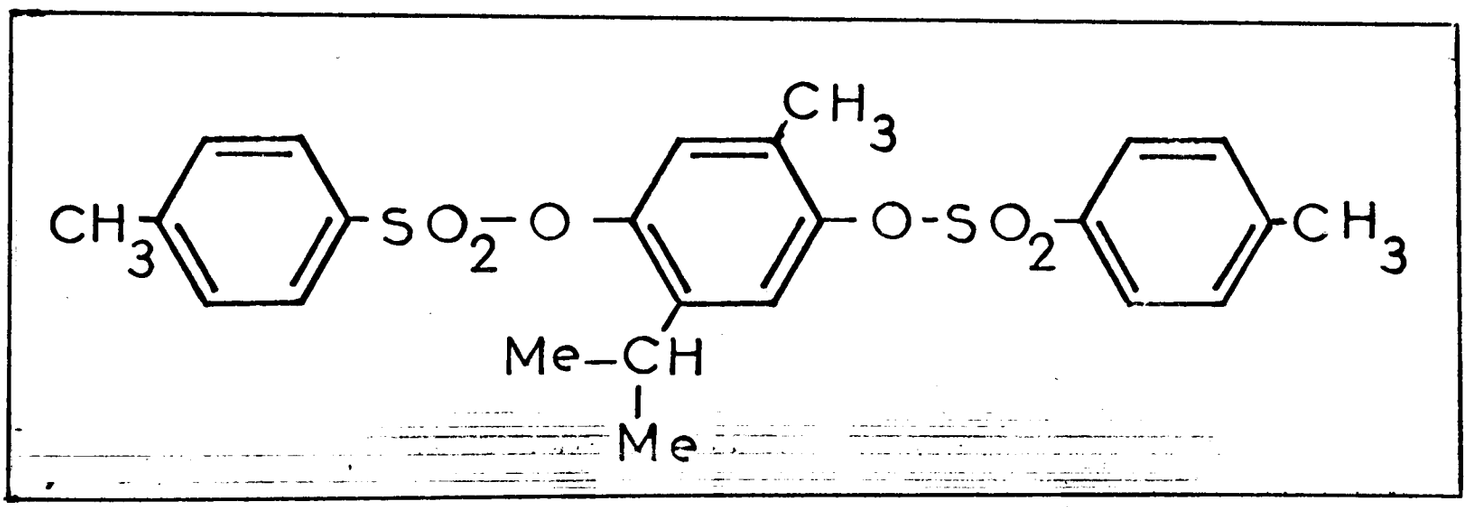
1,4-Substitution-1090(m),1020(w) and 1010(w) cm^{-1}

Sulphur bands

$-SO_2-O-$ stretching-1375(s) and 1145(s-m) cm^{-1}

Bands at 1180 and 1200 cm^{-1} were also present.

The compound is probably 2-methyl-5-isopropyl-hydroquinone--di-p-toluenesulphonate:



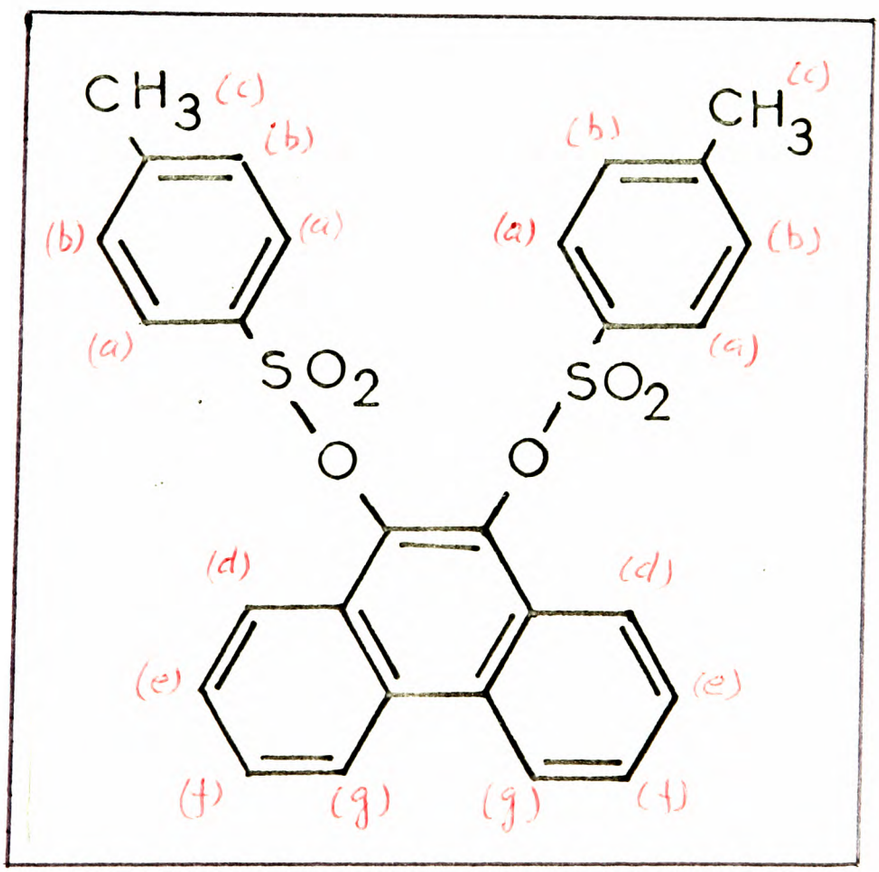
1.2.10 - Reaction with 9,10-phenanthraquinone.

A mixture af p-toluenesulphonyl iodide(38.0 g.,0.135 mole), phenanthraquinone(7.0 g.,0.0338 mole),copper bronze(8.5 g., 0.135 g.atom) and carbon tetrachloride(250 ml.) was heated under reflux for seven hours.The reaction mixture was filtered and a grey solid separated.A Lassaigne test on this solid

indicated the absence of sulphur.

The filtrate was cooled and washed with 10% alkaline sodium dithionite solution (4 × 100 ml.), and water (2 × 100 ml.), and dried (sodium sulphate). The solvent was removed under reduced pressure leaving a pale yellow solid (0.5 g.), m.p. 193-8°. Recrystallization from acetone gave very small crystals, 0.4 g., m.p. 200-1°.

This solid was identified as 9,10-di-hydroxyphenanthrene--di-p-toluenesulphonate by comparison of i.r. spectrum and mixed m.p. with an authentic specimen (p. 288). The structure of the compound was confirmed by n.m.r. in deuterated chloroform:



and may be interpreted as follows(p.205):

Proton	τ(P.P.M.)	J(c/sec.)	Relative intensity	Obs.
b	2.75	8.6	4	Doublet
c	7.55	-	6	Singlet
a,e,f	2.20-2.55	-	8	Complex
d	1.70-2.00	-	2	Complex
g	1.20-1.50	-	2	Complex

Protons (g) were assumed to be those with the greatest shift relative to cyclohexane protons by comparison with the n.m.r. spectrum of phenanthrene[157].

The i.r. spectrum of this di-ester in nujol showed the following(206):

Aromatic

C:CH skeletal in-plane vibrations-1605(m),1640(w) and 1500(w)

C-H out-of-plane deformations:

Two adjacent hydrogen atoms-820(s) cm^{-1}

Four adjacent hydrogen atoms-740(s) cm^{-1}

Region 1225-950 cm^{-1}:

1,4 and 1,2-Substitution-1090(s) or 1010(s) cm^{-1} ?

Sulphur bands

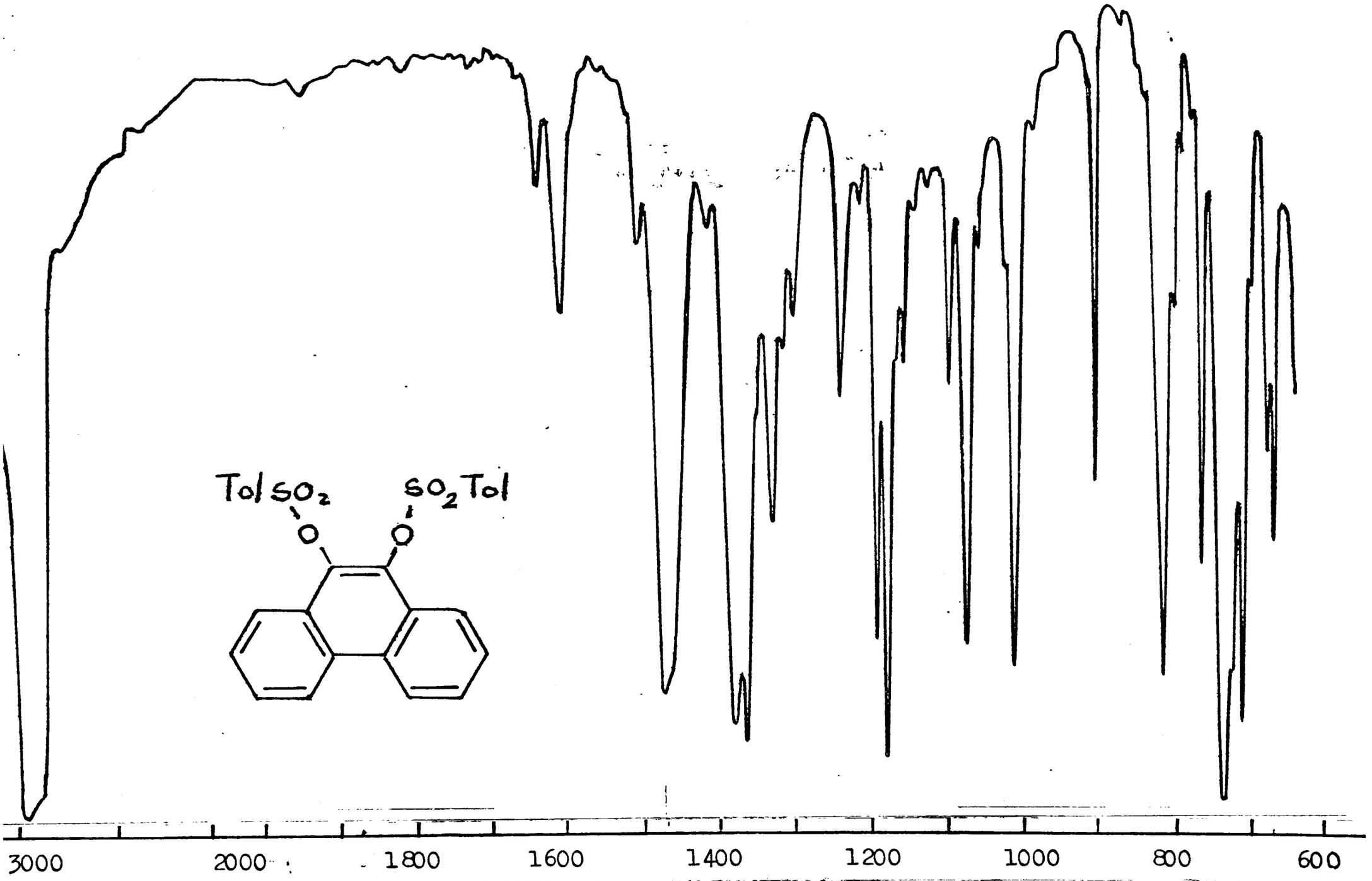
$-SO_2-O-$ stretching - ? 1180 and 1200,1380 or 1375(s) cm^{-1}

The usual band near 1150 cm^{-1} had disappeared,but bands at 1180 and 1200 cm^{-1} were present,as usual.

Bands at 715(s),735(s),820(s) and 1010(s) cm^{-1} were also present in the i.r. spectrum of phenanthrene[158].

DATE	DEC. SHIFT	REF. STD.	R.F. FIELD	R.F. GAIN	REMARKS	SENSITIVITY	SWEEP RATE	TIME CONST.	SCALE FACTO
21 APR 1955						NORM: 2 INT: 4	UNITS PER MIN	SECS D.I.S. M.SECS	6 C.S. PER UNIT





Infra red spectrum of 9,10-dihydroxyphenanthrene-di-p-toluenesulphonate

(Nujol film)

1.2.11 - Reactions with duroquinone (tetramethyl-p-benzoquinone), 9,10-Phenanthraquinone and 1,2-Acenaphthaquinone.

These reactions were carried out under the same conditions as previous reactions with a mixture of p-toluenesulphonyl iodide (18.0 g., 0.064 mole), copper bronze (4.15 g., 0.065 g.atom) and quinone (0.032 mole).

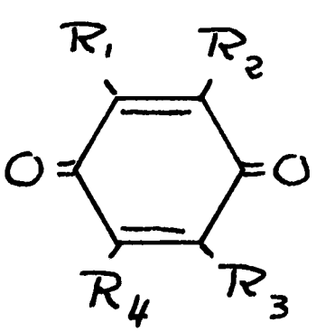
The reactions mixtures were worked out in the same manner as the reactions with P-benzoquinone (1.2.1) but no p-toluenesulphonates were detected.

Duroquinone was prepared as described at p.286.

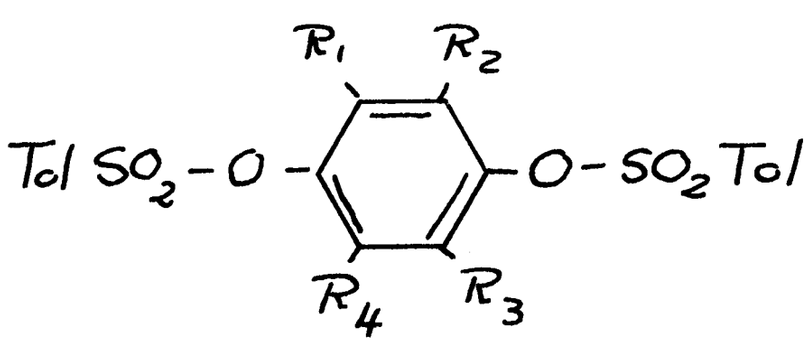
1.2.12 - Results

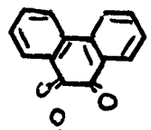
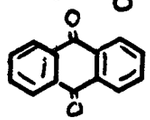
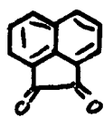
Results of reactions of p-toluenesulphonyl iodide with quinones are summarised in the table next page:

Quinone:



Di-ester:



Quinone	R_1-	R_2-	R_3-	R_4-	Di-ester m.p.	Di-ester yield	Synthetic di-ester m.p.	Synthetic di-ester i.r.	Synthetic di-ester n.m.r.	Reference
p-Benzoquinone	H	H	H	H	162-3°	46.5	163-4°	p.175	p.176,7	54
Toluquinone	Me	H	H	H	148-53°	28.0	152-4°	p.186	p.187	New
Chloranil	Cl	Cl	Cl	Cl	227-8°	2.4	-	p.191	p.190	New
m-Xyloquinone	Me	H	H	Me	160-2°	0.66	161-3°	p.195	p.194	New
p-Xyloquinone	Me	H	Me	H	191-3°	12.0	192-4°	p.199	p.198	New
Thymoquinone	^{i}Pr	H	Me	H	160-2°	2.8	-	p.201	-	?
Duroquinone	Me	Me	Me	Me	-	0	-	-	-	-
9,10-Phenanthraquinone					200-1°	2.4	201-2°	p.206	p.205	New
9,10-Anthraquinone					-	0	-	-	-	-
1,2-Acenaphthaquinone					-	0	-	-	-	-

1.3 - Further indications of the free radical nature of reactions of p-toluene sulphonyl iodide.

1.3.1 - The reaction of p-toluenesulphonyl iodide with anthracene.

A - Reaction in the presence of copper bronze

The reaction was carried out in a 500 ml. flask, fitted with a mechanical stirrer, a reflux condenser and a calcium chloride guard tube. Heating was by means of a water bath.

p-Toluenesulphonyl iodide (17.0 g., 0.0605 mole), anthracene (6.5 g., 0.0365 mole) and copper bronze (5.0 g., 0.078 g. atom) in benzene (220 ml.) were refluxed together for four hours. The mixture was filtered hot and a yellow-green solid (A) was separated. The solid (A) was extracted with boiling benzene (B). The benzene filtrate of (A) was added to the extract (B). The combined solution was concentrated to 50 ml. cooled and filtered (C). 5.88 g. of white crystals were obtained (D), m.p. = 140-147°. A Lassaigne test on the solid (D) showed the presence of sulphur, but iodine was absent. The analysis of the solid (D) by their layer chromatography and i.r. spectroscopy showed it consisted of unreacted anthracene, a little p-toluenesulphonic anhydride and p-tolyl-p-toluenethiosulphonate, and another product with very low Rf.

2.0 g. of the solid (D) were treated with 200 ml. of benzene. A small amount of the solid could not be dissolved

(0.10 g.) and it was separated by filtration (solid E). The filtrate was chromatographed on 200 g. of deactivated alumina. The products obtained from the column were:

I - Anthracene - 0.21 g.

II - Yellow product with anthracene - 1.20 g.

III - Brown oil

The yellow mixture (II) was washed with chloroform (20 ml.) and filtered. 0.26 g. of insoluble anthracene were separated. The chloroform filtrate was distilled. The residue was a bright yellow solid (F). A Lassaigne test on this solid showed the presence of sulphur. Analysis of (F) by thin layer chromatography and i.r. spectroscopy showed that it still contained anthracene. 0.6 g. of (F) were dissolved in 50 ml. of benzene and the solution was chromatographed on 60 g. of activated alumina.

The following products were obtained:

- 0.30 g. of anthracene
- 0.30 g. of yellow solid, m.p.180-182° (G)

The solid (G) was analysed:

Found: C = 74.22% H = 4.64% S = 9.16%

The product seemed to be a substituted anthracene, since it was fluorescent when examined under u.v. light and when dissolved in benzene in very small concentration.

The required analysis calculated for p-tolylsulphonylanthra-

cene is:

C = 75.89% H = 4.85% S = 9.63%

The i.r . spectrum of this solid showed no carbonyl absorption band so no anthraquinone was present.

This yellow product (G) was later characterized as 9-p-tolylsulphonylanthracene by comparison with an authentic specimen. It is not completely certain whether the product (G) was already present in the solid (D) since a clear decision could not be reached by examination of the infrared spectra of (G) and (D). We also cannot conclude anything from analysis of thin layer chromatoplates of (D) and (G) because the white mixture (D) when left in contact with silica gel on alumina turns yellow.

The infrared spectrum of (D) showed strong absorption bands not present in the spectra of anthracene and 9-p-tolylsulphonylanthracene. These absorption bands are also present in the spectrum of 9,10-di-p-tolylsulphonyl-9,10-dihydroanthracene. This product was also isolated. The yellow product (G), 9-p-tolylsulphonylanthracene is thought to be formed by decomposition of 9,10-di-p-tolylsulphonyl-9,10-dihydroanthracne in the column.

To see if the yellow product (G) was formed in the column the following experiment was carried out: 9,10-di-p-tolylsulphonyl-9,10-dihydroanthracene (0.50 g.) was dissolved in chloroform (50 ml.). The colourless solution was

percolated through 100 g. of alumina in a column. A strong yellow band appeared in the column. Chloroform was passed through the column. The yellow chloroform solution was compared with the initial one:

The thin layer chromatoplate showed one more spot, with the same Rf value as 9-p-tolylsulphonylanthracene.

The infra-red spectra of this yellow chloroform solution showed the presence of the absorption bands of the initial solution as well as new bands of the product (G) and a very strong CO band at 1.740 $cm.^{-1}$ (9,10 anthraquinone-CO- absorption band lies at 1670 $cm.^{-1}$).

The benzene solution (C) (p. 209) was distilled under reduced pressure, To the residue in the distillation flask a little carbon tetrachloride was added. The solid was triturated with a glass rod and heated to boiling. The hot solution was filtered (H) and 0.30 g. of white solid obtained as an insoluble product.(I) The carbon tetrachloride filtrate of (H) was kept in a refrigerator and 1.2 g. of white crystals (J), m.p. 101-103° were separated. These crystals were characterized as p-toluene sulphonic anhydride by comparison of i.r. spectra and mixed m.p. with an authentic specimen. The solid (I) was seen to be identical with solid (E) (p.209) and similar to the initial mixture of solids (D) (p.209). The carbon tetrachloride filtrate of (J) was distilled under

reduced pressure. A trace of residue was obtained. The yellow-green solid (A) separated from the reaction mixture (p.209)was extracted several times with hot chloroform. The combined extracts of chloroform were distilled under reduced pressure. A solid was obtained as residue. This solid was washed with a diluted aqueous solution of ammonia. A white solid was obtained (1.0 g.). This solid (L) was identical with 9,10-di-p-tolylsulphonyl-9,10-dihydroanthracene. Solids (I), (E) and (L) were put together and recrystallised from glacial acetic acid. The yield of this recrystallisation was very low. Colourless crystals, m.p. 149° were obtained (M). The i.r. spectra of this solid and solids (I), (L) and (E) were identical. The product m.p. - 149°C was analysed.

Found: C = 67.19% H = 4.97% S = 13.63%

Required to 9,10-di-p-tolylsulphonyl-9,10-dihydroanthracene:

C = 68.84% H = 4.95% S = 13.10%

This solid is not fluorescent when examined under u.v. light. The spectrum of this solid showed the following characteristics (p. 217).

Aromatic:

C=CH skeletal in-plane vibrations - 1600 cm^{-1} (m)

1500 cm^{-1} (w)

C-H out-of-plane deformations:

Four adjacent hydrogens - 790 cm^{-1} (s)

Two adjacent hydrogens - 830 cm^{-1} (s)

Region 1225-950 cm^{-1}:

1-2 and 1-4 substitution - 1200 cm^{-1} (s)?

1130 cm^{-1}(s) or 1095 cm^{-1}(s)

1040 cm^{-1}(w)

1060 cm^{-1}(w)

1-2 substitution: 975 cm^{-1} (w)

1600 cm^{-1} (m)

Non-aromatic:

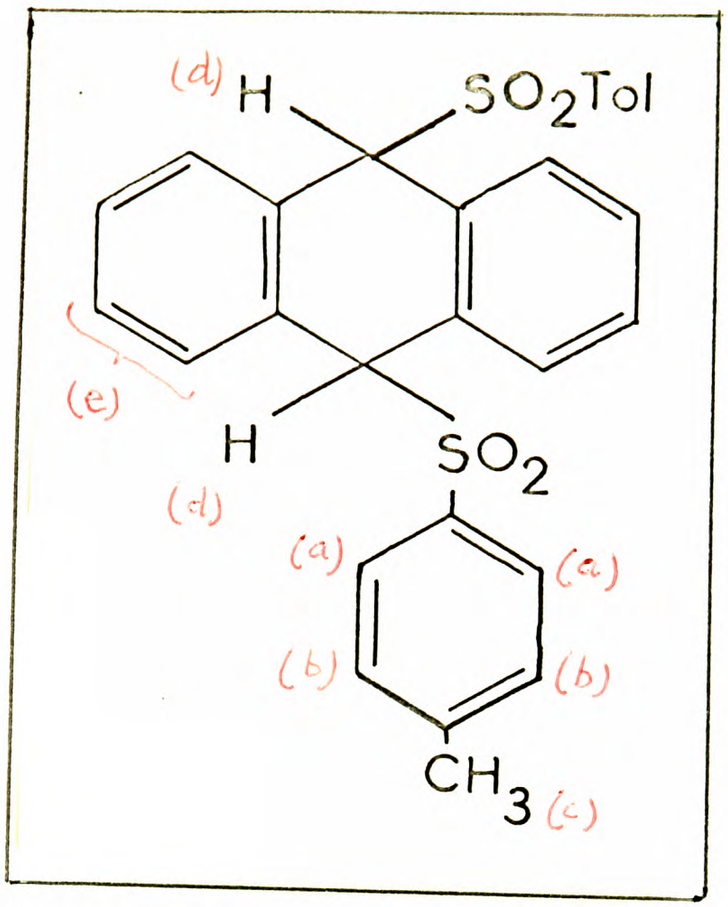
SO_2 stretching - 1180 cm^{-1}(s)

1310 cm^{-1}(s)

C-S stretching - 710 cm^{-1}(w) or 715 cm^{-1} (w)

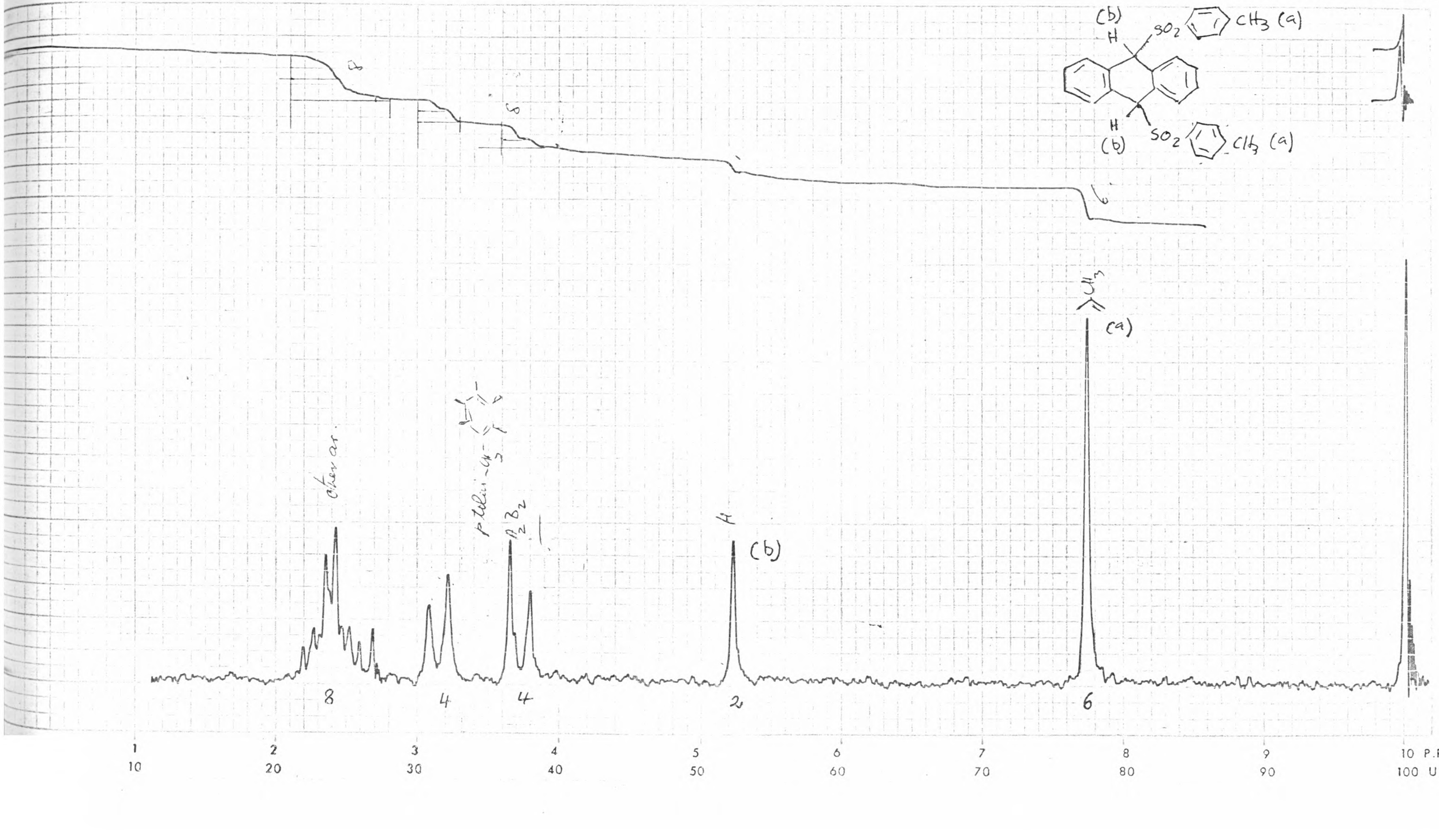
Nujol: 2.930 cm^{-1}, 1470 cm^{-1} and 1380 cm^{-1}

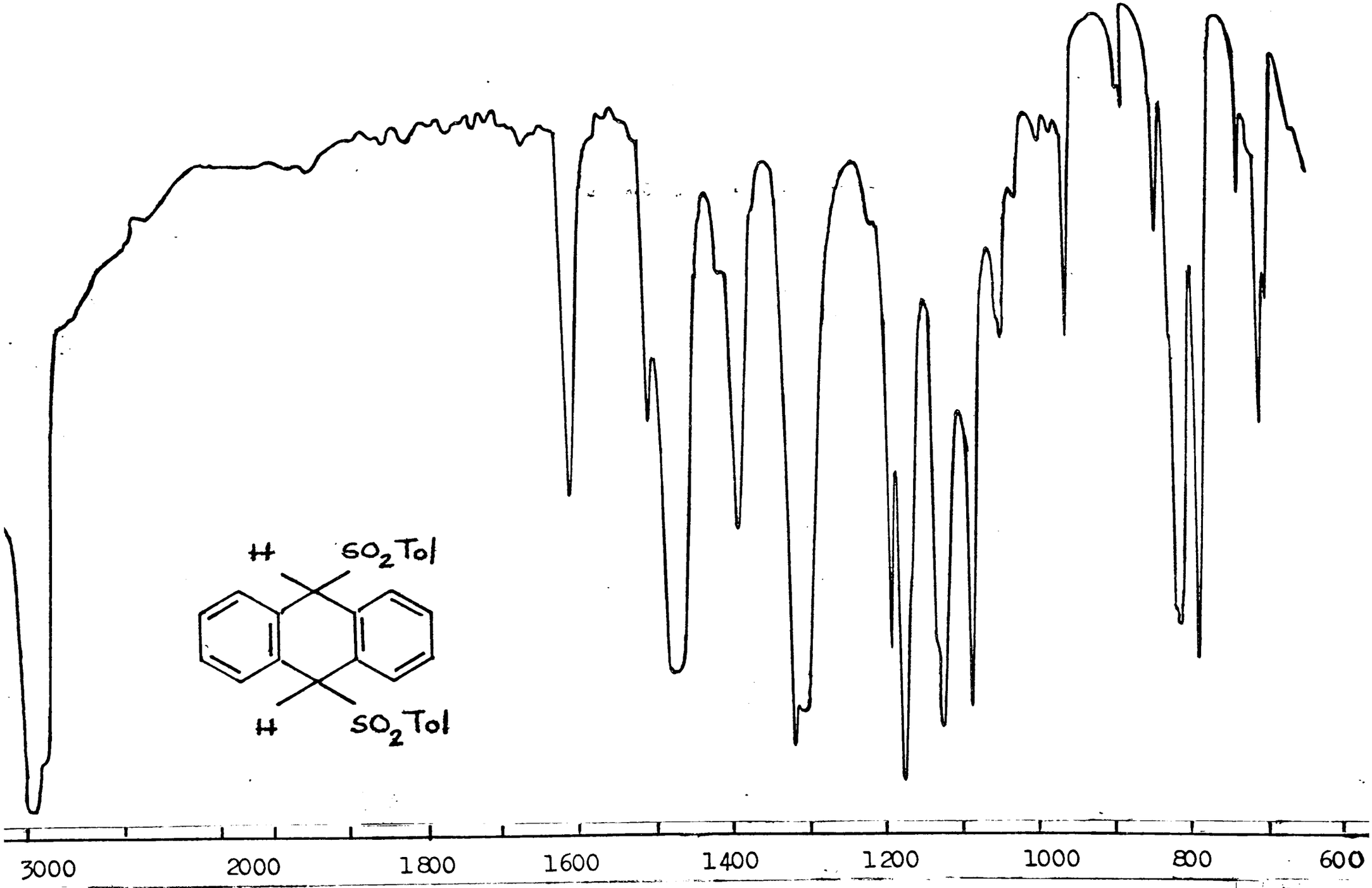
The analysis of this solid by nuclear magnetic resonance spectroscopy (n.m.r.) confirmed the following structure (b.216):



Protons	τ (PPM)	J($^{c}/_{sec}$)	Relative Intensity	Obs.
a	3.16	J_{ab}=8.4	4	Doublet
b	3.72		4	Doublet
c	7.75	-	6	Singlet
d	5.23	-	2	Singlet
e	2.45	-	8	Complex

DATE JUL 1965	DEC. SHIFT	REF. STD.	R.F. FIELD 1.25	R.F. GAIN	REMARKS	SENSITIVITY NORM: 4 INT: 4	SWEEP RATE 32 UNITS PER MIN	TIME CONST. 2 SECS 0.5 M SECS	SCALE FACTOR 6 C/S PER UNIT





Infra red spectrum of 9,10-di-p-tolylsulphonyl-9,10-dihydro-anthracene

(Nujol film)

The experiment was repeated, and a larger excess of p-toluenesulphonyl iodide was used.

p-Toluenesulphonyl iodide, (34.0 g., 0.121 mole), anthracene (6.5 g., 0.0365 mole) and copper bronze (10.0 g., 0.156 g.atom) in benzene (350 ml.) were refluxed together for four hours. The reaction was carried out in the presence of solid calcium carbonate (20 g., 0.2 mole) to keep the reaction mixture neutral if any hydrogen iodide were formed. The hot reaction mixture was filtered from a grey solid (N). The filtrate was cooled (8-10°C) and filtered (O). 1.5 g. of crystals (P) m.p. 148.5-149° were obtained. This product was characterised as 9,10-di-p-tolylsulphonyl-9,10-dihydroanthracne by comparison with an authentic specimen of the previous reaction by using m.p., mixed m.p. and i.r. spectrum. The crystals (P) were recrystallized from glacial acetic acid (low yield): m.p. = 150-150.5°.

The benzene filtrate (O) was concentrated by distillation under reduced pressure to 50 ml. This solution was cooled (6-8°C) and filtered (Q). 3.8 g. of white crystals (R) were separated, m.p. 148-149°. This product was examined by thin layer chromatography and by i.r. spectroscopy. Product (R) was a mixture of two products with very close Rf values. Anthracene was not present and 9,10-di-p-tolylsulphonyl-

9,10-dihydroanthracene was one of the two components of the mixture (R). The separation of (R) was attempted by extraction with solvents (hot benzene and hot methanol) but no separation could be obtained.

Product (R) was analysed:

Found: C = 68.58% H = 5.36% S = 12.82%

This result is not very far off that one required to 9,10-di-p-tolylsulphonyl-9,10-dihydroanthracene:

C = 68.84% H = 4.95% S = 13.10%

The separation of the mixture (R) could not be carried out by chromatography (alumina or silica gel) because the solid decomposed in the column yielding bright yellow products.

The benzene filtrate (Q) (p.218) was distilled under reduced pressure. 20 ml. of carbon tetrachloride were added to the residue and the solid was tritured with a glass rod. The mixture was filtered and 1.12 g. of p-toluene-sulphonic anhydride was separated m.p. 99-100° (T). This product was characterised by comparison with an authentic specimen. The carbon tetrachloride filtrate of (T) was distilled. A small residue of anthracene (0.20 g.) was obtained.

The solid (N) separated from the reaction mixture (p.218) was refluxed with chloroform. The hot mixture was filtered (U) and the filtrate was distilled under reduced pressure.

A pale green residue was obtained. This residue contained copper salts (flame test). The green residue was washed with an aqueous solution of ammonium hydroxide and filtered. 2.4 g. of white solid, m.p. 149-150° were obtained. This product was characterised as 9,10-di-p-tolylsulphonyl-9,10-dihydroanthracene by comparison with an authentic specimen obtained in the previous experiment. The yield of this product (not including the product present in the mixture (R)) was 3.9 g. (22%).

B - Reaction in the absence of copper bronze

p-Toluenesulphonyl iodide (36.0 g., 0.128 mole), anthracene (15.0 g., 0.084 mole) and calcium carbonate (20 g., 0.2 mole) in benzene (350 ml.) were refluxed together for 8 hours.

The reaction mixture was filtered hot, and a solid was separated. This solid was washed with hot benzene and separated (A). The benzene filtrate was added to the main filtrate solution. This solution was left overnight and 4.0 g. of brown solid were separated (B) by filtration. This solid was mixed with 30 ml. of carbon tetrachloride and the mixture was left two days. Then the mixture was filtered and a solid was separated (C). This solid was washed with a little acetone: yield, 2.8 g., m.p. 149-151°,

characterised as 9,10-di-p-tolylsulphonyl-9,10-dihydroanthracene (D). The carbon tetrachloride filtrate of (C) and the acetone filtrate of (D) were distilled under reduced pressure, yielding tars and iodine.

The benzene filtrate of the solid (B) was washed with an aqueous alkaline solution of sodium thiosulphate to remove the excess of unreacted sulphonyl iodide and iodine. The organic layer was then washed with water and dried (sodium sulphate). The dry organic layer was distilled under reduced pressure and a yellow-green residue was obtained. This residue was washed with a little hot carbon tetrachloride. The mixture was cooled. A yellow solid (E) was separated by filtration: 2.43 g., m.p. 185-190°. The carbon tetrachloride filtrate was distilled and 1.0 g. of a dark-brown oil was obtained. This oil was not characterised.
The yellow solid (E) was recrystallised twice from carbon tetra-chloride: crystals, m.p. = 190-191°C. The product was analysed:

Found: C = 75.24% H = 4.83% S = 9.66%

Required to p-tolylsulphonylanthracene:

C = 75.89% H = 4.85% S = 9.63%

This product showed fluorescence when observed under u.v. light. Its i.r. spectrum in a nujol suspension showed the following characteristics (p.225):

Aromatic:

C=CH skeletal in-plane vibrations	1620 cm^{-1}(w) (Anth.)
	1595 cm^{-1} (w) (Tolyl)
	1500 cm^{-1} (w)
(conjugated rings)——	1560 cm^{-1} (w)?

C-H out-of-plane deformations:

Four adjacent hydrogens ———	735 cm^{-1}(s)
Two adjacent hydrogens ———	830 cm^{-1}(m)
One isolated hydrogen ———	910 cm^{-1} (m)

Region 1225-950 cm^{-1}:

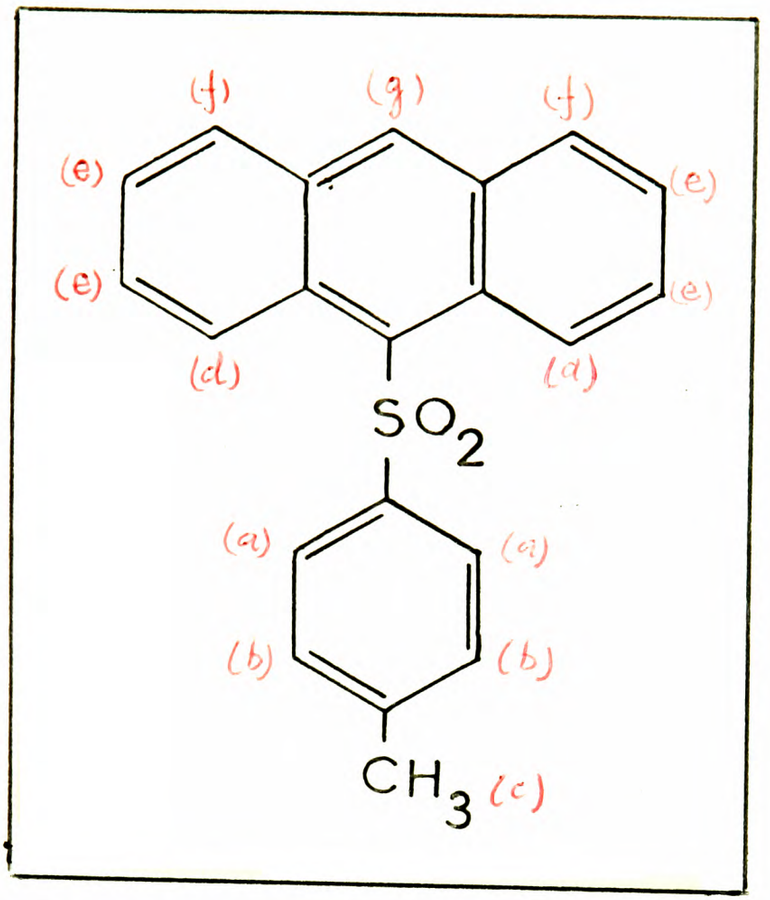
1-2 and 1-4 substitution ——	1090 cm^{-1}(m)
	1020 cm^{-1} (w)
	1030 cm^{-1} (w)

Non-aromatic:

SO_2 stretching ————	1150 cm^{-1}(two bands)(s)
	1320 cm^{-1} (s)
S-C stretching ————	700 cm^{-1} (m) ?

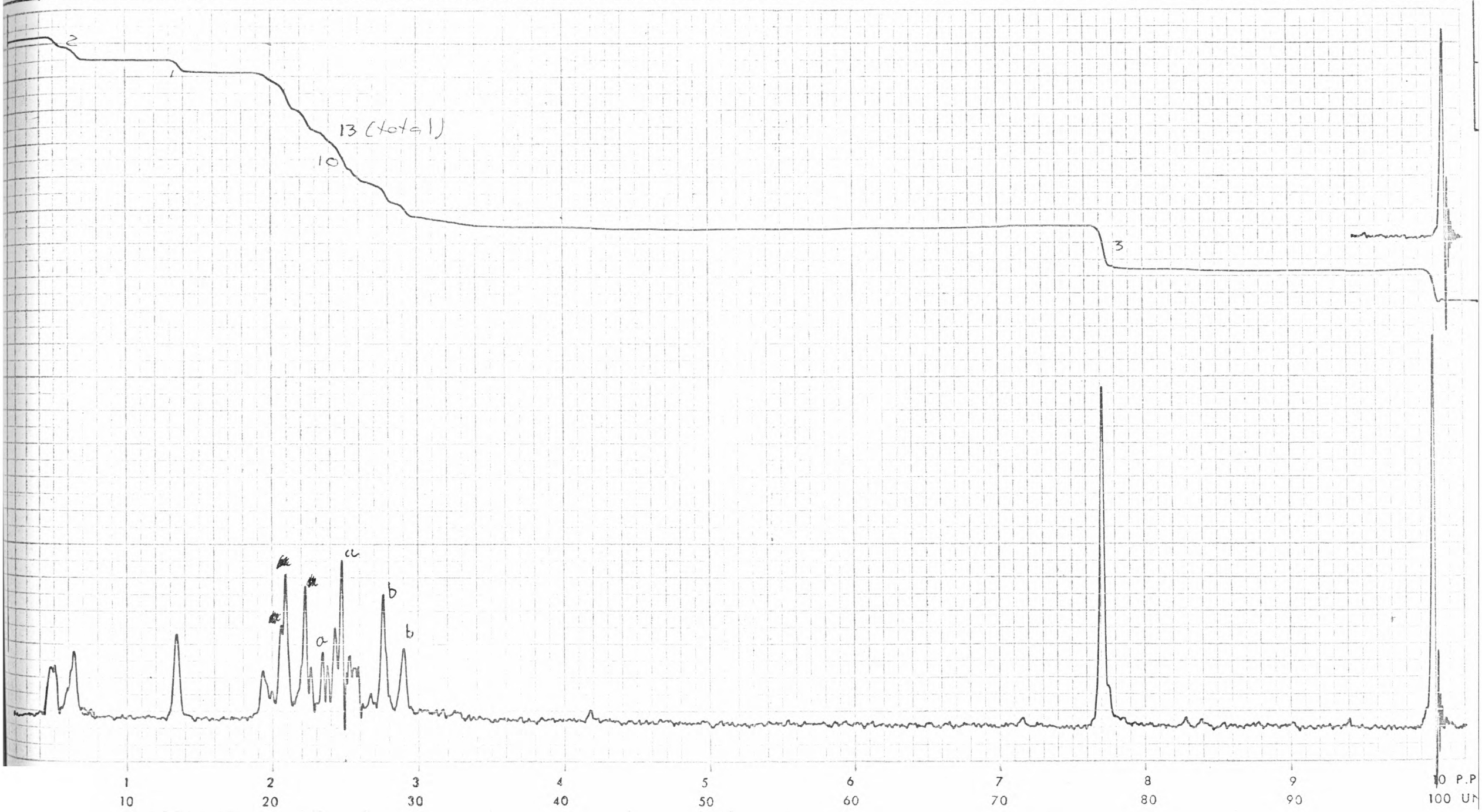
Nujol: 2.930 cm^{-1} , 1470 cm^{-1} and 1380 cm^{-1}.

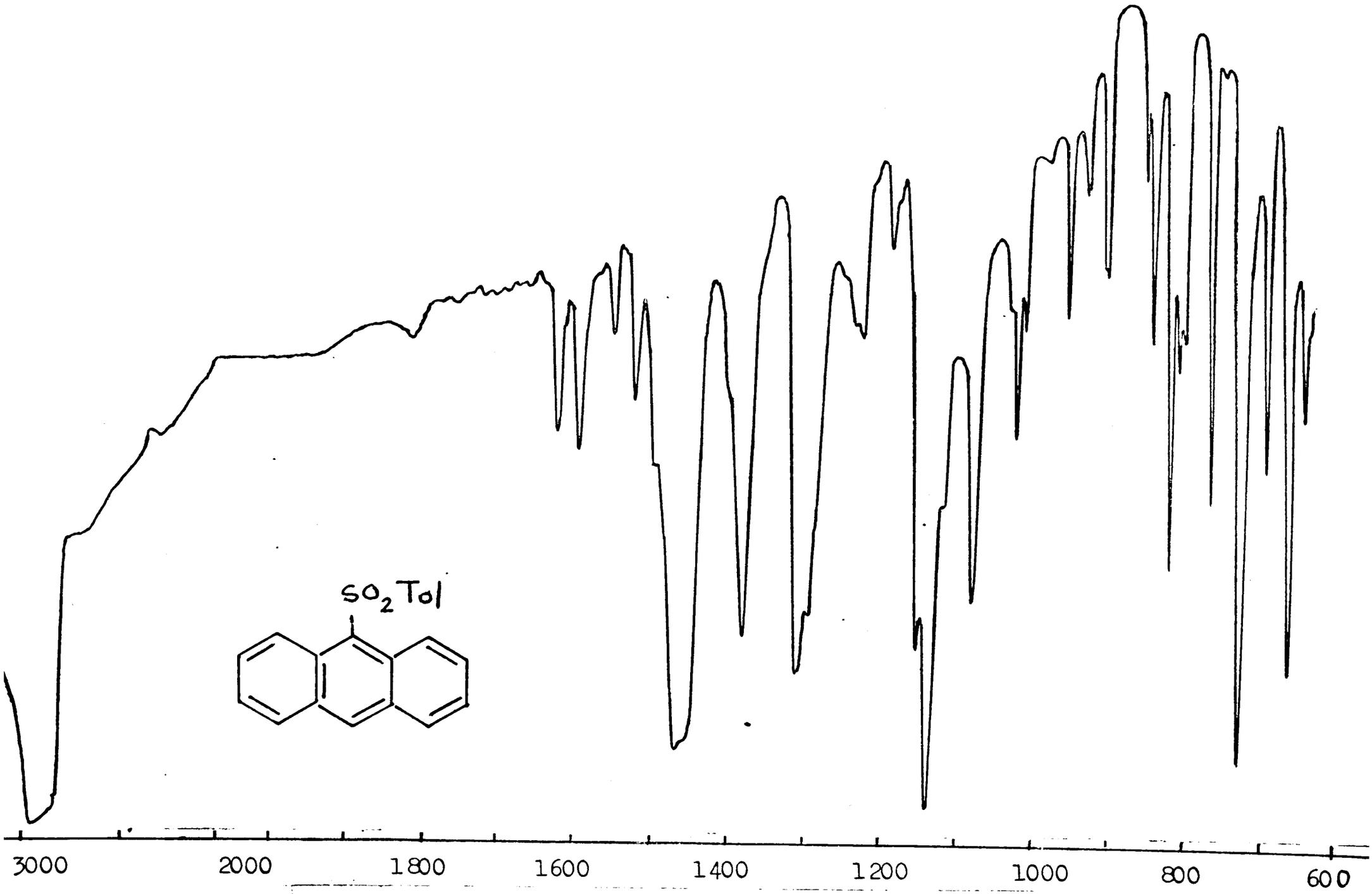
The n.m.r. spectrum of this product in $CDCl_3$ was consistent with the following structure(p. 224):



Proton	τ(PPM)	J(c/sec.)	Relative Intensity	Obs.
a,e and f or d	1.90-2.70	-	8	Complex
b	2.83	8.6	2	Doublet
c	7.72	-	23	Singlet
d or f	0.57	~ 8.6	2	Doublet; each peak shows a small splitting.
g	1.34	-	1	Singlet

DATE 28 SEP 1965	DEC. SHIFT	REF. STD.	R.F. FIELD	R.F. GAIN	REMARKS	SENSITIVITY	SWEEP RATE	TIME CONST.	SCALE FACTOR
			1.0	11		NORM: 1 INT: 2	UNITS PER MIN	SECS 0.15 M SECS	6 C/S PER UNIT





Infra red spectrum of 9-p-tolylsulphonyl-anthracene

(Nujol film)

Solid (A) was refluxed with chloroform and the hot mixture was filtered. The chloroform filtrate was distilled under reduced pressure to yield a white solid (5.3 g.), m.p.149-50°.

This solid (1.0 g.) was recrystallized from methanol. Colourless crystals, 0.8 g., m.p. 152°.

Found: C=68.64% H=4.68% S=13.00%

Required for $C_{28}H_{24}S_2O_4$:

C=68.84% H=4.95% S=13.10%

This product was identical with products (I), (E) and (L) of experiment A, and it was identified as 9,10-di-p-tolylsulphonyl-9,10-dihydroanthracene (i.r. and n.m.r. spectrum). Absorption light in chloroform: maximum at 2370A° (ε ,15,600), indicating no anthryl group.[180]

Solid (A) after extraction with chloroform weighed 20.0 g (calcium carbonate).

9-p-tolylsulphonylanthracene was examined by u.v. spectroscopy: absorption maxima in chloroform 2620A° (ε, 106,00), 3650 A° (ε 5,600) and 3900 A° (ε , 6,200), indicative of an anthryl group.[180]

Yields of products were:

-9,10-di-p-tolylsulphonyk-9,10-dihydroanthracene: 7.1 g.,17%

-9-p-tolylsulphonylanthracene: 2.43 g.,8.8%.

1.3.2 - The reaction of p-toluenesulphonyl iodide with 9,10-dimethylanthracene

p-Toluenesulphonyl iodide (11.0 g., 0.039 mole), 9,10-dimethylanthracene (2.0 g., 0.0097 mole) and copper bronze (3.0 g., 0.0472 g.atom) in benzene (100 ml.) were refluxed together for five hours.

The hot reaction mixture was filtered and a grey solid (A) was separated. This solid was boiled with 100 ml. of chloroform and the hot mixture was filtered. The chloroform filtrate was distilled under reduced pressure and a small yellow residue was obtained. This residue was added to the benzene filtrate of (A). This solution was cooled but no insoluble solid was obtained. The solution was then concentrated by distillation under reduced pressure to 20 ml and left two days.

A yellow solid separated during this time. The solid was collected by filtration (1.74 g., m.p. 209-213) (C). This solid contained adsorbed iodine. Iodine was removed with 50 ml. of cold carbon tetrachloride. 1.2 g. of yellow solid (B), m.p. = 210-213°C was obtained. The carbon tetrachloride filtrate of (B) was distilled under reduced pressure. A brown residue was obtained. This was treated with a little methanol and 0.5 g. of a yellow solid with an i.r. spectrum identical to (B) was obtained. The solid (B) was recrystall-

ized twice from ethanol. Small yellow needles, m.p. 214-215° were obtained. The i.r. spectra of the product recrystallized and of (B) were identical.

The crystals, m.p. 214-215°, were analysed:

Found: C = 76.14% H = 5.47% S = 8.88%

Required for tolylsulphonyl-9,10-dimethyl anthracene:

C = 76.65% H = 5.59% S = 8.88%

Required for 9,10-di-tolylsulphonyl-9,10-dimethyl-9,10-dihydroanthracene:

C = 69.75% H = 5.46% S = 12.39%

This product is fluorescent when observed under u.v. light.

The i.r. spectrum of the solid in nujol film showed the following characteristics (see p.231):

Aromatic:

C=CH skeletal in-plane vibrations:

1595 cm^{-1} (w) (Tolyl)

1620 cm^{-1} (w) (Anth.)

1500 cm^{-1} (w)

C-H out-of-plane deformations:

Four adjacent hydrogens - 730 cm^{-1} (s)

Two adjacent hydrogens - 830 cm^{-1} (s)

Hexasubstitution - 760 cm^{-1} (s) (*)

* This band was absent on the corresponding compound derived from 9-methylanthracene; as the band is not attributed to the methyl group, it is likely to be due to the hexasubstitution.

Region 1225-950 cm^{-1}:

1-2 and 1-4 substitution - 1180 cm^{-1} (w)
1090 cm^{-1} (m)
1030 cm^{-1} (w)
1043 cm^{-1} (w)

Non-aromatic:

SO_2 stretching - 1145 cm^{-1} (s)
1310 cm^{-1} (s)

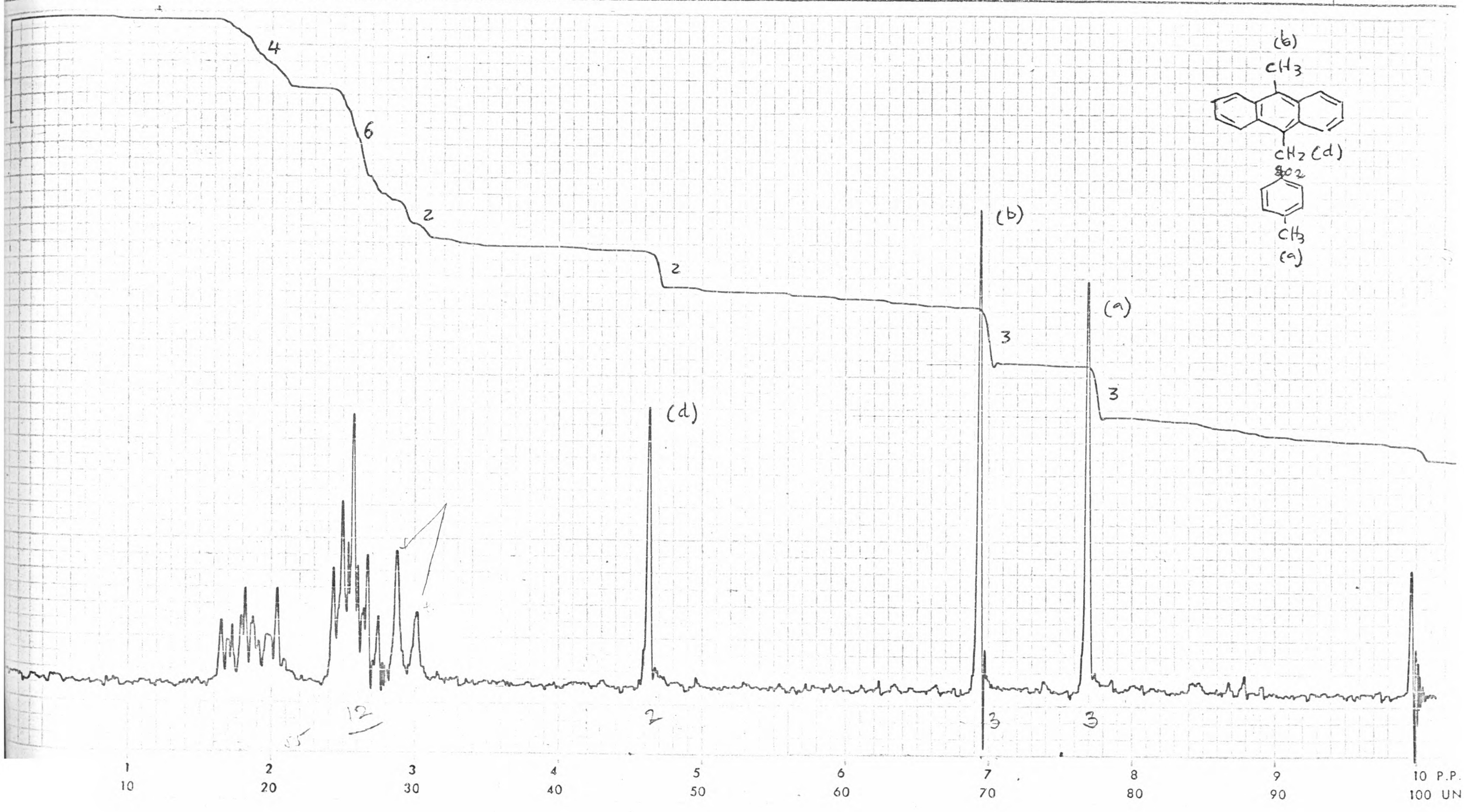
Nujol: 2.930 cm^{-1}, 1470 cm^{-1} and 1380 cm^{-1}.

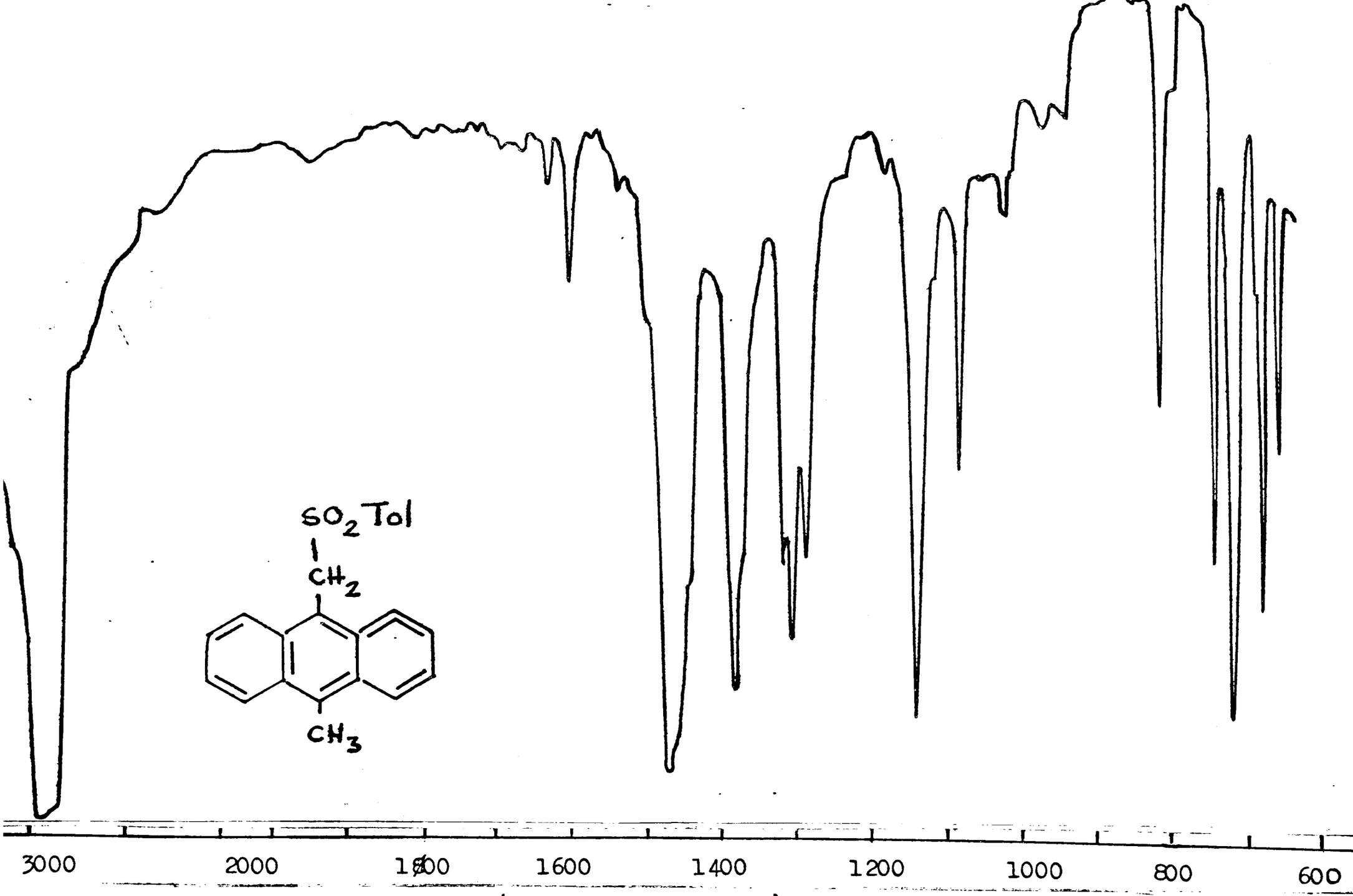
The benzene filtrate of solid (C) (p.227) was examined by thin layer chromatography in the presence of samples of p-toluenesulphonic anhydride (D), p-tolyl-p-toluene-thiosulphonate (E), 9,10-dimethylanthracene(F) and product (B).

The filtrate was distilled under reduced pressure and a very small amount of brown solid was obtained. The residue was dissolved in a little chloroform and analysed by i.r. spectroscopy. The combined result of analysis by this process and by thin layer chromatography showed that the mixture was formed by (D), (E), traces of (F) and of (B). Iodine was also present (starch test).

The grey solid (A) (p.227) was also extracted with hot ethanol. The mixture was filtered hot and the ethanolic

DATE	DEC. SHIFT	REF. STD.	R.F. FIELD	R.F. GAIN	REMARKS	SENSITIVITY	SWEEP RATE	TIME CONST.	SCALE FACTOR
2 SEP 1965						NORM: 1 INT: 9	1 UNITS PER MIN	0.1 SECS. 0.15 M SECS.	6 C/S PER UNIT

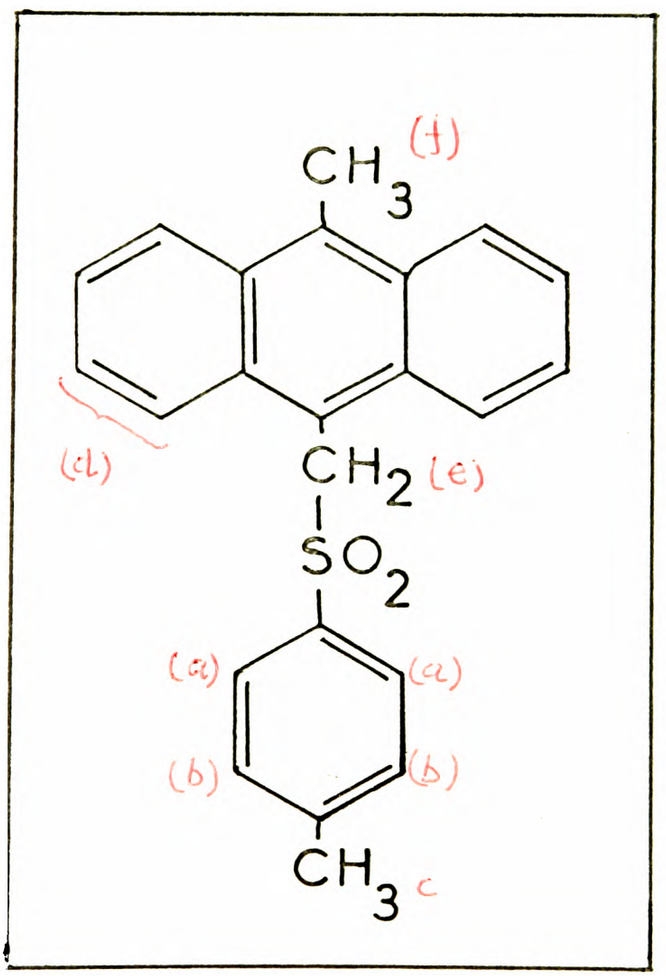




Infra red spectrum of (10-methyl-9-anthryl)-p-tolylsulphonyl methane

(Nujol film)

filtrate was distilled under reduced pressure. Some drops of dark liquid was obtained. This product contained copper (flame test). The i.r. spectrum of this residue was very broad and no anthracene derivative bands were detected. Thus the only product of this reaction that could be isolated was (B). The total yield was 1.7 g. (49%). The structure of this product was determined by n.m.r. ($CDCl_3$ solution): p.230



Proton	τ(PPM)	J(c/sec)	Relative Intensity	Obs.
a,d	1.64-2.04 and 2.43-2.75	-	8	Superposition of (a) and (d); complex
b	2.87 3.02	Jab = 8.6	4	Doublet
c	7.70	-	3	Singlet
e	4.63	-	2	Singlet
f	6.95	-	3	Singlet

The u.v.spectrum in chloroform showed absorption maxima:

2630 Å(ε, 95000), 3440 Å(ε, 2850), 3620 Å(ε, 6000), 3700 Å(ε, 11050) and 4020 Å(ε, 8600).

1.3.3. Reaction of p-toluenesulphonyl iodide with 9-methylanthracene.

9-Methylanthracene (0.9 g., 0.00047 mole), p-toluenesulphonyl iodide (5.0 g., 0.00178 mole) and copper bronze (1.5 g. 0.00237 mole) were refluxed in benzene (50 ml.) for six hours.

The resulting grey suspension was filtered hot and a solid collected (A). The benzene filtrate was cooled to 5-8° and filtered. Colourless crystals (0.08 g.) were collected, m.p. 131-5° (decomp.). Recrystallization of these crystals was attempted using a great number of solvents but was unsuccessful due to the insolubility of this product in all these solvents. The i.r. spectrum of these crystals in nujol was very similar to that of 9,10-di-p-tolylsulphonyl-9,10-dihydroanthracene. The product could not be examined by n.m.r. because no suitable solvent could be found.

The benzene solution was then evaporated in vacuo to a yellow solid. This solid was mixed with carbon tetrachloride (10 ml.) and collected by filtration, 0.50 g., (B). The carbon tetrachloride filtrate was evaporated to 2-3 ml and cooled, but no solid product separated. This solution was examined by i.r. spectroscopy which indicated the presence of p-toluenesulphonic anhydride and p-tolyl-p-toluenethiosulphonate. Several other bands were present in weak intensity.

The carbon tetrachloride solution was evaporated in vacuo

and gave a small brown residue. This residue was treated with 4-5 ml of hot petroleum ether and the mixture was decanted leaving a brown oil which was left for several days in the refrigerator. However, no solid product was obtained. The petroleum ether solution was evaporated in vacuo and gave a yellow solid (0.18 g.) which was examined by i.r. spectroscopy and thin layer chromatography. These analyses indicated it to be a mixture of p-tolyl-p-toluenethiosulphonate and unreacted 9-methylanthracene.

Extraction of solid (A) with boiling chloroform gave a yellow solid (0.08 g.) identical to product B.

Product B was recrystallized from ethanol containing a trace of chloroform (Yield 0.46 g., m.p. 212-4°).

Analysis gave:

Found: C=74.84 H=5.41 S=9.55

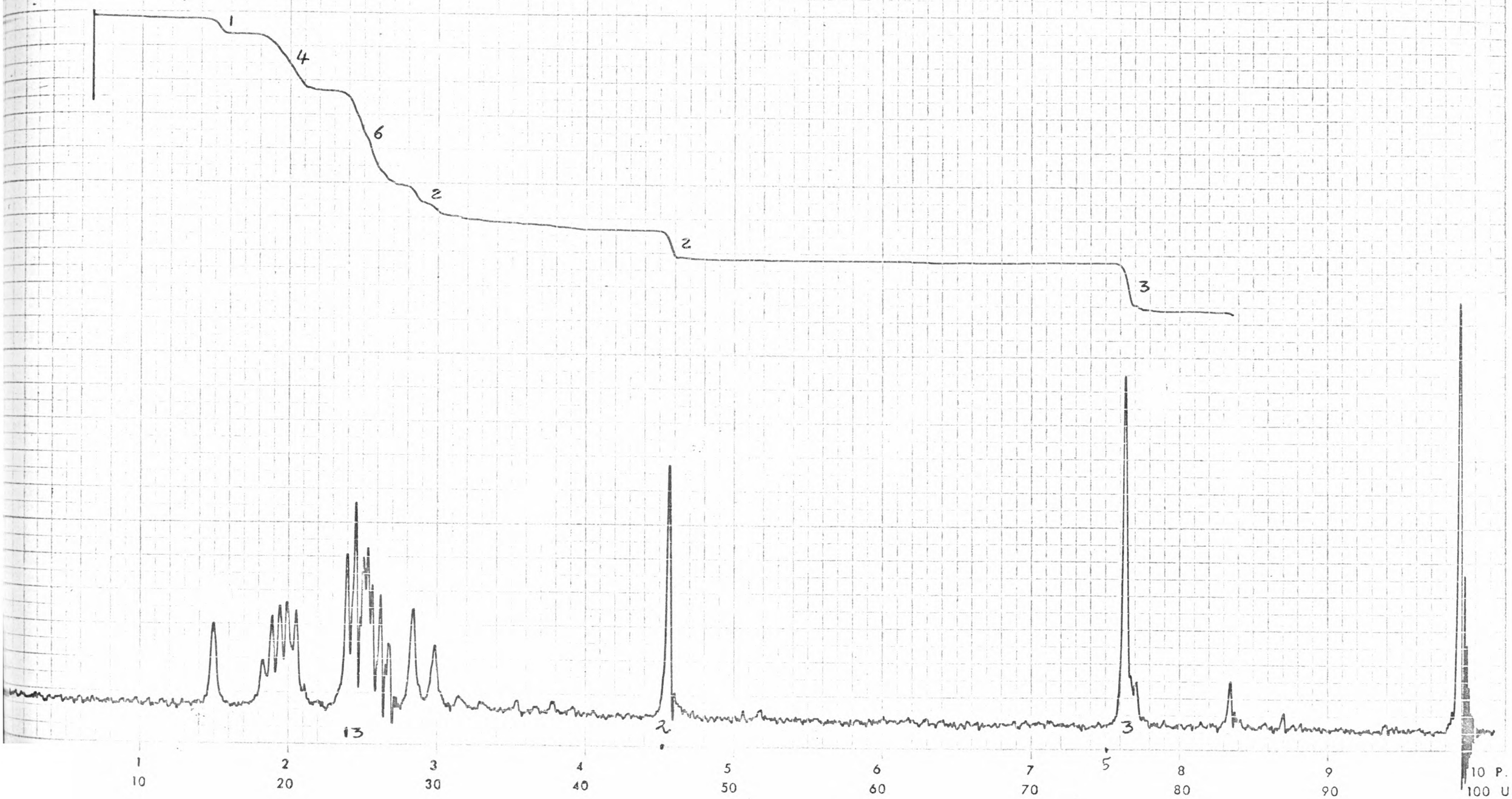
Req. for p-tolylsulphonyl-9-anthylmethane:

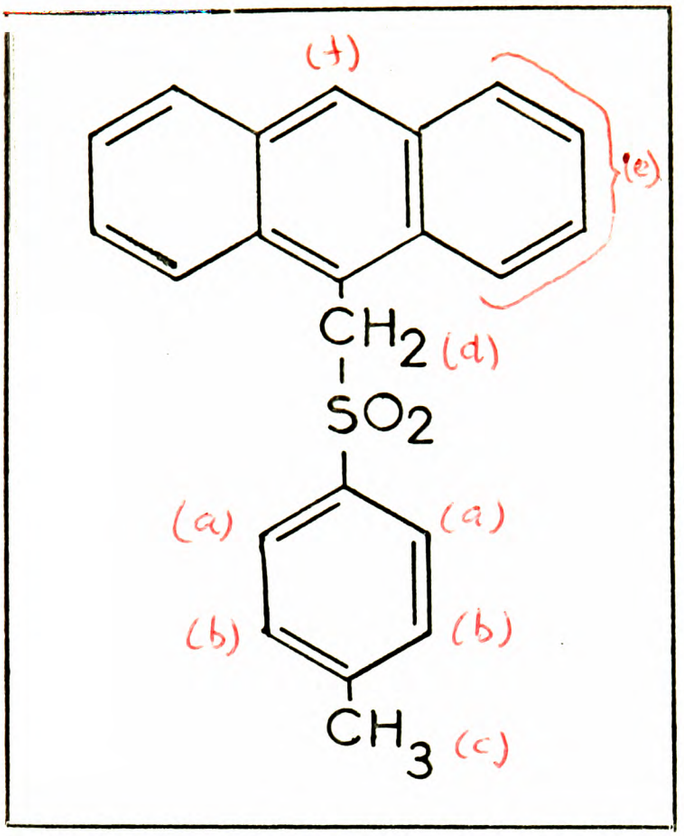
C=76.3 H=5.24 S=9.24

The n.m.r. spectrum of this compound in deuterated chloroform showed the following characteristics (p. 236):

Proton	(PPM)	J(c/sec.)	Relat.Intensity	Obs.
b	3.03	8.6	2	Doublet
c	7.73	-	3	Singlet
d	4.67	-	2	Singlet
e,a	2.90-3.10	-	10	Complex
f	1.60	-	1	Singlet

DATE	DEC. SHIFT	REF. STD.	R.F. FIELD	R.F. GAIN	REMARKS	SENSITIVITY	SWEEP RATE	TIME CONST.	SCALE FACTO
29 OCT. 1963						NORM: 1 INT: 2	32 UNITS PER MIN	.05 SECS. .015 M SECS.	6 C/S PER UNIT





This spectrum indicated substitution on the methylene group.

The i.r. spectrum in nujol (p. 238) showed:

Aromatic:

C=CH skeletal in-plane vibrations: 1590 (w), 1620 (w) and 1500 (w) cm^{-1}

C-H out-of-plane deformations:

Four adjacent hydrogen atoms-735 (s) cm^{-1}

Two adjacent hydrogen atoms-825 (m) cm^{-1}

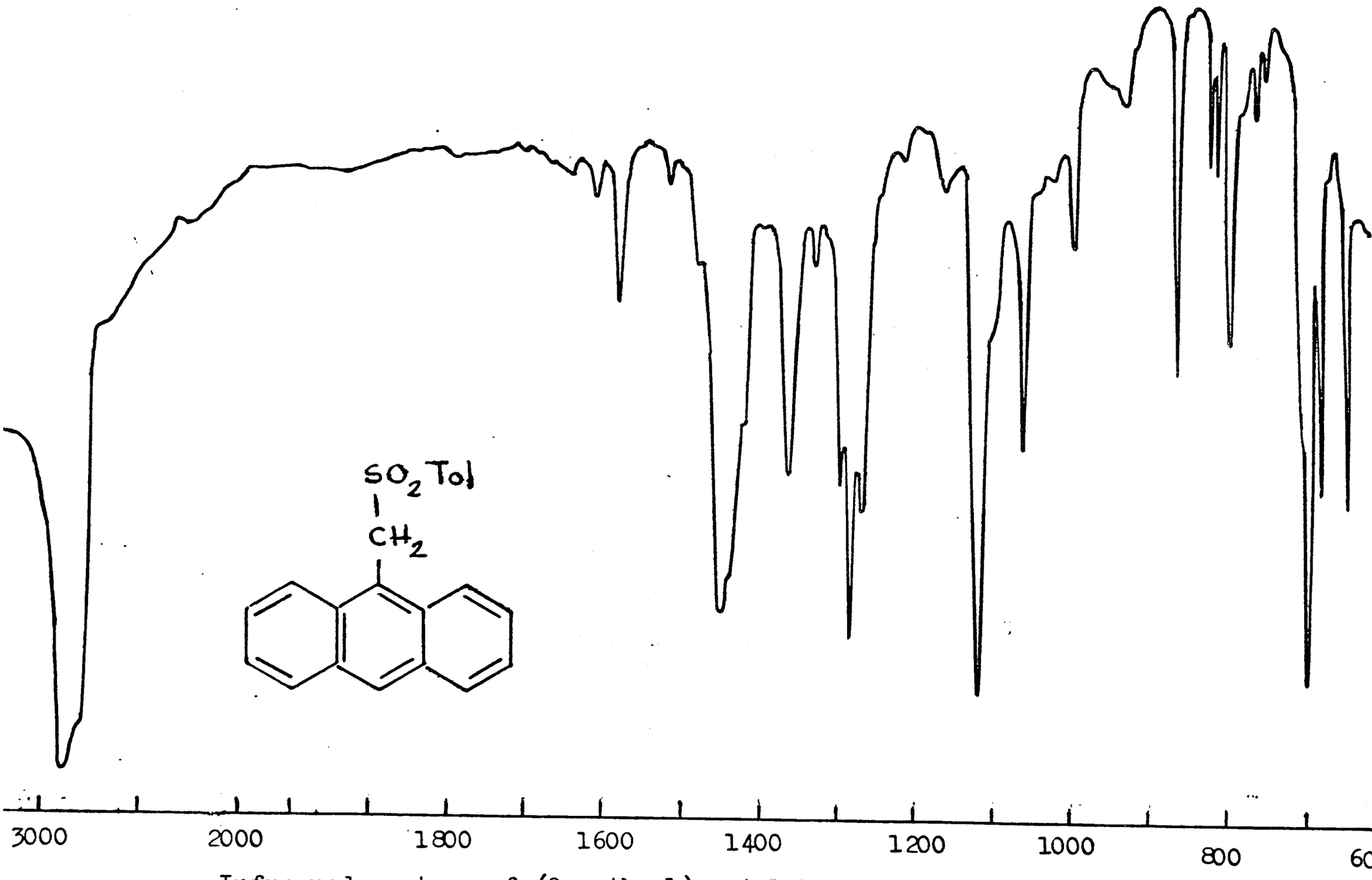
Region 1225-950 cm^{-1}:

1,2 and 1,4 Substitution-1025 (s) and 1090 (m) cm^{-1}

Sulphur bands: $-SO_2-$ stretching at 1140 (s) and 1310 (s) cm^{-1}

The u.v. spectrum showed light absorption in chloroform:

maxima 2590 Å (ε, 55500), 3370 Å (ε, 2360), 3530 Å (ε, 5350),



Infra red spetrum of (9-anthryl)-p-tolyl sulphonyl methane

(Nujol film)

3720 A° (ε, 8,500) and 3920A° (ε,7,650). These absorption bands indicated the presence of an anthryl group.[180] The solid was characterised as p-tolylsulphonyl-9-anthryl methane, (yield 35.8%).

1.3.4. Reaction of p-toluenesulphonyl iodide with 2,3-benzanthracene.

A mixture of p-toluenesulphonyl iodide (18.0 g., 0.064 mole), 2,3-benzanthracene (5.0 g., 0.0219 mole) and copper bronze (5.0 g., 0.0786 g.atom) in benzene (250 ml.) was refluxed for five hours. The reaction mixture was filtered hot and a solid separated (A). The filtrate was reduced to 75 ml and cooled. A white solid (0.73 g.) separated and was collected (B).

The filtrate was evaporated in vacuo to a dark residue which was treated with petroleum ether (15 ml) and filtered. A pale yellow solid (0.40 g.) was collected and identified as a mixture of p-toluenesulphonic anhydride and p-tolyl-p-toluenethiosulphonate (i.r. spectroscopy and thin layer chromatography). The petroleum ether filtrate was evaporated in vacuo to yield a small amount of a brown residue which was discarded.

Solid (A) was extracted several times with 100 ml portions of boiling chloroform. The chloroform extracts were evaporated to yield a white solid (6.50 g.), m.p.

183-6°, identical to (B). 1.0 g of this product was recrystallised several times from a methanol-chloroform mixture to yield small colourless crystals, m.p. 190-1°. The i.r. spectra of solids m.p. 190-1° and 183-6° were identical.

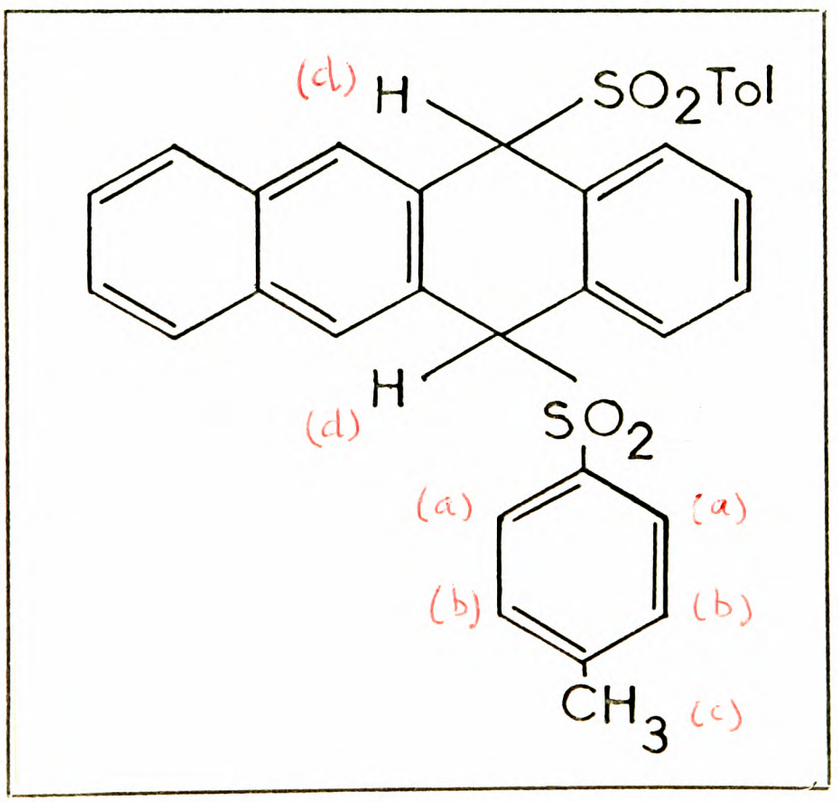
Analysis gave:

Found: C=71.35% H=4.78% S=12.25%

Required for 9,10-di-p-tolylsulphonyl-9,10-dihydro-2,3-benzanthracene,

C=71.36% H=4.87% S=11.88%

The n.m.r. spectrum of the product in chloroform could not be integrated accurately as the compound was very insoluble. The n.m.r. spectrum is shown on p.242 and may be interpreted as



Protons	τ(P.P.M.)	J(c/sec.)	Obs.
a	3.25	8.6	Doublet
b	3.83	8.6	Doublet
c	7.75	-	Singlet
d	4.99	-	Singlet

The u.v. spectrum in chloroform gave absorption maximum at 2400 A° (ε, 5,600), 2820 A° (4.065) and 2925 A° (ε, 3575). The position of these bands indicated the absence of the 2,3-benzanthryl group and the presence of two annellated benzene rings.[180] The i.r. spectrum in nujol (p.243) showed:

Aromatic Characteristics:

C=CH skeletal in-plane vibrations:

1590(m) and 1500(m) cm^{-1}

C-H out-of-plane deformations:

Four adjacent hydrogens: 760 cm^{-1} (s)

Two adjacent hydrogens: 830 (m) cm^{-1}

One isolated hydrogen: 900 (m) cm^{-1}

Region 1225-950 cm^{-1}:

1,2 and 1,4 Substitution: 1020(w), 1080(s) and 1120(s) cm^{-1}

Sulphur bands

$-SO_2-$ stretching: 1170(s) and 1315(s) cm^{-1}

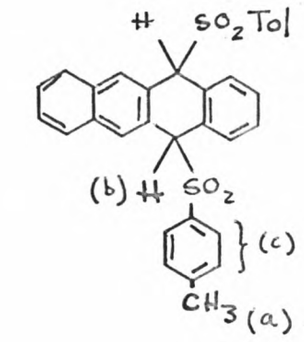
From these results it is thought this product is 9,10-di-p-tolylsulphonyl-9,10-dihydro-2,3-benzanthracene (61.4%).

EC. SHIFT	REF. STD.	R.F. FIELD	R.F. GAIN	REMARKS	SENSITIVITY	SWEEP RATE	TIME CONST.	SCALE FACTOR	SPECTRUM
____	____	1·0	1/2	Insufficient concn for integration	NORM: 4 INT: ____	10 UNITS PER MIN	·25 SECS 0·15 M SECS.	6 C/S PER UNIT	No. 4147

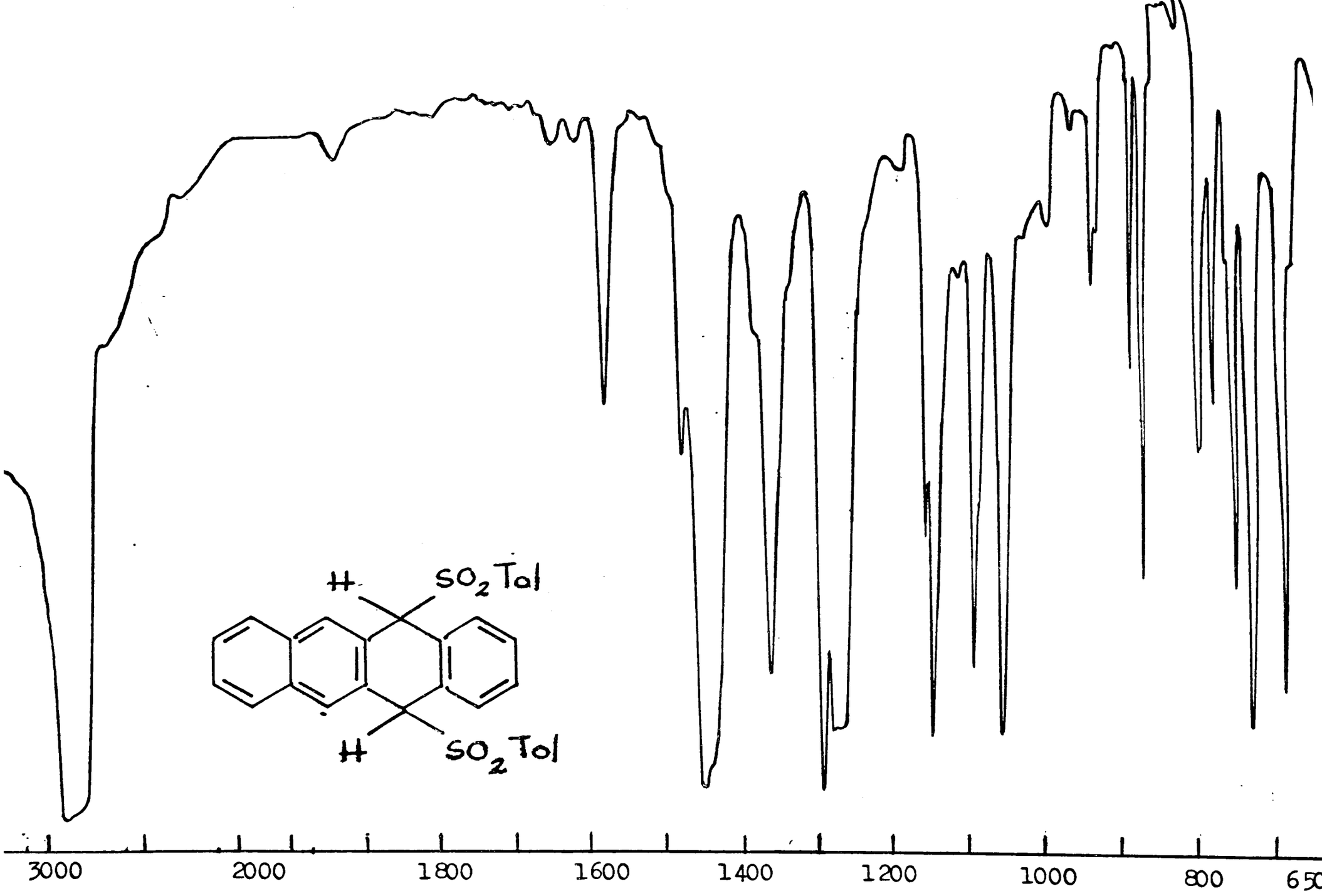
NUCLEUS ____

SUBMITTED BY Correa

COMPOUND



SOLVENT	CONC.	OPERATOR
CDCl3	v. sp. Sol. only	E.R.



Infra red spectrum of 9,10-di-p-tolyl sulphonyl-9,10-dihydro-2,3-benzanthracene
(Nujol film)

2143

1.3.5. Reaction of p-toluenesulphonyl iodide with 1,2-benzanthracene.

A -Reaction in the presence of copper bronze.

A mixture of p-toluenesulphonyl iodide (19.0 g., 0.0675 mole), 1,2-benzanthracene (5.0 g., 0.0219 mole) and copper bronze (5.0 g., 0.0787 mole) in benzene (250 ml.) was refluxed for five hours. The hot reaction mixture was filtered and a solid collected (A). The filtrate was cooled and left at room temperature for one day but no solid separated. The solution was then concentrated under reduced pressure to 50 ml and cooled. As no solid separated, the solution was mixed with petroleum ether (200 ml.) and cooled. p-Toluenesulphonic anhydride (0.70 g.) separated and was collected, m.p. 99-103°. Identification was by comparison with an authentic specimen (i.r. spectrum and mixed m.p.) The filtrate was left in the refrigerator at 0° for some hours during which a pale yellow solid (2.46 g.) separated which was identified as a mixture of p-toluenesulphonic anhydride and unreacted benzanthracene (i.r. spectroscopy and thin layer chromatography). The filtrate was again stored at 0° for one day. A pale yellow solid (1.82 g.) separated and i.r. spectroscopy and thin layer chromatography indicated to be p-tolyl-p-toluenethiosulphonate with a trace of benzanthracene. The filtrate from this solid was evaporated to 20 ml and examined by i.r. spectroscopy and thin layer chromatography which indicated a mixture of unreacted benz-

anthracene and thiosulphonate. No other product was detected.

Solid (A) was extracted with boiling chloroform but no product could be found by evaporating the chloroform extracts. Extraction with boiling benzene gave similar results. Boiling ethanol extracted a copper salt, probably a sulphinate or a sulphonate. The i.r. spectrum of this product showed no sulphone type bands. The product contained copper (flame test).

B - Reaction in the absence of copper bronze

A mixture of p-toluenesulphonyl iodide (7.0 g., 0.025 mole) and 1,2-benzanthracene (3.5 g., 0.0154 mole) in benzene (400 ml.) was refluxed for nine hours. The resulting solution was concentrated in vacuo to 150 ml and cooled (6-8°), but no solid separated. The cold solution (B) was washed with an alkaline solution of 10% sodium thiosulphate and 5% potassium iodide (2 x 100 ml.).

The aqueous layer was extracted with chloroform and a small amount of black tar was obtained from the combined extracts.

The organic layer of (B) was washed with water (2 x 100 ml.) and dried (magnesium sulphate). It was then evaporated under reduced pressure to a yellow solid. This was then mixed with hot petroleum ether and a dark tar filtered off and the filtrate cooled. 1,2-benzanthracene (2.0 g.) separated as yellow powder, and was removed by filtration,

m.p. 157-8° (identification by comparison with an authentic specimen.) The petroleum ether filtrate was evaporated in vacuo yielding a brown oil containing some solid. This mixture was treated with hot ethanol (15 ml.), cooled and filtered. Unreacted benzanthracene (1.2 g.) was separated, m.p. 158-9°, (identification as before).

The ethanol filtrate was concentrated to about 5 ml., cooled and filtered. A further amount of benzanthracene (0.1 g.) separated and was collected. The ethanol filtrate on being evaporated gave a brown oil that was discarded. The amount of benzanthracene recovered from the reaction mixture was 3.3 g. (94%),

1.3.6. The reaction of p-toluenesulphonyl iodide with phenanthrene

A mixture of p-toluenesulphonyl iodide (18.0 g., 0.064 mole) phenanthrene (4.5 g., 0.0253 mole) and copper bronze (5.0 g., 0.0786 g.atom) in benzene (250 ml.) was refluxed for five hours. The reaction mixture was filtered hot and the insoluble solid was collected (A).

The filtrate (B) was cooled to 7-9° but no insoluble product was obtained. A portion of this filtrate (50 ml.) was mixed with 2 ml of aniline. Phenylammonium p-toluenesulphonate (0.36 g.) crystallized after 5-10 minutes and was identified by comparison with an authentic specimen. The corresponding yield of p-toluenesulphonic anhydride was 1.94 g.

The remainder of solution (B) was concentrated in vacuo to 50 ml but on cooling no solid separated. The solvent was then evaporated off completely, leaving a white residue. Petroleum ether (100 ml.) was added to this residue. The mixture was well stirred and the insoluble solid collected by filtration (2.35 g.) This solid was examined by i.r. spectroscopy and thin layer chromatography which indicated to be p-toluenesulphonic anhydride with traces of p-tolyl-p-toluenethiosulphonate and phenanthrene. The petroleum ether filtrate was evaporated in vacuo to give a white solid (3.5 g.) identified as phenanthrene by comparison with an authentic specimen.
A trace of a pale green solid was extracted by boiling chloroform from solid (A). The extracted solid was examined by i.r.

spectroscopy and showed no sulphone type bands.

1.3.7. Reaction of p-toluenesulphonyl iodide with cumene.

A mixture of p-toluenesulphonyl iodide (15.0 g., 0.053 mole) and copper bronze (4.0 g., 0.0635 mole) in cumene (190 ml) was heated at 80° for five hours. The reaction mixture was filtered hot and a grey solid separated (A). The filtrate was stored at 0° in a refrigerator and p-toluenesulphonic anhydride (0.35 g., m.p. 101-103°) separated. This product was identified by comparison with an authentic specimen.

40 ml. of the filtrate was treated with 2 ml. of aniline, phenylammonium p-toluenesulphonate (0.16 g.) was obtained as small white crystals. This corresponds to 0.94g. (13 %) of sulphonic anhydride. The remaining filtrate was distilled under reduced pressure to remove cumene. The residue was a liquid (1-2 ml.) that soon solidified to a pale yellow solid. This was treated with hot ethanol (5 ml.) and then cooled. The mixture was filtered and yielded p-tolyl-p-toluenethiosulphonate (1.0 g., m.p. 73-76°) as a white insoluble solid, identified by comparison with an authentic specimen. The ethanol filtrate gave a trace of brown oil that could not be solidified. The i.r. spectrum of this oil indicated the presence of cumene. Solid (A) was extracted with boiling chloroform but no product was obtained when the chloroform extracts were evaporated. Solid (A) was mixed with water

(250 ml.) and stirred for half an hour. The mixture was left to settle and then decanted. The solution was pale blue and gave an acidic reaction (B.D.H. wide range indicator). The u.v. spectrum showed absorption maximum at 2220 A^{o}. The blue solution gave a negative ferric chloride test for sulphinic acids. 50 ml. of this solution were treated with benzylthioronium chloride, p.295 $PhCH_2SC(NH)\overset{+}{N}H_3\bar{C}l$, (1.0 g.) in water (10 ml.). A white solid separated (0.56 g.), m.p. 179-80^{o} identified as the derivative benzyl thioroniuum-p-toluenesulphonate, $PhCH_2SC(NH)\overset{+}{N}H_3\overset{-}{S}O_3Tol$, by i.r. spectrum and a mixed m.p.,181^{o}. The total yield of derivative was 2.80 g. This corresponds to 1.42 g. of p-toluenesulphonic acid in the aqueous solution. The experiment was repeated and the sulphonic acid was again formed. It was not possible to find dicumyl in the reaction mixture.

1.3.8. - The reaction of p-toluenesulphonyl iodide with acrylonitrile (vinyl cyanide).

A - Reaction in the presence of copper bronze

p-Toluenesulphonyl iodide (11.0 g., 0.039 mole), acrylonitrile (2.66 g., 0.05 mole) and copper bronze (3.0 g., 0.047 g. atom) in carbon tetrachloride (150 ml.) were refluxed together for three hours. The hot reaction mixture was filtered and a grey solid (A) was separated. The filtrate was left over night in refrigerator. 1.06 g. of white crystals (B) separated; m.p.=137-145°C. This solid contained iodine (decomposition when heated with liberation of violet vapours).

The carbon tetrachloride filtrate of (B) was distilled under reduced pressure. The small residue obtained was completely soluble in benzene (20 ml.). This benzene solution was separated into two parts:

- Part I (10 ml.) was treated with some drops of aniline. The solution was shaken and left 10-15 minutes. White crystals separated and were collected by filtration: 0.04 g. of phenylammonium p-toluenesulphonate (formed from p-toluenesulphonic anhydride).

- Part II (10 ml) was distilled and petroleum ether was added to the small residue. The mixture was triturated with a glass rod and the insoluble solid was separated by filtration

0.03 g.). This solid was examined by thin layer chromatography and i.r. spectroscopy. It was concluded to be formed by a mixture of p-toluene sulphonic anhydride and p-tolyl-p-toluene-thiosulphonate.

The grey solid (A), (p.250) was extracted with boiling chloroform. The hot mixture was filtered and the filtrate was kept in a refrigerator overnight. 6.0 g. of white crystals (C), m.p. 145-150° were obtained. The i.r. spectra of this product was identical with that of solid (B) (p.250), m.p. 137-145°. Solid (C) was recrystalised from benzene yielding colourless crystals, m.p. 149-152° (D).

These crystals were analysed:

Found: C = 35.66% H = 2.93% I = 38.19%

Required for $TolSO_2CH_2CHICN$:

C = 35.63% H = 3.01% I = 37.87%

1.0 g. of crystals (D) were dissolved in 50 ml. of ethyl acetate. To this solution 3 ml. of tri-ethylamine in 5 ml. of ethyl acetate were added. The mixture was shaken and a white precipitate was obtained. This white solid (0.5 g.) was separated by filtration (E). This solid was very soluble in water and it contained the iodide ion ($Ph\overset{+}{N}H_3\,I^-$).

The filtrate from (E) was neutralized with dilute hydrochloric acid and separated. The organic layer was washed with water and dried (calcium chloride). The dry organic layer

was distilled and a white solid residue was obtained. A little ethanol was added to the residue. The mixture was heated under a reflux condenser and filtered. The filtrate was cooled and crystals were obtained. Crystals were separated by filtration: 0.45 g., m.p. 131-133° . This product showed unsaturation (test with an acidic solution of potassium permanganate). The i.r. spectrum of this product in chloroform showed the following characteristics (see p.256):

Aromatic:

C=CH skeletal in-plane vibrations:

1595 cm^{-1} (m)

1500 cm^{-1} (w)

C-H out-of-plane deformations:

Two adjacent hydrogens - 830 cm^{-1} (s)

Region 1225-950 cm^{-1}:

1-4 substitution - 1110 cm^{-1} (w)

1080 cm^{-1} (s)

1050 cm^{-1} (w)

1020 cm^{-1} (w)

Olefinic:

C=C stretching (aromatic conjugated) - 1620 cm^{-1} (w)

-CH=CH-(trans):

CH stretching - 3.040 cm^{-1} (m)

CH out-of-plane deformation - 945 cm^{-1} (s)

CH in-plane deformation - 1300 cm^{-1} (m)

Nitrile:

CN stretching - 2.250 cm^{-1} (w)

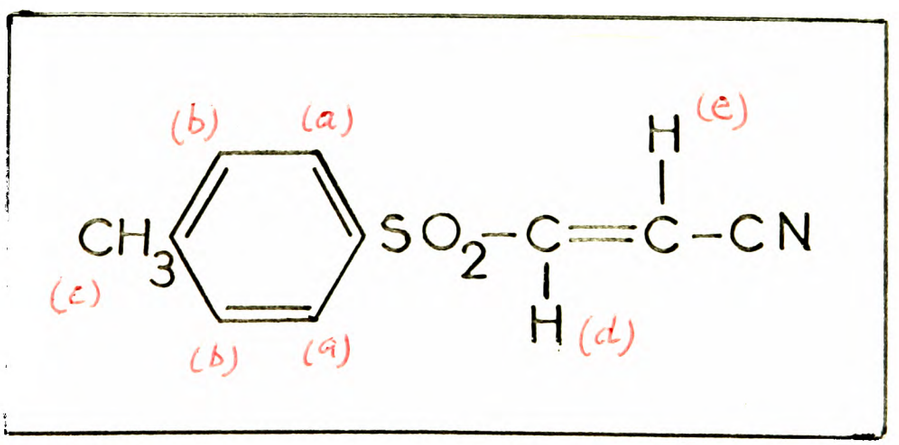
sulphur groups:

SO_2 stretching - 1145 cm^{-1} (s)

1330 cm^{-1} (s)

S-C stretching - 700 cm^{-1} (w)

The structure was confirmed by n.m.r.($CDCl_3$ solution), p.255:

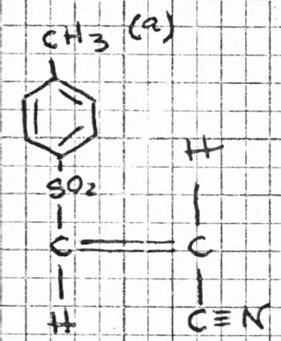


Proton	τ (PPM.)	J(c/sec)	Relative Intensity	Obs.
a	2.18	J_{ab}=8.6	2	Doublet
b	2.57		-	Doublet
c	7.48	-	3	Singlet
d or e	2.73	J_{de}=15.6	1	Doublet
e or d	3.49		1	Doublet

The coupling constant J_{de} showed that the isomer was the <u>trans</u> (lit.[156, p. 85] J_{trans} = 11-18; J_{cis} = 6-14).

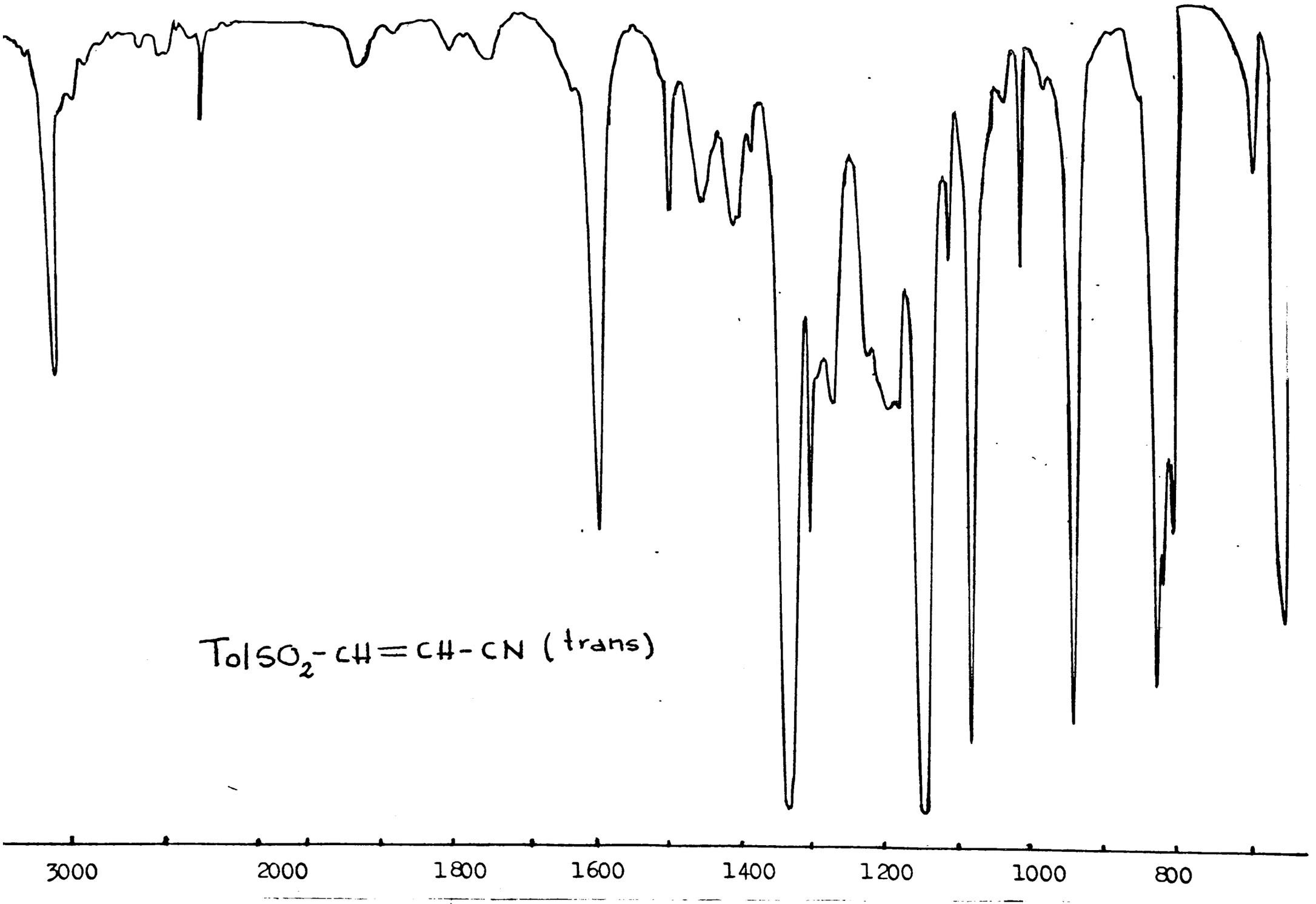
The chloroform filtrate of (C) was distilled under reduced pressure. To the residue a little benzene was added and the mixture was heated. The insoluble tar was separated by filtration and the filtrate was cooled. White crystals separated and they were collected by filtration: 1.07 g., m.p. = 146-149°. The i.r. spectrum of these crystals was identical with that of crystals (D). From the benzene filtrate no more solid could be obtained. The total amount of adduct like (D) 3-<u>p</u>-tolylsulphonyl-2-iodopropanenitrile was 8.13 g. (62.5%). The infrared spectrum of this product (nujol film) showed the following characteristics (see p. 258):

DATE JAN 1966	DEC. SHIFT	REF. STD.	R.F. FIELD	R.F. GAIN	REMARKS	SENSITIVITY NORM: 2 INT: 4	SWEEP RATE 32 UNITS PER MIN	TIME CONST. 0.1 SECS. 0.15 M SECS.	SCALE FACTO 6 C/S PER UNIT
			1	½					



(a)

1 10 2 20 3 30 4 40 5 50 6 60 7 70 8 80 9 90 0 P. 00 U



Infra red spetrum of 3-p-tolylsulphonyl-2-propenenitrile
(Chloroform solution)

Aromatic:

C=CH skeletal in-plane vibrations: 1590 cm^{-1} (w)

C-H out-of-plane deformations:

Two adjacent hydrogens - 825 cm^{-1} (m)

Region 1225-950 cm^{-1}:

1-4 substitution - 1020 cm^{-1} (w)
1050 cm^{-1} (w)
1090 cm^{-1} (m)
1175 cm^{-1} (m)

Nitrile

CN stretching - 2.250 cm^{-1} (w)

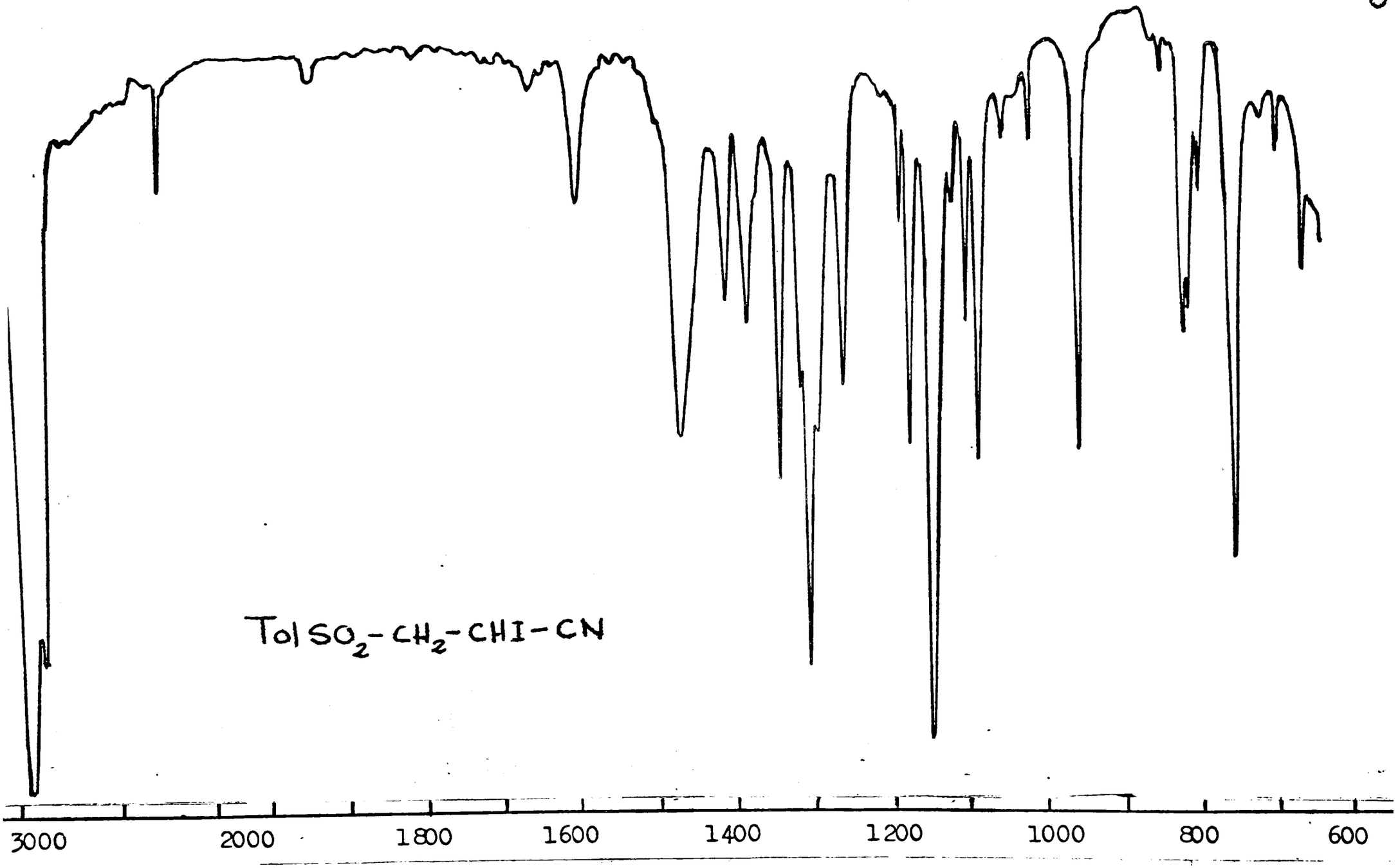
Sulphur bands

SO_2 stretching - 1150 cm^{-1} (s)
1300 cm^{-1} (s)

S-C stretching 700 cm^{-1} (w)

B - Reaction in the absence of copper bronze at room temperature

p-Toluenesulphonyl iodide (14.0 g., 0.0495 mole), and acrylonitrile (3.0 g., 0.056 mole) were dissolved in ether (250 ml.). The mixture was left for about twenty hours. After this time a large amount of small crystals had separated



Infra red spectrum of 2-iodo-3-p-tolylsulphonyl-propionitrile
(Nujol film)

out. The solution was filtered and 14.3 g. of white crystals (F), m.p. = 152-152.5°C were separated. The infrared spectra of this solid was identical with that of 3-p-tolylsulphonyl-2-iodopropanenitrile. The ether filtrate of (F) was kept in refrigerator for two days. Then the mixture was filtered and 0.15 g. of white crystals (G) were obtained. This solid was identical with (F) (i.r. spectroscopy and mixed m.p.).

The ether filtrate of (G) was a red solution. This solution was distilled and a tar containing iodine was obtained. The yield of addition product was 87%.

C - Reaction in the presence of aluminium chloride.

p-Toluenesulphonyl iodide (13.5 g., 0.048 mole) was dissolved in anhydrous ether (200 ml.). This solution was cooled in ice-water, anhydrous aluminium chloride (12.8 g., 0.096 mole) was added. The mixture was stirred until dissolution of the aluminium chloride.

To this solution acrylonitrile (3.0 g., 0.0566 mole) in 100 ml. of anhydrous ether was slowly added. The resulting solution was then stirred for one hour and then left overnight. At morning the mixture was mixed with cracked ice and stirred until complete melting of the ice. The mixture was filtered and a yellow inorganic solid was collected. This solid was insoluble in organic solvents and its i.r. spectrum showed no

sulphone absorption bands.

The filtrate was separated into two layers:

-Organic layer: it was dried (magnesium sulphate) and distilled. The brown residue was treated with petroleum ether, but no solid could be separated. The solution was washed with an aqueous solution of sodium thiosulphate, with water and dried (magnesium sulphate). The petroleum ether solution was distilled and a very small white residue was obtained.

-Aqueous layer: it was extracted with chloroform. The organic layer was dried (magnesium sulphate) and distilled under reduced pressure. The pink residue was treated with a little ethanol and filtered. 0.20 g. of white solid were obtained (H). The ethanol filtrate of (H) was concentrated and cooled: 1.0 g. of white solid separated (I). Solids (H) and (I) had m.p. 150-151° and were characterized as the addition product 3-p-tolylsulphonyl-2-iodo-propionitrile by comparison with an authentic specimen. The yield of addition product was 7.5%.

D - Reaction of p-toluenesulphonyl chloride and benzenesulphonyl chloride in the presence of aluminium chloride with acrylonitrile.

p-Toluenesulphonyl chloride (10.0 g.; 0.0525 mole) was dissolved in anhydrous ether (160 ml.). The solution was cooled in an ice bath and anhydrous aluminium chloride (14.0 g. 0.105 mole) was dissolved in this solution. To the well stirred

solution acrylonitrile (3.0 g., 0.0566 mole) in 40 ml of anhydrous ether was added slowly. The mixture was stirred for two hours and left overnight. The reaction mixture was then mixed with cracked ice and stirred till the ice melted. The mixture was then separated into two layers:
-The aqueous layer was extracted with chloroform and the extract was dried (magnesium sulphate). The dry chloroform layer was distilled and a small amount of p-toluenesulphonyl chloride was obtained as residue.

-The organic layer was washed with water and dried (magnesium sulphate). The solution was distilled under reduced pressure. 8.60 g. of white solid was obtained. This solid was examined by thin layer chromatography and infrared specroscopy, and it was characterized as pure p-toluenesulphonyl chloride (90% recovered).

No addition product to acrylonitrile was detected.

The reaction was repeated with liquid benzene-sulphonyl chloride as described by Catch et al.[162]

Aluminium chloride (53.3 g., 0.40 mole) was dissolved in a well stirred cooled solution of benzenesulphonyl chloride (71 g., 0.40 mole). Cooling was made by means of an ice bath. To the cold and well stirred solution acrylonitrile (21.2 g., 0.40 mole) was added drop by drop. The mixture was stirred

for one and a half hours. Then the cooling mixture was removed and the reaction mixture was left in a stoppered flask for fifty hours.

Then the solution was added to cracked ice and stirred till the ice melted. The mixture was extracted with chloroform. The chloroform layer was separated and dried (magnesium sulphate). The dry solution was distilled and benzenesulphonyl chloride (65.5 g., 92.5%) was obtained as residue. This was characterised by comparison of i.r. spectra, boiling points, and by thin layer chromatography, with an authentic specimen.

E - The reaction of p-toluenesulphonyl iodide with acrylonitrile in the absence of light.

p-Toluenesulphonyl iodide (7.0 g., 0.0248 mole) and acrylonitrile (1.5 g., 0.0283 mole) were dissolved in ether (150 ml.). The solution was placed in a 250 ml. conical flask wrapped in black paper. The mixture was left 24 hours at room temperature. Then the mixture was filtered and 0.90 g. of 3-p-tolylsulphonyl-2-iodopropionitrile (J) were separated. The colour of the filtrate was still the initial yellow. The filtrate was left in a stoppered flask without any protection from daylight for half an hour. The solution turned brown and a solid started to separate. The solid was removed by filtration (2.50 g.) and it was characterized again as (J). Several filtrations were carried out at different

times and the same product (J) was collected.

Results are given:

Time of reaction (hours)	Solid separated each time (g)	Time of formation (hours)	Light conditions	%
24	0.90	24	Dark	11.8
24½	2.50	½	Light	30.0
25	1.34	½	Light	16.0
27½	0.43	2½	Light	5.2
51½	0	24	Light	-
72½	0	21	Light	-

F - Reaction in the absence of light and in the presence of inhibitors.

p-Toluenesulphonyliodide (17.0 g., 0.0605 mole) and acrylonitrile (3.5 g., 0.06 mole) were dissolved in 200 ml of ether (peroxide free). To this solution hydroquinone (1.0 g., 0.0091 mole) was added. The solution was placed in a 250 ml. conical flask wrapped in black paper. The mixture was left for 22 hours and then cooled in the refrigerator (still in the dark). Then the black paper was removed. The solution was yellow with a small amount of separated solid. This solid was filtered off (1.0 g.) and it was characterised as unreacted p-toluenesulphonyl iodide. The yellow filtrate was

separated into two parts:

- Part (i) was washed with an aqueous solution of sodium thiosulphonate with a little potassium iodide to remove the unreacted sulphonyl iodide. The organic layer was dried (magnesium sulphate). The mixture was filtered and the magnesium sulphate was washed with chloroform. The chloroform and the ether filtrates were distilled and hydroquinone (0.35 g.) was obtained as residue. No addition product (J) could be found.

-Part (ii): to this solution excess of petroleum ether was added. The solution was left in refrigerator overnight and a yellow solid separated (6.0 g., m.p. = 85°C). This solid was characterized as p-toluenesulphonyl iodide. The filtrate of this solid was left some hours under the light. 0.72 g. of product (J) was very quickly separated.

The reaction was repeated in the presence of smaller amounts of inhibitor.

Mixture A: (6.8% of hydroquinone)

$TolSO_2I$ - 7.5 g. (0.0266 mole)

Acrylonitrile - 1.5 g. (0.0283 mole)

Quinol - 0.2 g. (0.0018 mole)

Ether (peroxide free) - 130 ml.

Mixture B: (3.4% of hydroquinone)

$TolSO_2I$ - 7.5 g. (0.0266 mole)

Acrylonitrile - 1.5 g. (0.0283 mole)

Quinol - 0.1 g. (0.0009 mole)

Ether (peroxide free) - 130 ml.

The reaction mixtures were placed in conical flasks and were kept in the dark for seventeen hours. The reaction mixtures were examined several times and the separated solid was collected.

Results are summarised in the following table:

Reaction A

Time of Reaction (hours)	Separated product (g.)	Time of formation (hours)	Light conditions	Adduct %
17	0	17	Dark	0
65	1.11	48	Dark	12.5
72	2.62	7	Light	29.0
96	0.32	24	Light	3.6

Reaction B

17	0.30	17	Dark	3.4
65	1.20	48	Dark	13.4
72	3.37	7	Light	37.5
96	0.10	24	Light	11.3%

2 - Some attempted reactions with sulphinyl chlorides.

2.1 - The decomposition of sulphinyl chlorides in the presence of copper bronze.

2.1.1 - Preparation of benzenesulphinyl chloride.

Benzenesulphinyl chloride was prepared as described by Douglass and Poole by reaction of diphenyl disulphide, gaseous chlorine and water (p.291). Several reactions were attempted with the sulphinyl chloride prepared following these authors but no reaction products were obtained. Closer examination of the starting material showed that it was in fact sulphonyl chloride and not sulphinyl chloride which had been prepared by the above method. Attempted preparations by Douglass and Poole method:

No. 1: liquid b.p. 83-84°/1 mm

Found: Cl = 19.80%

Req. for PhSOCl: Cl = 22.1%

Req. for $PhSO_2Cl$: Cl = 20.1%

No.2: liquid b.p. 81-84°/ 1mm

Found: Cl = 19.45%

No.3: liquid b.p. 71-75°/0.8-0.9 mm

Found: Cl = 20.50%

The i.r. spectra of these products showed strong absorption bands of the sulphonyl chloride type and was identical with

that of authentic benzenesulphonyl chloride. The sulphonamide derivative $PhSO_2NH_2$ was prepared, m.p. 152-154° (lit.[178] 156°).

Benzenesulphinyl chloride was then prepared as described by Barnard by reaction of benzene sulphinic acid with thionyl chloride (p. 291). The i.r. spectrum was identical with that described in literature ([165]). The derivative benzenesulphinamide, $PhSONH_2$, was prepared, m.p. 120-122° (lit.[166] m.p. 122°C).

2.1.2 - The decomposition of benzenesulphinyl chloride.

A mixture of benzenesulphinyl chloride (8.0 g., 0.08 mole), copper bronze (3.2 g., 0.0505 g. atom) and carbon tetrachloride (100 ml.) was refluxed for three hours. The hot reaction mixture was filtered and a grey solid (6.3 g.) separated. The filtrate was a pale yellow solution and was stored overnight in the refrigerator. No product separated. On removal of the solvent under reduced pressure, a liquid (4.5 g.) which could not be crystallized was obtained as residue.

The i.r. spectrum of this liquid was very similar to that of phenyl benzenethiosulphonate ([167]). Attempted distillation of the liquid residue caused it to decompose. The m.p. of phenyl benzenethiosulphonate is 37-38°C ([167]).

2.1.3 - The decomposition of p-toluenesulphinyl chloride.

p-Toluenesulphinyl chloride was prepared as described in Org.Synth. by reaction of sodium p-toluenesulphinate with thionyl chloride (p.292) and had b.p. 115-120°/4mm. A mixture of the sulphinyl chloride (4.0 g., 0.0229 mole) and copper bronze (3.0 g., 0.0472 g. atom) in carbon tetrachloride (50 ml.) were stirred for six hours at room temperature. The mixture was then left overnight. It was then filtered warm and the filtrate was distilled under reduced pressure. A yellow liq uid which solidified was obtained as residue. Petroleum ether (20 ml.) was added to this residue. The mixture was heated and cooled and the white solid was removed by filtration, 1.16 g., 36.5%, m.p. 74-75°C. This product was identified as p-tolyl-p-toluenethiosulphonate by comparison of i.r. spectrum and m.p. with an authentic specimen ([48]), prepared by reaction of p-toluenesulphonyl chloride with copper bronze in pyridine.

2.2 - The attempted addition of benzene sulphinyl chloride to olefins.

2.2.1 - The reaction with cyclohexene.

Benzenesulphinyl chloride (8.0 g., 0.05 mole), cyclohexene (5.0 g., 0.061 mole) and copper bronze (0.5 g., 0.0079 g.atom) in carbon tetrachloride (100 ml.) were refluxed together for five hours. The hot reaction mixture was filtered and 0.76 g. of dark solid (A) was separated. The brown filtrate was

kept twelve hours at 0^{o} but no solid separated. The solvent was concentrated under reduced pressure to a brown liquid (10.5 g.). This liquid was left in refrigerator for one week but no solid was obtained. This product was examined by i.r. spectroscopy and showed no sulphoxide absorption band.

2.2.2. The reaction with α-methyl styrene.

Benzenesulphinyl chloride (8.0 g., 0.05 mole), α-methyl styrene (6.0 g., 0.051 mole) and copper bronze (0.5 g., 0.0079 g. atom) in carbon tetrachloride (100 ml.) were heated under reflux for three hours. The grey suspension was filtered hot and the filtrate was cooled in a refrigerator, but no solid separated. The solvent was then removed by distillation under reduced pressure and a brown liquid (16 g.) was obtained. The i.r. spectrum of this liquid showed complete absence of sulphoxide absorption bands.

2.3. The attempted addition of p-toluenesulphinyl chloride to olefins.

2.3.1. The reaction with cyclohexene.

p-Toluenesulphinyl chloride (10.0 g., 0.0575 mole), in carbon tetrachloride (50 ml.) was added to a well stirred solution of cyclohexene (5.0 g., 0.061 mole) in carbon tetrachloride (50 ml.) in the presence of copper bronze (6.0 g.,

0.0945 mole). The mixture was stirred for four hours at room temperature. The reaction mixture was warmed and filtered. The filtrate was concentrated to 30 ml. and cooled. No solid separated. The solution was distilled again under reduced pressure leaving a residue which rapidly solidified.

Petroleum ether (15 ml.) was added to the residue and a white solid was obtained. This solid was separated by filtration, 3.52 g. (44%), m.p. 73-76° and it was identified as p-tolyl-p-toluenethiosulphonate by comparison with an authentic specimen. The petroleum ether filtrate was distilled under reduced pressure and a very small amount of yellow oil was obtained. The i.r. spectrum of this oil was very similar to that of p-tolyl-p-toluenethiosulphonate and showed no sulphoxide absorption band.

The reaction was repeated, but using traces of copper bronze and at about 80°.

p-Toluenesulphinyl chloride (10.0 g., 0.0575 mole), cyclohexene (5.0 g., 0.061 mole) and copper bronze (0.5 g., 0.0079 g. atom) in carbon tetrachloride (75 ml.) were boiled and refluxed for three hours. The hot reaction mixture was filtered and the filtrate was kept in the refrigerator for twelve hours but no solid separated. The brown filtrate was

distilled under reduced pressure. The brown liquid residue (14.3 g.) was analysed by thin layer chromatography and i.r. spectroscopy. No sulphoxide band could be detected and the residue was found to contain p-tolyl-p-toluenethiosulfonate.

2.3.2. The reaction with styrene.

p-Toluenesulphinyl chloride (10.0 g., 0.0575 mole), styrene (5.5 g., 0.0528 mole) and copper bronze (0.5 g., 0.0079 g. atom) in carbon tetrachloride were heated under reflux for three hours. The grey suspension was filtered hot and a solid separated. The filtrate was a brown solution which was examined by i.r. spectroscopy and showed no sulphoxide absorption band.

The reaction was repeated without the solvent by using p-toluenesulphinyl chloride (11.0 g., 0.063 mole), styrene (7.0 g., 0.0672 mole) and traces of copper bronze, at room temperature. The mixture was stirred for six hours. Again no sulphoxide absorption band could be detected in the i.r. spectrum of the products.

2.3.3 - The reaction with ethyl cinnamate

p-Toluenesulphinyl chloride (10.0 g., 0.0575 mole), ethyl cinnamate (10.0 g., 0.0568 mole) and copper bronze (0.5 g., 0.0079 g. atom) in carbon tetrachloride (100 ml.) were heated under reflux for three hours. The reaction mixture was filtered

hot and the filtrate was stored overnight at 0°. No solids separated out. The carbon tetrachloride filtrate was examined by thin layer chromatography and i.r. spectroscopy. The mixture was found to contain p-tolyl-p-toluenethiosulphonate, unreacted p-toluenesulphinyl chloride and ethyl cinnamate. No sulphoxide absorption bands could be detected in the i.r. spectrum of this mixture.

2.4 - The attempted addition of β-naphthalenesulphinyl chloride to styrene.

β-Naphthalenesulphinyl chloride (p.293) (6.0 g., 0.0286 mole), styrene (5.0 g., 0.058 mole) in benzene (50 ml.) were irradiated by a "Hanovia" u.v. lamp (1 kw) at 70-80° for six hours. The brown solution was kept overnight in the refrigerator but no solid separated. The solvent was removed in vacuo and the solution was concentrated to a brown oil that examined by i.r. spectroscopy showed no sulphoxide absorption band.

2.5. Attempted reaction of p-toluenesulphinyl chloride with p-benzoquinone.

2.5.1. Reaction at room temperature

p-Toluenesulphinyl chloride (6.5 g., 0.0372 mole), p-benzoquinone (2.0 g., 0.0186 mole) and copper bronze (2.5 g., 0.0395 g.atom) in carbon tetrachloride (100 ml.) were stirred at room temperature for three hours. The mixture was then

left for two days in a stoppered flask. Then the reaction mixture was warmed and filtered. The orange-brown filtrate was left in the refrigerator overnight; a small amount of dark solid (A) was separated off and characterized as p-benzoquinone with a little tar. The filtrate of (A) was separated into two parts:

-Part (i) was distilled under reduced pressure. A red residue was obtained. It was treated with a little petroleum ether (20 ml.),(B). A red solid separated and was collected by filtration. The solid was washed with 2-3 ml. of methanol (C), leaving a white insoluble solid identified as p-tolyl-p-toluenethiosulphonate (0.83 g.), m.p. 75-76°, mixed and alone. The methanol (C) and petroleum ether (B) filtrates were concentrated in vacuo to a red solid. The i.r. spectrum of this solid and its analysis by thin layer chromatography indicated it to be p-benzoquinone and p-tolyl-p-toluenethiosulphonate.

-Part (ii) was washed with a 10% aqueous sodium dithionite (non alkaline) solution to remove unreacted p-benzoquinone. The organic layer was washed with water and dried (magnesium sulphate). The dry organic layer was then distilled under reduced pressure. The residue was a liquid that soon solidified. The residue was treated with hot petroleum ether (15 ml.) and then the mixture was cooled. p-Tolyl-p-toluenethiosulphonate (1.0 g.) separated as white small crystals,

m.p. 72-75°, (D). This product was identified by comparison of i.r. spectrum and mixed m.p. with an authentic specimen. The mother liq uor of (D) was concentrated *in vacuo* to a trace of (D). The i.r. spectrum of this solid was identical with that of *p*-tolyl-*p*-toluenethiosulphonate.

2.5.2. Reaction at about 80°

A mixture of *p*-toluenesulphinyl chloride (11.5 g., 0.066 mole), *p*-benzoquinone (4.0 g., 0.037 mole) and copper bronze (4.5 g., 0.071 g.atom) in carbon tetrachloride (100 ml.) was heated under reflux for two hours.

The reaction mixture was filtered hot and 8.0 g. of grey solid (A) was separated. The orange filtrate was kept in the refrigerator for twelve hours and an orange-red solid (1.32 g.), (B), separated, m.p. 113-114°. The i.r. spectrum of this solid was identical with that of *p*-benzoquinone.
The orange filtrate of (B) was analysed by i.r. spectroscopy and the spectrum was identical with that of a mixture of *p*-benzoquinone and *p*-tolyl-*p*-toluenethiosulphonate. This filtrate was washed with a 10% aqueous sodium dithionite solution (*non* alkaline), with water and dried (magnesium sulphate). The dry organic layer was then examined by thin layer chromatography and i.r. spectroscopy. *p*-Tolyl-*p*-toluenethiosulphonate was detected only. The solution was concentrated *in vacuo* to a liquid residue that soon solidified.

The residue was washed with petroleum ether (20 ml.) and the mixture filtered. p-Tolyl-p-toluenethiosulphonate, 3.76 g. (40.7%) was obtained, m.p. 74-75°. It was identified by comparison of i.r. spectrum and mixed m.p. with an authentic specimen. The mother liquor was concentrated to 5 ml. and cooled. Traces of p-tolyl-p-toluenethiosulphonate separated and were collected by filtration. The filtrate was distilled under reduced pressure and a yellow liquid was obtained as residue (near 1 g.). The i.r. spectrum of this oil was identical with that of p-tolyl-p-toluenethiosulphonate with two extra bands: 1.380 cm^{-1}(m) and 1.170 cm^{-1}(s). This product was probably formed by decomposition of the thiosulphonate since heating the thiosulphonate to about 150-180° gave a similar oil.

Solid (A) was extracted with hot chloroform. The chloroform extract was distilled and a trace of brown oil was obtained. This oil was not identified. The extraction was repeated with hot ethanol but no product was obtained.

2.6. Attempted reaction of β-naphthalenesulphinyl chloride with anthracene.

β-Naphthalenesulphinyl chloride (3.0 g., 0.0143 mole), anthracene (2.0 g., 0.0112 mole) and copper bronze (2.0 g., 0.0317 g.atom) in benzene (100 ml.) were heated under reflux

for three hours. The reaction mixture was filtered hot and a solid (A) was separated from the yellow filtrate which was kept at 6-8° for several hours. As no solid separated from this, the solution was distilled under reduced pressure. Carbon tetrachloride (20 ml.) was added to the residue; anthracene (0.60 g.) separated and was identified by i.r. spectroscopy. The filtrate was again distilled under reduced pressure; boiling petroleum ether (10 ml.) was added to the residue. A brown tar separated and was removed by decantation. The hot solution was cooled and a white solid (0.27 g.) was obtained, m.p. 101-104°, (B). The solid was recrystallized from ethanol, 0.22 g., m.p. 105-106°.

Analysis gave: C = 81.1% H= 4.66% S = 7.39

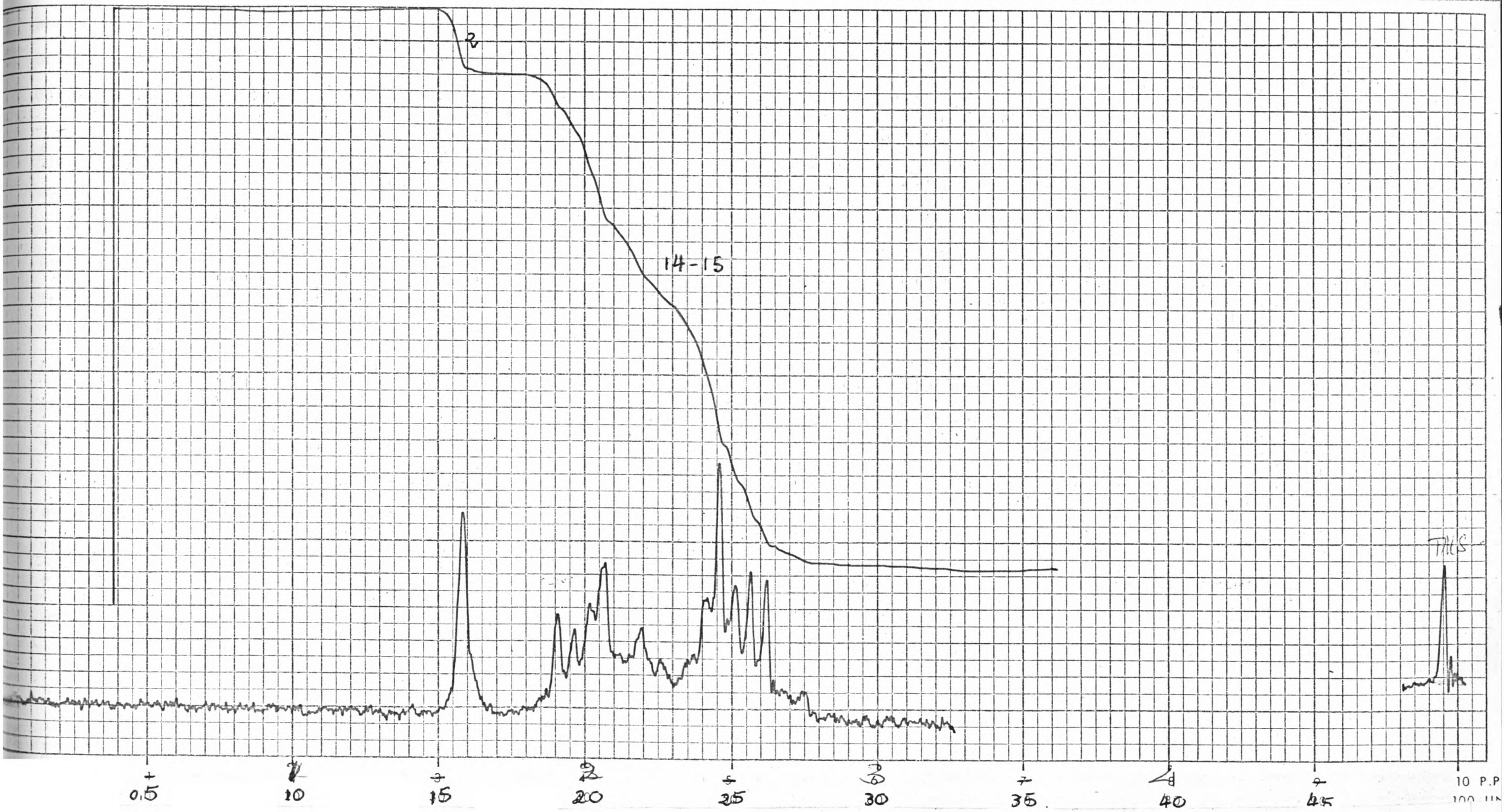
Required for $C_{20}H_{14}O_2S_2$: C= 68.6 H= 4.03 S= 18.3

The i.r. spectrum of this product in nujol showed the following absorption bands ($cm.^{-1}$):

660(s), 730(s), 755(s), 775(w), 820(s), 827(m), 870(m), 895(s), 920(w), 950(w),985(m), 980(w), 1000(w), 1030(w), 1070(m), 1125(s), 1145(s), 1240(w), 1270(w), 1330(s), 1350(m), 1380(nujol), 1470(nujol), 1500(m), 1580(m), 1620(m) and 2900(nujol).

The two strong bands at 1145 and 1330 cm^{-1} are due to the sulphonyl group, $-SO_2-$. The dimer, β-naphthyl-β-naphthalenethiosulphonate has m.p. 106-108° (177).

DATE	DEC. SHIFT	REF. STD.	R.F. FIELD	R.F GAIN	REMARKS	SENSITIVITY	SWEEP RATE	TIME CONST.	SCALE FACTOR
MAY 1965						NORM: ___ INT: 4	___ UNITS PER MIN	___ SECS .015 M SECS	3 C/S PER UNIT



The solid (A) was extracted with boiling chloroform. The extract was distilled under reduced pressure. A white solid (0.12 g.) was obtained. This solid did not contain sulphur and was not identified. The filtrate of (B) was distilled and a trace of brown oil was obtained.

2.7. Attempted reaction of 2,4-dinitrobenzenesulphinyl radicals with p-benzoquinone.

2,4-dinitrobenzenesulphenyl chloride (8.20 g., 0.035 mole) (p.294) was dissolved in dry acetonitrile (160 ml.), (p.295). This solution was stirred and cooled in acetone/dry ice.

To the cold solution silver nitrate (5.85 g., 0.0344 mole) in dry acetonitrile (160 ml.) was added, drop by drop, with good stirring. Silver nitrate was dried in a stream of dry air at 150-180°C.

After the addition of the silver nitrate solution was completed, the mixture was allowed to stand for three hours. Then the precipitate of silver chloride was removed and the filtrate was concentrated to small volume (50 ml.) under a stream of dry air at room temperature.

A solution of p-benzoquinone (3.0 g., 0.277 mole)in ethanol (50 ml.) was added to the acetonitrile solution, and the concentration of the ethanol-acetonitrile solution was continued down to about 40 ml. This solution was then separated into two parts:

-Part (i) was mixed with ethanol (200 ml.). The mixture was left overnight and then filtered. Yellow crystals (1.50 g.) separated, m.p. 126-127°. This product was identified as 2,4-dinitrophenyl-2,4-dinitrobenzenethiosulphonate by comparison of i.r. spectrum and mixed m.p. with an authentic specimen, m.p. 126.5-127°, obtained by decomposition of 2,4-dinitrobenzene-sulphenyl nitrate ([147]).

The filtrate of (A) was cooled in acetone/dry ice but no solids were obtained. The solution was then left overnight and more 0.11 g. of solid (A) was separated by filtration.

50 ml. of this filtrate (total 210 ml.) were mixed with 50 ml. of water. The mixture was then extracted with chloroform. The chloroform layer was separated and dried over magnesium sulphate. Then it was distilled under reduced pressure and a dark red residue was obtained. The i.r. spectrum of this residue indicated it was a mixture of p-benzoquinone and thiosulphonate.

-Part (ii) was mixed with ethanol (50 ml.). The solution was left twenty hours at room temperature. Yellow crystals (1.30 g.) separated, m.p. 126-127°. This product was identical with (A), 2,4-dinitrophenyl-2,4-dinitrobenzenethiosulphonate. The filtrate of these crystals was kept at 0° for one day and product (A), 0.40 g., was obtained (B).

Half the filtrate of (B) was diluted with water and

extracted with chloroform. The same result of part (i) was obtained: a mixture of p-benzoquinone and (A).

The total yield of dimer, 2,4-dinitrophenyl-2,4-dinitrobenzenethiosulphonate, was about 3.30 g.(44%).

No addition of the sulphinyl radical to the quinone molecule was obtained.

3. Preparation of reference compounds.

3.1. Preparations concerning the decomposition of p-toluenesulphonyl iodide.

3.1.1. p-Toluenesulphonyl iodide.

A-Sodium p-toluenesulphinate:

This was prepared as described in Org.Synth.[181] using one half of the stated quantities, by reduction of p-toluenesulphonyl chloride with zinc dust followed by treatment with sodium carbonate.

B-p-Toluenesulphonyl iodide:

This was prepared after Whitmore and Thurman[53] by the reaction of sodium p-toluenesulphinate with iodine. The compound was dried in the dark at room temperature in a vacuum dissecator in the presence of sodium hydroxide or phosphorus pentoxide. The compound melted with decomposition at 84-85° (lit.[53] m.p. 84-85°). It was contaminated with a little iodine. The solid was recrystallized from carbon tetrachloride and the m.p. was improved to 90-91° (decomp.). The i.r. spectrum of solid m.p. 84-5° and crystals 90-91° were identical.
Yield 60% (lit.90%).

3.1.2 - p-Toluenesulphonic anhydride:

This was prepared after Field and Settlage[152] by reaction of p-toluenesulphonyl chloride with mercurous oxide, m.p.

98-102° (lit.128-129.5°). Analysis gave:

Found: C=51.46% H=4.71% S=19.62%

Required for $C_{14}H_{14}O_5S_2$:

C=51.50 H=4.32% S=19.65%

3.1.3 - p-Tolyl-p-toluenethiosulphonate:

This was prepared by reaction of p-toluenesulphonyl chloride with copper bronze in pyridine as described by Karrer[48] The product had m.p. 76° (lit.76°) and the yield was 35%.

3.1.4. Phenylammonium p-toluenesulphonate.

p-Toluenesulphonic acid (2.0 g., 0.0116 mole) was dissolved in hot aniline (5 ml.) The solution was cooled in an ice-bath and then mixed with benzene (50 ml.) The white solid which separated was washed with benzene (3 x 25 ml.) and dried by suction in the Buchner funnel. Phenylammonium p-toluenesulphonate, $PhNH_3^+SO_3^-Tol$, was obtained (1.6 g., 84%) as small colourless crystals, m.p. 226-8° (lit.[182] m.p. 216°, 223°, 230-1 and 238°).

3.1.5. p-Tolyldisulphone:

This was prepared by oxidation of p-toluene sulphinic acid with an acidic ceric sulphate solution. The reaction was carried out by adding a ceric sulphate solution (0.1M) in 2N sulphuric acid to a solution of sodium p-toluenesulphinate in water until the colour of the mixture turned yellow (50% excess). The solid that separated was collected and dried.

After recrystallization from benzene, p-tolyldisulphone was obtained as colourless crystals, 20% yield, m.p. 218-9° (lit.[33] 221°).

3.1.6 - 2-Iodo-2-methylpropanenitrile

This compound was prepared as described by Ford and Waters[183] by decomposition of α,α'-azo-bis-isobutyronitrile in toluene in the presence of iodine.

3.1.7- 1,1'-bis(1-cyanomethylcyclohexane) and 1-iodo-1-cyanomethylcyclohexane.

Azo-bis-cyanomethylcyclohexane (5.0 g., 0.0204 mole) and iodine (5.0 g., 0.0196 g. atom) were refluxed in toluene (50 ml.) for about fifty hours. The reaction mixture was diluted with benzene (100 ml.) and washed with an alkaline solution of sodium thiosulphate (5%) to remove unreacted iodine. The organic layer was washed with water, dried with sodium sulphate and then distilled under reduced pressure. All fractions with bp $\leq 40^{\circ}$/ 80 mm were removed. The residue was a liquid containing some crystals. This residue was mixed with acetone (20 ml.) and filtered. 1,1'-bis(1-cyanomethylcyclohexyl) was collected by filtration (2.0 g., 45%) and had m.p. 220-5° (lit.[184] 224-225.5°) (A). Recrystallization from acetone gave 1.83 g., m.p. 224-5°.

The acetone filtrate of (A) was evaporated and a pale red

liquid residue (2.0 g.) was obtained. This liquid decomposed with liberation of iodine vapour. Its i.r. spectrum was identical with that obtained by the decomposition of the azo-compound in the presence of p-toluenesulphonyl iodide (p. 95).

3.2. Preparations concerning the reaction of p-toluenesulphonyl iodide with quinones.

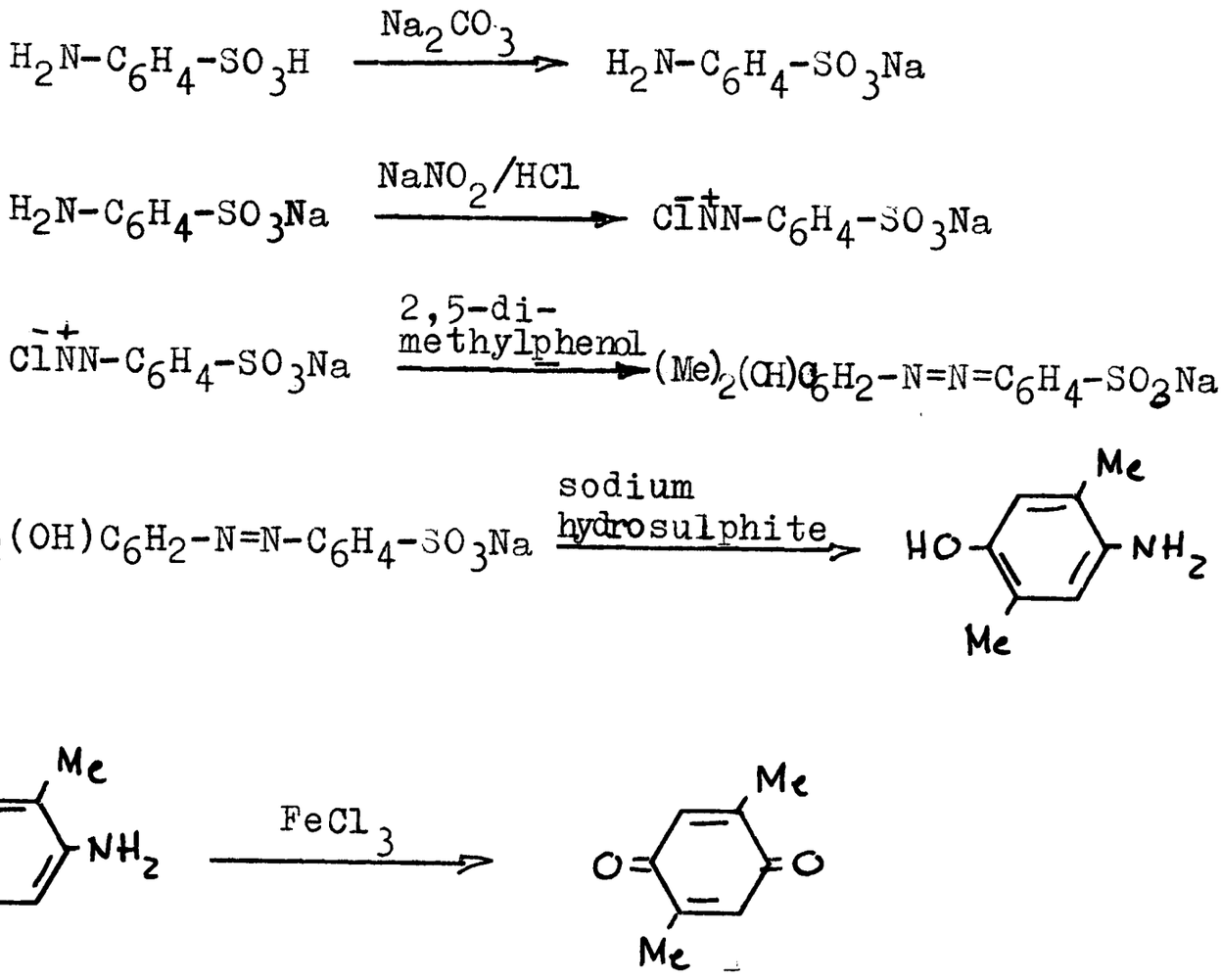
3.2.1. Toluquinone (methyl-p-benzoquinone)

Toluquinone was prepared by oxidation of o-toluidine by potassium dicromate [185] . A solution of o-toluidine (30 g., 0.28 mole) in a mixture of water (900 ml.) and conc. sulphuric acid (240 g.) was cooled in an ice bath and finely powdered potassium dichromate (78 g., 0.265 mole) was added slowly with vigorous stirring.

Stirring of the mixture was continued for about half an hour after all the potassium dicromate had been added and then the mixture was left overnight. The dark solid that had separated was filtered off and distilled in small amounts in a current of superheated steam. The distillate was cooled in an ice bath and the quinone was collected by filtration (6.1 g., 41.5%), m.p. 66-67° (lit.[185] 67-8°).

3.2.2- p-xyloquinone (2,5-dimethyl-p-benzoquinone)

This was prepared from p-aminobenzenesulphonic acid as described by Smith and Opie [186] :



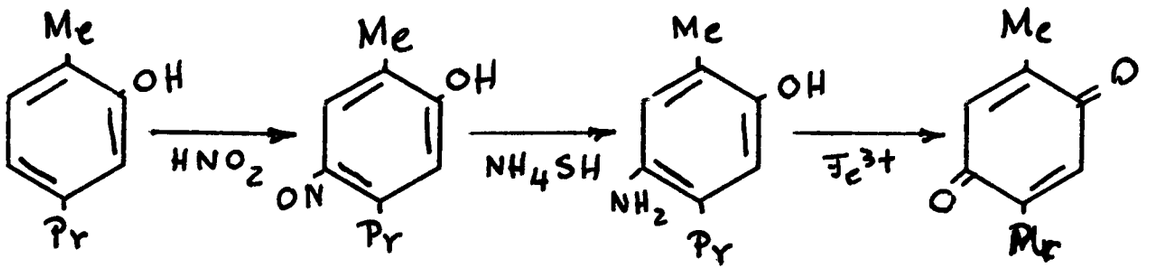
The quinone had m.p. 123-5° (lit. 123.5-125°). Yield about 50% (lit.50-80%)

3.2.3. - m-xyloquinone (2,6-dimethyl-p-benzoquinone)

This quinone was prepared by using the same method as 4.2.2. and had m.p. 73-4° (lit.[186] 73-5°). Yield about 69% (lit.[186] 74.5%).

3.2.4. - Thymoquinone (2-methyl-5-isopropyl-p-benzoquinone):

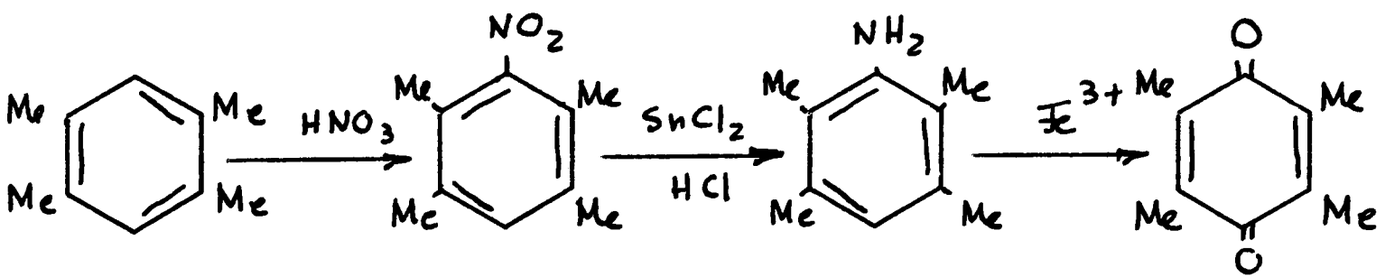
This was prepared as described in Org.Synth.[187], m.p.



45-6°(lit.45-8°). Yield very poor, 43% (lit.80-87%).

3.2.5. Duroquinone (tetramethyl-p-benzoquinone)

This quinone was synthesized by oxidation of durene with nitric acid followed by reduction with stannous chloride and subsequent oxidation of the amine with ferric chloride[188]:



The yield of pure quinone was quite low (42%, lit.90%), m.p. 109-10° (lit. 109-10°).

3.2.6. Methylhydroquinone

This was prepared by reduction of p-toluquinone with tin-amalgam[189] in glacial acetic acid.

Tin amalgam was prepared as follows:

To a flask containing 15 g. of mercuric chloride and 100 ml of water was added tin powder (100 g.). The flask was stoppered and shaken for a few minutes until all the tin appeared to have a shiny coating of mercury. The tin amalgam was then repeatedly washed with water until the washings were clear, and stored under distilled water.

The hydroquinone was prepared as follows: Methylhydroquinone (2.0 g., 0.0164 mole) and tin amalgam (3.5 g.) in acetic acid (20 ml.) were heated on a steam bath for ten minutes. The mixture was filtered and the solvent removed in vacuo. Recrystallization of the residue from benzene gave 1.47 g., (73%), m.p. 123-5° (lit.[190] m.p. 124°).

3.2.7. p-xylohydroquinone (2,5-dimethylhydroquinone).

This was obtained by reduction of the corresponding quinone as described by Smith and Opie[191] for other quinones.

2,5-Dimethyl-p-benzoquinone (1.4 g., 0.0103 mole) was dissolved in a mixture of acetic acid (7 ml.) and water (5 ml.) Zinc dust (2 g., 0.0305 g.atom) was added and the mixture refluxed until it became colourless (3-4 minutes). Boiling water (15 ml.) was added and the hot solution was decanted off from the zinc. The zinc was washed with another portion of hot water. The solution was cooled to 0° and the hydroquinone (0.99 g., 71%) was separated, m.p. 208° (lit.[191] 208°).

3.2.8 - m-xylohydroquinone (2,6-dimethylhydroquinone).

This was prepared by using the same process as the preparation of the isomeric 2,5-dimethylhydroquinone. Yield 54%, m.p. 211-20° (lit.[190] 213°).

3.2.9 - 9,10-Dihydroxyphenanthrene.

This was prepared by reduction of 9,10-phenanthraquinone with zinc powder in acetic acid as described by Schmit and Jumpp[192] and used without further purification. Yield 42%.

3.2.10 - 2-p-tolylsulphonylhydroquinone.

This was synthesized as described by Walker ([176] from p-toluenesulphinic acid and p-benzoquinone. The yield of the reaction was about 94%; m.p. 211-4° (lit.m.p. 211-2°).

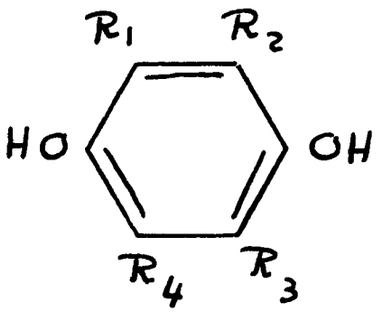
3.2.11 - Hydroquinone-di-p-toluenesulphonate and similar di-esters.

These were prepared as described by Drahowzal and Klamann to the hydroquinone di-ester. p-Toluenesulphonyl chloride (9.5 g., 0.05 mole) and hydroquinone (5.5 g., 0.05 mole) were dissolved in 50 ml of acetone. The solution was kept in an ice bath and a solution of sodium hydroxide (2 g. in 10 ml. of water) added slowly, with stirring.

p-Toluenesulphonyl chloride (9.5 g., 0.05 mole) was then added in small portions and the mixture stirred for a further

15 minutes. Another 10 ml. of the sodium hydroxide solution were added and the mixture stirred one hour. It was then poured into 100 ml. of water. A white solid (14.9 g.) was obtained by filtration and was then recrystallized from a benzene-carbon tetrachloride mixture (1:6) yielding 13.5 g. (65%) of small colourless crystals of hydroquinone-di-p-toluene-sulphonate, m.p. 162-3° (lit.[154] 163-4°).

The di-esters of p-toluenesulphonic acid and other hydroquinones were prepared in the same manner. Details are given in the following table:



Hydroquinone					$TolSO_2Cl$	NaOH	Acetone	Di-ester		
R_1	R_2	R_3	R_4	(g)	(g.)	(g.)	(ml.)	Yield	m.p.	No.
H	H	H	H	(5.5)	19	4	50	65%	162-3°	1
Me	H	H	H	(1.4)	4.3	1.45	10	45%	152-4°	2
Me	H	Me	H	(1.1)	3.1	1.19	10	61%	192-4°	3
Me	H	H	Me	(1.5)	3.0	1.0	10	62%	161-3°	4
9,10-dihydroxy-phenanthrene				(1.0)	2.7	0.5	10	17%	200-1°	5

Analysis

Diester nº	Found			Required		
	C	H	S	C	H	S
2	58.3	4.69	14.8	58.3	4.66	14.8
3	58.7	5.09	14.6	59.2	4.97	14.3
4	59.1	5.04	14.3	59.2	4.97	14.3
5	64.2	4.31	12.7	64.9	4.28	12.3

N.m.r. and i.r. spectra (pages)

Diester nº	n.m.r.	i.r.
1	p.175	p.176,7
2	p.186	p. 187
3	p. 198	p. 199
4	p. 194	p. 195
5	p. 205	p. 206

3.3. Preparations concerning reactions of sulphinyl chlorides

3.3.1 - Preparations of benzenesulphinyl chloride

(a) Method of Douglass and Poole[163]

Thiophenol (22 g., 0.2 mole) and dry methylene chloride (150 ml.) were introduced into a 1 l. 3-neck flask fitted with stirrer, gas inlet and outlet tubes. The flask and contents were cooled in acetone/dry ice while gaseous chlorine was passed in above the surface of the stirred solution for about two hours. Water (3.6 g. 0.2 moles) was introduced slowly to the cold mixture, the temperature of which was allowed to rise slowly to about -15°.

The mixture gradually melted and was allowed to come to room temperature. Most of the solvent was removed at atmospheric pressure and the residue was distilled under vacuum:

	1st Experiment	2nd Experiment	3rd Experiment
Boiling point:	$83-4^{\circ}$/1mm	$81-4^{\circ}$/1 mm	$71-5^{\circ}$/0.8-0.9 mm
Analysis (Cl%):	19.80	19.45	20.50

Required to PhSOCl: 22.08%

Required to $PhSO_2Cl$: 20.19%

The i.r. spectrum of the product showed strong $-SO_2-$ bands and was identical with that of benzenesulphonyl chloride. This was confirmed by preparing the sulphonamide derivative, m.p.

152-4° (lit.[178] m.p. 156°).

This preparative method was abandoned.

(b) Method of Barnard[145]

Sodium benzenesulphinate was dissolved in a small amount of warm water. This solution was acidified with sulphuric acid and cooled in an ice bath. The white solid which appeared was separated by filtration and dried in a vacuum desicator over phosphorus pentoxide at 0-5°.

The benzenesulphinic acid (14.2 g., 0.1 mole) was suspended in dry ether (60 ml.); thionyl chloride (18 ml.) was added slowly with stirring, the reaction flask being cooled in an ice bath.

Dry benzene (50 ml.) was added and the solvent and excess of thionyl chloride distilled off under reduced pressure. This operation was repeated three times with an equal volume of benzene, leaving the sulphinyl chloride (80%) that was used without purification.

The i.r. spectrum of the sulphinyl chloride was identical with that shown in the literature.[165]

The derivative sulphinamide, $PhSONH_2$, was prepared, m.p. 120-2° (lit.[166] 122°).

3.3.2. p-Toluenesulphinyl chloride.

This was prepared as described in Org.Synth.[168] by reaction of thyonyl chloride with sodium p-toluenesulphinate. The

The yield was about 61% and the liquid had b.p. 115-20°/4 mm. (lit.[166] b.p.99-102/0.5 mm; 113-5/3.5 mm)

3.3.3. β-Naphthalenesulphinyl chloride.

This product was prepared from naphthalene by using the following processes:

(a) Sulphonation of naphthalene[193] with concentrated sulphuric acid to give the β-naphthalenesulphonic acid.

(b) Conversion of β-naphthalenesulphonic acid into the sulphonyl chloride using phosphorus trichloride.[194]

(c) The sulphonyl chloride was reduced with sodium sulphite to give sodium β-naphthalenesulphinate.[195]

(d) The sodium salt could not be converted directly into the acid by acidification because the complex acid-salt was formed. The sodium sulphinate was transformed into ferric sulphinate. The ferric sulphinate was separated, dried, and stored. When necessary the ferric salt was dissolved in diluted ammonia, filtered and the filtrate acidified. The mixture was cooled and the acid collected.[196]

(e) The sulphinyl chloride was obtained from the β-naphthalene-sulphinic acid by reaction with thionyl chloride.[177]

3.3.4. Bis(2,4-dinitrophenyl)disulphide

was prepared from 2,4-dinitrochlorobenzene by the same method used to prepare bis(o-nitrophenyl)disulphide from o-nitro-chlorobenzene.[197]

Sodium sulphide (120 g., 1.54 mole) was mixed with 95% ethanol (500 ml.) and the mixture refluxed in a water bath until the sulphide dissolved. Then finely ground sulphur (16 g., 0.5 g. atom) was added to the solution and the heating was continued until all the sulphur had dissolved.

A solution of 2,4-dinitrochlorobenzene (162 g., 0.80 mole) in 95% ethanol (165 ml.) was prepared and placed in a 2 l. flask fitted with reflux condenser. The sodium disulphide solution was added slowly to this solution through a funnel placed in the top of the reflux condenser.

The mixture was then heated on a steam bath, gently at first and then more strongly for three hours. The mixture was then cooled and filtered. The solid collected was stirred with water (3 x 250 ml.) and filtered. The resulting yellow solid was washed with ethanol (3 x 50 ml.) Yield 62%, m.p. 245-80° (decomp.) (lit.[198] m.p. 240-280° decomp.).

Sodium sulphide was dried by heating several hours on a water bath in vacuo.

3.3.5. - 2,4-dinitrobenzenesulphenyl chloride.

This was prepared as described by Kharasch[199] by reaction of bis(2,4-dinitrophenyl)disulphide with sulphuryl chloride in the presence of a small amount of pyridine as catalyst. The sulphenyl chloride was recrystallised from carbon tetrachloride. Yield 67%, m.p.94-5° (lit.71-83%[199], m.p.95-5.5°[200] 94-5°[198]).

SOURCES AND PURIFICATION OF MATERIALS

Material	Source	Characteristics	Obs.
Acenaphthaquinone	Dept.	m.p.258-59°	UWP
Acetonitrile	H&W	b.p.80-82°	DD
Acrylonitrile	BDH	m.p.76-8°	UWP
Alumina	Spence	H-type	-
Alumina(deactivated)	Spence	H-type	AcOH
Aluminium chloride	BDH	Anhydrous	UWP
Aniline	H	Technical	UWP
Anthracene(blue fluors.)	BDH	m.p.214-6°	UWP
Anthraquinone	BDH	m.p.282-7°	UWP
Azobis(1-cyano-1-cyclohexyl)	Dept.	m.p.112-3°	UWP
Azobis(2-cyano-2-propyl)	ICI	m.p.103-4°	R(ether)
1,2-Benzanthracene	L	m.p.156-58°	UWP
2,3-Benzanthracene	L	m.p.>350°	UWP
Benzene	M&B	-	D
p-Benzoquinone	BDH	m.p.115°	R(Pet.ether)
Benzyl thiouronium chloride	Prep. as Chambers & Watts, J.O.C., 1941,6,373		
Carbon tetrachloride	H	-	D
Chloranil	H&W	97%	UWP
Copper bronze	BDH	-	UWP
Cumene	BDH	b.p.152°	DD
Cyclohexene	BDH	-	UWP
9,10-Dimethylanthracene	KL	m.p.177-9°	UWP
3,5-Dimethylphenol	BDH	m.p.63-6°	UWP

Material	Source	Characteristics	Obs.
2,5-Dimethylphenol	BDH	-	UWP
2,4-DinitroChlorobenzene	BDH	m.p.48-52°	UWP
Durene	BDH	-	UWP
Ethyl cinnamate	BDH	b.p.82-4°/0.1mm	DD
Ferric chloride	H	Technical	UWP
Hydroquinone	BDH	m.p.170-4°	UWP
Iodine	H	Resublimed	UWP
α-methylstyrene	BDH	b.p.59°/18mm	DD
Naphthalene	BDH	m.p.79.5-80°	UWP
9-Methylanthracene	KL	m.p.78-80°	UWP
Petroleum ether	-	b.p.60-80°	UWP
9,10-Phenanthraquinone	BDH	m.p.206-11°	UWP
Phenanthrene	BDH	m.p.99-100°	UWP
Phosphorus pentachloride	BDH	99%	UWP
Siver Nitrate	BDH	Pure	UWP
Sodium benzenesulphinate	BDH	-	UWP
Sodium dithionite	H	-	UWP
Sodim sulphide	H	Crystals	D
Sodium nitrite	H	96%	UWP
Sodium sulphite	BDH	Anhydrous	UWP
Sodium thiosulphate	BDH	Analar	UWP
Stannous chloride	BDH	95%(oxidim.)	UWP
Sulphanilic acid	BDH	99%(acidim.)	UWP
Styrene(stabil.with t_{Bu}-catechol)	BDH	Ref.index 1.546--1.548	UWP
Tetramethylsuccinonitrile	Dept.	m.p.162-3°	UWP
Tri-ethylamine	BDH	m.p.170-5°(picrate)	UWP

Material	Source	Characteristics	Obs.
Sulphur	BDH	Sublimed	UWP
Thionyl chloride	BDH	97-103%(iodom.)	UWP
Thymol	BDH	-	UWP
p-Toluenesulphonic acid	BDH	m.p.90-2°	UWP
p-Toluenesulphonyl chloride	BDH	m.p.66-70°	UWP
o-Toluidine	BDH	b.p.198-201°	UWP
p-Xylidine	BDH	-	UWP
m-Xylidine	BDH	-	UWP

Notes; BDH-British Drug House

UWP-Used witout purification

Dept.-Sample belonging to the Department.

H&W-Hopkin & Williams

DD-Dried and distilled

AcOH-1 Kg treated with 50ml 10% acetic acid

H-Harrington

ICI-Imperial Chemical Industries

R(ether)-Recrystallized from ether

L-Light Ltd.

D-Distilled

M&B-May & Baker,Ltd

KL-Koch-Light Laboratories

SPECTRA AND OTHERS

All infra-red and ultra-violet spectra were recorded at room temperature(20°) on a Unicam SP.200 and SP.800 spectrophotometers respectively.
Nuclear magnetic ressonance spectra were recorded on a Perkin Elmer R 10 N.M.R. Spectrophotometer at 34°.
Analysis were by Drs.Weiller and Strauss.
N.M.R. spectra were determined by Mrs.Richards.
Melting points are uncorrected.

Interpretation of spectra was made by using the following:

-Infra-red:

Bellamy,The infra-red spectra of complex molecules, Methuen & Co.,1954

Jones,Infra-red spectra of organic compunds,National Research Council,Ottawa,1959

Meakins,Notes on applications of spectrographic techniques to organic chemistry,Dyson Perrins Lab.,Oxford

Colthup,Spectra-structure correlations(probable positions of characteristic infra-red absorption bands),American Cyanamid Co.(1950).

Bellamy and Kharasch,Organic Sulphur Compounds,Pergamon Press, 1961,p.48,49.

-N.M.R.,Varian Catalogues,nºI,II.

Dyer,Applications of absorption spectroscopy of organic compounds,Prentice Hall,Englewood Cliffs,New Jersey,1965.

Jackman,Applications of nuclear magnetic resonance spectroscopy in organic chemistry,Pergamon Press,1959.

ACKNOMLEDGEMENTS

The author wishes to express his deep gratitude to his supervisor, Dr.W.A.Waters, F.R.S., for his guidance and encouragement throughout the investigation.

He also wishes to thank Dr.W.G.B.Huysmans for helpful advise and discussions and all collegues for reading parts of the manuscript.

He also wishes to thank the Fundação Calouste Gulbenkian, Portugal, who supported this investigation.

REFERENCES

(1) Fehnel and Paul, J.A.C.S., 1955, 77, 4241

(2) Arndt et al., Liebigs Ann., 1932, 499, 228; Ber., 1941, 74, 423; Ang.Chem., 1941, 54, 101

(3) N.Kharacsh, "Organic Sulphur Compounds", Pergamon Press, 1961, vol.1

(4) Lister and Sutton, Trans.Far.Soc., 1939, 35, nº1, 495

(5) Phillips et al., J., 1945, 146

(6) Phenel and Carmack, J.A.C.S., 1949, 71, 231; Koch, J., 1949, 408

(7) Amstutz, Hunsberger and Chessick, J.A.C.S., 1951, 73, 1220

(8) Toussaint, Bull.Soc.Chim.Belg., 1945, 54, 319

(9) Doering and Levy, J.A.C.S., 1952, 74, 1058
Parham and Motter, ibid., 1959, 81, 2146
Szmant and Planinsek, ibid., 1950, 72, 4042, 4981
Cilento et al., ibid., 1953, 75, 3749; 1954, 76, 4469
Price et al., ibid., 1953, 75, 4749, 4750
Bordwell et al., ibid., 1957, 79, 376
Fehnel et al., ibid., 1949, 71, 84, 889
Longuet-Higgins, Trans.Far.Soc., 1949, 45, 173
Mangini, Gazz.Chim.Ital., 1958, 88, 1063
Knott, J., 1955, 916, 927, 933, 937, 949
Lumbrogo and Passerini, Bull.Soc.Chim. Biol.France, 1957, 311

(10) Fehnel and Carmack, J.A.C.S., 1949, 71, 231
Wepster et al., Rec.trav.chim., 1952, 71, 108
Kloosterziel and Backer, ibid., 1952, 71, 295
Bordwell and Cooper, J.A.C.S., 1952, 74, 1058

(11) Cumper, Read and Vogel, J, 1965, 5323

(12) Szmaut et al., J.A.C.S., 1951, 73, 4175; ibid., 1952, 74, 4395

(13) Solonina, J.Russ.Phys.Chem.Soc., 1898, 30, 826

(14) Seyer and King, J.A.C.S., 1933, 55, 3140

(15) Frederick, Cogan and Marvel, J.A.C.S., 1934, 56, 1815,
Hunt and Marvel, ibid., 1935, 57, 1691,
Ryden and Marvel, ibid., 1935, 57, 2311

(16) Standinger and Ritzenhaler, Ber., 1935, 68 B, 455

(17) Dainton, Ivin and Sheard, Trans.Farad.Soc., 1956, 52, 414

(18) Jobard and Virloget, Fr.Pat., 1957, № 1,138,557

(19) Backer and Bottema, Rec.trav.chim., 1932, 51, 294

(20) Eigenberger, J.prakt.Chem., 1930, 127(2), 307

(21) Sorokin and Puzitzkii, Sintet.Kauchuk, 1933, 6, 12

(22) Snow and Frey, Ind.Eng.Chem., 1938, 30, 176

(23) Dainton and Ivin, Trans.Farad.Soc., 1950, 46, 374

(24) Ibid., 382

(25) Schenck and Schmidt, Ann., 1953, 584, 199

(26) Ayscough, Ivin and O'Donnell, Proe.Chem.Soc., 1960, 71

(27) Kuri, Ueda and Shida, J.Chem.Phys., 1960, 32, 371

(28) Squire and Waters, J., 1962, 2o68

(29) Squire, Part II, Oxford, 1960

(30) Lindsay, Part II, Oxford, 1962

(31) Masters, Part II, Oxford, 1961

(32) Correia, Thesis to be submitted at Oporto, Portugal

(33) Hilditch, J., 1908, 1524

(34) Alimarin and Sotnikov, Doklady Akad.Nauk., S.S.S.R., 1957,
113, 150

(35) Forrest and Ryan, Can.J.Chem., 1958, 36, 1677

(36) Alimarin and Kusnetsov, Vestnik Moscov Uni.Ser.Fiz.Mat.,
Estesteven.Nauk.3

(37) Gringras and Sjostedt, Act.Chem.Scand., 1961, 15, 433

(38) McMillan and Waters, J.(B), 1966, 422

~~(38) McMillan(Miss) and Waters,personal communication(J.,in press~~

(39) Olivier,Rec.trav.chim.,1917,36,124

(40) Asinger,Schmidt and Striengler,U.S.Dept.Comm.,O.T.S. Report,PB 850(1941)

(41) Smook,Pietski and Hammer,Ind.Eng.Chem.,1953,45,2731

(42) Schumacker and Stauff,Die Chemie,1942,55,341

(43) Herbrandson,Kelly and Versnel,J.Am.Chem.Soc.,1958,80,3301

(44) M.Kharasch,Chao and Brown,J.A.C.S.,1940,62,2393

(45) Bain,Blackman,Cummings,Hughes and Lynch,Proc.Chem. Soc., 1962,186

(46) Geisler and Reinhardt,Z.physik.chem.,1961,28,24,33; ibid.,1962,33,264.

(47) Inamoto,Yûki Gôsei Kagaku Kyôkay Shi,1958,16,528

(48) Karrer et al.,Helv.Chem. Acta,1928,11,233

(49) Pearl,Ivans and Dehn,J.A.C.S.,1938,60,2478

(50) Otto et al.,Ber.,1899,24,478

(51) Otto,Rössing and Tröger,J.prakt.chem.(2),1893,47,99

(52) Kohler and McDonald,Am.Chem.J.,1899,22,222

(53) Whitmore and Thurman,J.A.C.S.,1923,45,1068

(54) Ladd,U.S. Patent 2,521,068(1950); 2,573,580(1951).

(55) M.Kharasch and Mosher,J.O.C.,1952,17,453

(56) Skell and McNamara,J.A.C.S.,1957,79,85

(57) Skell,McNamara and Woodworth,ibid.,1957,79,1253

(58) McNamara,Dissert.Abstr.,1957,17,226

(59) Cristol and Reeder,J.O.C.,1961,26,2182

(60) Cristol and Davies,ibid.,1964,29,1282

(61) Asscher and Vofsi,J.,1964,4962

(62) Asscher and Vofsi,ibid.,1963,1887

(63) Goldwhite,Gibson and Harris,Tetrahedron,1965,21,2743

(64) Gibson and Harris,Tetrahedron,1964,20,1649

(65) Gibson and Harris,ibid.,1964,20,1657

(66) Pinnell,Huyser and Kleissberg,J.O.C.,1965,30,38

(67) Huyser,J.A.C.S.,1960,82,5246

(68) Kice and Pawlowski,ibid.,1964,86,4898

(69) Overberger and Rosenthal,ibid.,1960,82,108,117

(70) Backer,Rec.trav.chim.,1950,69,304

(71) Stone andWaters,J.,1964,213

(72) Dixon and Norman,J.,1964,4857

(73) Stone and Waters,Proc.Chem.Soc.,1962,253
Dixon and Norman,J.,1963,3122

(74) Chantsy,Horsfield,Morton,Rowlands and Whiffen,Mol.Phys.,
1962,5,233

(75(Price and Simpson,Proc.Roy.Soc.,1938,A 165,272

(76) Berthoud and Ponet,Helv.Chem.Acta,1934,17,694

(77) Gibbs,Philippine J.Sci.,1912,7,57

(78) Benrath and Von'Meyer,J.prakt.Chem.,1914,89,258

(79) Schönberg and Mustafa,J.,1944,67

(80) Waters,Ann.Reports,1945,42,155; Trans.Faraday Soc.,1946,
42,184

(81) Moore and Waters,J.,1953,3405

(82) Walling,Free Radicals in Solution,p.165,Jonh Wiley,1957

(83) Fieser and Oxford,J.A.C.S.,1942,64,2060

(84) Kvalnes,ibid.,1934,56,2478

(85) Cohen,ibid.,1947,69,1057

(86) Breitenbach and Renner,Can.J.Research,1950,28B,509

(87) Bickel and Waters,J.,1950,1764

(88) Aparicio and Waters,J.,1952,4666

(89) Dunn,Waters and Wickham-Jones,J.,1952,2427

(90) Moore and Waters,J.,1952,2432

(91) Breitenback and Breitenback,Z.physik.Chem.,1942,361

(92) Bartlett,Hammond and Kwart,Disc.Faraday Soc.,1947,2,342

(93) Kice,J.A.C.S.,1954,76,6274

(94) Branch and Calvin,The Theory of Organic Chemistry,N.Y., Prentice Hall,1941

(95) Evans and De Heer,Quart.Revs.,1950,4,94

(96) Rembaum and Szwarc,J.A.C.S.,1955,77,4468

(97) Fueno and Furukawa,Bull.Inst.Chem.Res.,Kyoto Univ.,1958,36,

(98) Hush,J.Polymer Sci.,11,289; Brown,Quart.Revs.,1952,6,63 81
Schmid and Heibronner,Helv.Chim.Acta,1954,37,1453

(99) Sykes,A Guidebook to Mechanism in Organic Chemistry,1965, Longmans,p.142

(100) Kharasch and Mayo,J.A.C.S.,1933,55,2468

(101) Hey and Waters,Chem.Revs.,1937,21,202

(102) Kharacsh,Engelmann and Mayo,J.O.C.,1937,2,288

(103) Vaugham,Rust and Evans,ibid.,1942,7,477

(104) Waters,The Chemistry of Free Radicals,Clarendon Press, Oxford,1948,p.182

(105) Barton,Nature,1948,162,182

(106) Mayo and Walling,Chem.Revs.,1940,27,373

(107) Cadogan and Hey,Quart.Revs.,1954,8,308

(108) Mayo and Walling,Chem.Revs.,1940,27,373

(109) Haszeldine,et al.,J.,1952,2504;1953,5527

(110) Henne and Nager,J.A.C.S.,1951,73,5527

(111) Tedder and Walton,Proc.Chem.Soc.,1964,420

(112) Augood and Williams,Chem.Revs.,1957,57,123

(113) Dermer and Edminson,Chem.Revs.,1957,57,77

(114) Lewis and Symons,Quart.Revs.,1958,12,230

(115) Sheppard,Ph.D.Thesis,Massachusetts Inst.Tech.,1954

(116) Price and Convery,J.A.C.S.,1958,80,4101

(117) De Tar and Long,ibid.,1958,80,4742

(118) Seaman,Taylor and Waters,J.,1954,4690

(119) Davis,Hey and Williams,J.,1958,1878

(120) Dannley and Gippin,J.A.C.S.,1952,74,332

(121) Roitt and Waters,J.,1952,2695

(122) Bickel and Kooyman,Rec.trav.chim.,1952,71,1137

(123) Mikhailov and Blokhina,Doklady Akad.Nauk.S.S.S.R.,1951, 80,373;Chem.Abst.,1952,46,5025

(124) Beckwith and Low,J.,1961,1304

(125) Beckwith and Low,Austral.J.Chem.,1963,16,845

(126) Beckwith and Low,ibid.,1964,17,109

(127) Beckwith and Low,J.,1964,2571

(128) Beckwith and Waters,J.,1957,1001

(129) Beckwith,Norman and Waters,J.,1958,171

(130) Norman and Waters,J.,1958,167

(131) Norman and Waters,J.,1957,950

(132) Sisido,Udô and Nozaki,J.A.C.S.,1960,82,434

(133) Bass and Nababsing,J.,1965,4395

(134) Beckwith and Waters,J.,1956,1108 ; Beckwith,D.Phil.Thesis, Oxford,1956

(135) Waters,J.,1939,864 ; Hanby and Waters,J.,1946,1029

(136) Mikhailov,Bull.acad.sci.U.R.S.S.,classe Sci.chim.,1945,627

(137) Mikhailov and Promyslov,Zhur.Obshchei.Khim.,1950,20,338

(138) Szwarc,J.Polymer Sci.,1955,16,367 ; Levy and Szwarc, J.A.C.S.,1955,77,1949 ; Levy,Newman and Szwarc,ibid., 1955,77,4225

(139) Bergman, Trans.Faraday Soc., 1954, 50, 829

(140) Dewar, J.A.C.S., 1952, 74, 3341

(141) Burkitt, Coulson and Longuet-Higgins, Trans.Faraday Soc., 1951, 47, 553 ; Pullman and Pullman, Le theries electroniques de la chimic organique, Mason, Paris, 1952

(142) Kooyman and Farenhorst, Trans.Faraday Soc., 1953, 49, 58

(143) Dunn, Waters and Roitt, J., 1954, 50

(144) Turner and Waters, J., 1956, 879

(145) Barnard, J., 1957, 4673

(146) Barnard and Percy, Chem.Ind.(London), 1960, 1332

(147) Topping and Kharasch, J.O.C., 1962, 27, 4353

(148) Stirling, J., 1957, 3597

(149) Kice and Pawlowsky, J.A.C.S., 1964, 86, 4898

(150) Suter, Organic Chemistry of Sulphur, J.Wiley, 1944

(151) Overberger, Biletch, Finestone, Lilker and Herbert, J.A.C.S., 1953, 75, 2078

(152) Field and Settlage, J.A.C.S., 1954, 76, 1224

(153) Stevens and Coffield, J.A.C.S., 1951, 53, 103

(154) Drahowzal and Klamann, Monatsh, 1951, 82, 452 ; Chem Abst., 46, 924a

(155) N.M.R. Varian Catalogue

(156) Jackman, Applications of N.M.R. spectroscopy in Org.Chem., Pergamon Press, 1959

(157) Bernstein, Schneider and Pople, Proc.Roy.Soc., 1956, 236A, 518

(158) Mosley, J.O.C., 1954, 19, 304

(159) Kvalnes, J.A.C.S., 1934, 56, 667, 670, 2487 ; Hunter and Kvalnes, ibid., 1932, 54, 2869

(160) Bruyn, Compt.rend., 1949, 228, 1953

(161) Cook, J., 1926, 2160

(162) Catch,Elliot,Hey and Jones,J.,1948,278

(163) Douglass and Poole,J.O.C.,1957,22,536

(164) Douglass and Poole,ibid.,1961,26,1996

(165) Detoni and Hadzi,J.,1955,3166(1955)

(166) Herbrandson,Dickerson and Weinstein,J.A.C.S.,1956,78,2578

(167) Cymerman and Willis,J.,1951,1334

(168) Org.Synth.,1954,vol.34,p.93

(169) Org.Synth.,1946,col.vol.I,p.220

(170) N.Kharasch,U.S.Pat.2,929,820(1960)

(171) Dost and VanMes,Rec.trav.chim.,1951,70,403;ibid.,1952,71,857

(172) Milyutinskaya,Bagdasasayan and Israelevitch,Zhur.Fiz. Khim.,1957,31,1019

(173)Olah,Friedel Crafts and Related Reactions,vol.III,p.1341, Interscience Publishers,1964

(174) Aleykutty and Baliah,J.Indian Chem.Soc.,1955,32,702; Baliah and Mathew,ibid.,1957,34,434

(175) Burton and Hopkins,J.,1952,4457

(176) Walker,J.,1945,633

(177) Trivedi,J.Indian Chem.Soc.,1956,33,359

(178) F.Wild,Characterization of Organic Compounds,p.200, Cambridge University Press,1960

(179) Ford and Waters,J.,1952,2240

(180) Bartlett,Hammond and Kwart,Disc.Faraday Soc.,1947,2,342

(181) Org.Synth.,1947,coll.vol.I,p.492

(182) Noller and Liang,J.A.C.S.,1932,54,670

(183) Ford and Waters,J.,1951,1853

(184) Overberger,Shaughnessy and Shalit,J.A.C.S.,1949,71,2661

(185) Harmen and Cason,J.O.C.,1952,17,1058;Chattaway and Parkes,J.,1925,1309

(186) Smith and Opie, J.O.C., 1941, 6, 432

(187) Org.Synth., 1941, coll.vol.I, p.511

(188) Org.Synth., 1943, coll.vol.II, p.254

(189) Schaefer, J.O.C., 1960, 25, 2027

(190) Rodd, The Chemistry of Carbon Compounds, vol.III_A, p.478, Elsevieer (1954).

(191) Smith and Opie, J.O.C., 1941, 6, 433

(192) Schmit and Lumpp, Ber., 1910, 43, 789

(193) Vogel, Practical Organic Chemistry, 1948, 529

(194) Joy and Bogert, J.O.C., 1936, 1, 238

(195) Org.Synth., 1932, coll.vol. II, p.7

(196) Balfe and Wright, J., 1938, 1490; Thomas, J., 1909, 344

(197) Org.Synth., coll.vol.I, 1946, p.220

(198) N.Kharasch, Wehrmeister and Tigerman, J.A.C.S., 1947, 69, 1613

(199) N.Kharasch, U.S.Pat. 2,929,820 (1960)

(200) N.Kharasch, Gleason and Buess, J.A.C.S., 1950, 72, 1796

ABSTRACT

The reactions of sulphonyl halides with olefins have been reviewed, with other processes of producing free sulphonyl radicals.

Reactions of polynuclear aromatic hydrocarbons and quinones with free radicals have also been presented.

The decomposition of p-toluenesulphonyl iodide was investigated. The sulphonyl iodide decomposed very slowly when refluxed in carbon tetrachloride for eight hours but in the presence of metals, e.g. silver and copper powders, the decomposition was achieved in less than three hours. The products of this decomposition were p-toluenesulphonic anhydride and p-tolyl-p-toluenethiosulphonate. Copper salts of p-toluenesulphonic acid seem to be formed. The expected dimer, p-tolyldisulphone could not be isolated.

Free radicals were used instead of metals to decide whether the sulphonic anhydride was formed by a homolytic or heterolytic reaction. It was expected that the free radicals would combine with the iodine atoms yielding sulphonyl radicals:

$$TolSO_2I + R\cdot \longrightarrow TolSO_2\cdot + R\text{-}I$$

The reaction mixtures were complex but the formation of p-toluenesulphonic anhydride could still be detected. The dimer, p-tolyldisulphone was also isolated but only in 3-18 % yield. Azobis-isobutyronitrile and azobis(1-cyano-1-cyclohexyl) were used as sources of free radicals. The other products of reaction were of the type R-I, R-R and R'-SO_2Tol (R = 2-cyano-2-propyl and 1-cyano-1-cyclohexyl; R' = 2-cyano-2-propyl).

Decomposition of the sulphonyl iodide under u.v. light gave also p-toluenesulphonic anhydride.

The mechanism proposed for the decomposition of the sulphonyl iodide was:

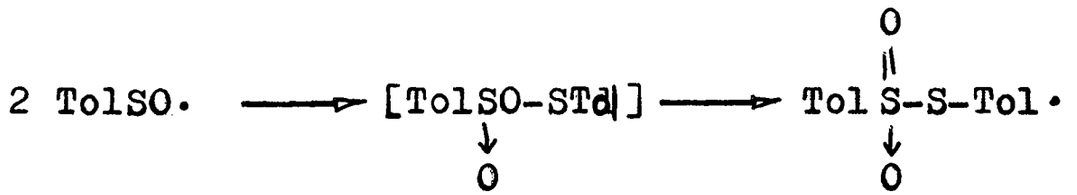
$$TolSO_2I + \begin{cases} M \\ R\cdot \end{cases} \longrightarrow \begin{cases} TolSO_2\cdot + IM \\ TolSO_2\cdot + IR \end{cases}$$

$$TolSO_2I \rightleftharpoons TolSO_2\cdot + I\cdot$$

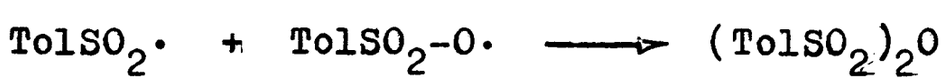
$$I\cdot + \begin{cases} M \\ R\cdot \end{cases} \longrightarrow \begin{cases} IM \\ IR \end{cases}$$

$$2\ TolSO_2\cdot \longrightarrow TolSO_2\text{-}O\cdot + TolSO\cdot$$

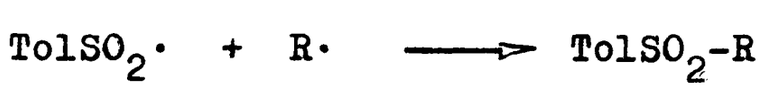
$$2\ TolSO_2\cdot \longrightarrow TolSO_2SO_2Tol$$



$$2\ TolSO\cdot \longrightarrow [TolSO\text{-}STol] \longrightarrow Tol\overset{\overset{O}{\downarrow}}{\underset{\underset{O}{\downarrow}}{S}}\!=\!S\text{-}Tol\cdot$$



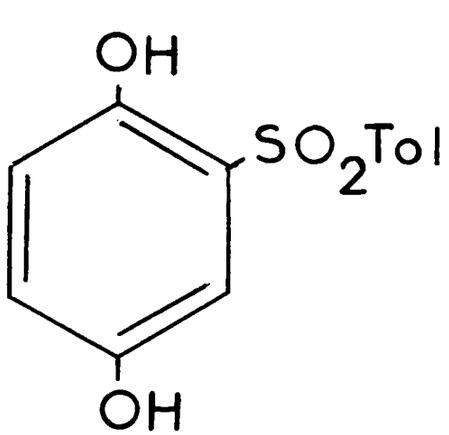
$$TolSO_2\cdot + TolSO_2\text{-}O\cdot \longrightarrow (TolSO_2)_2O$$



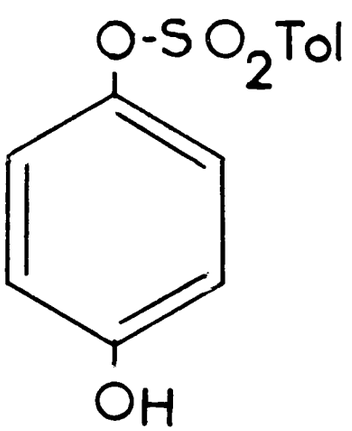
$$TolSO_2\cdot + R\cdot \longrightarrow TolSO_2\text{-}R$$

R· = Free radical; M = Metal

p-Toluenesulphonyl iodide reacts with quinones in the presence of copper bronze. Attack by the sulphonyl group concerned exclusively the oxygen atoms of quinones. Di-p-toluenesulphonates of 1,4-dihydroxybenzenes were obtained. p-Toluenesulphonic anhydride did not react with quinones. The sulphonyl iodide attacked hydroquinone at the nucleus to give a sulphone and not a sulphonate, i.e.



not



The mechanism proposed for the reaction of p-toluene-sulphonyl iodide with quinones was as follows:

$$TolSO_2I + Cu \longrightarrow TolSO_2\cdot + CuI$$

$$TolSO_2\cdot + Q \longrightarrow TolSO_2\text{-}Q\cdot$$

$$TolSO_2\text{-}Q\cdot + TolSO_2\cdot \longrightarrow TolSO_2\text{-}Q\text{-}SO_2{}^{Td}$$

Quinones of higher redox potential were more reactive towards tolylsulphonyl radicals than quinones of low potential. Shielding of the quinone oxygen atoms by methyl or chlorine groups also reduced the reactivity.

Further indications of the free radical nature of the reactions of p-toluene sulphonyl iodide were obtained by reactions with polynuclear aromatic hydrocarbons. In the presence of copper bronze the sulphonyl iodide reacted with anthracene to give 9,10-di-p-tolylsulphonyl-9,10-dihydro-anthracene.

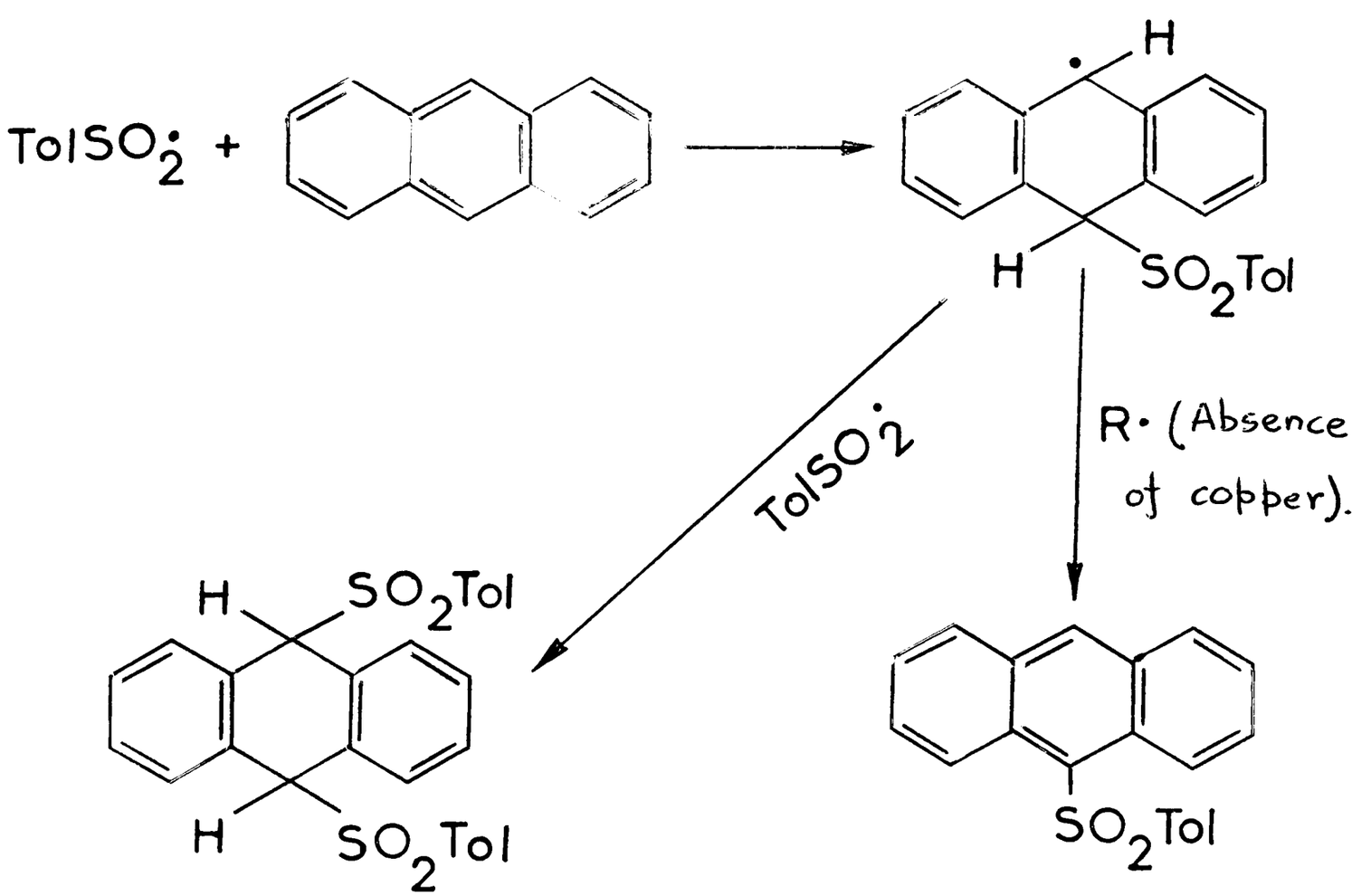
In the absence of metal, 9-p-tolylsulphonylanthracene was also formed. 2,3-Benzanthracene gave 9,10-di-p-tolyl-sulphonyl-9,10-dihydro-2,3-benzanthracene. 1,2-Benz-anthracene, phenanthrene did not react.

Evidence for free radical reactions were obtained with 9,10-di-methylanthracene and 9-methylanthracene. Substitution

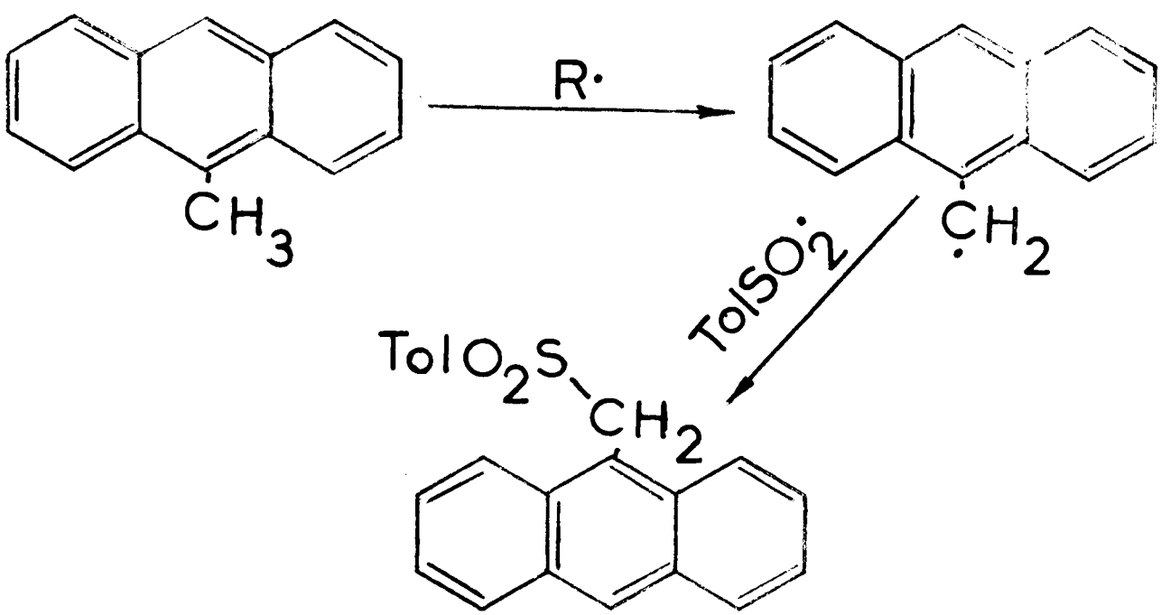
products of the methyl group were obtained in both cases, which indicated the presence of species able to abstract hydrogen from the side chain.

The reaction with cumene gave no bicumyl but p-toluene-sulphonic acid was formed; which could indicate that p-tolyl-sulphonyloxy radicals, $TolSO_2-O\cdot$, have been produced.

The mechanism proposed to the reaction of p-toluenesulphonyl iodide with anthracene was as follows:



9-Methyl- and 9,10-dimethylanthracene reacted as follows:



The effect of light and inhibitors (hydroquinone) on the addition of p-toluenesulphonyl iodide to acrylonitrile was studied. The reaction was accelerated by light and retarded by hydroquinone and darkness.

The production of sulphinyl radicals by reaction of sulphinyl chlorides, Ar·SO·Cl with copper bronze was investigated.

No evidence for the formation of sulphinyl radicals was obtained since no reaction occurred with olefins, p-benzoquinone or anthracene. Sulphinyl radicals produced

by decomposition of 2,4-dinitrobenzenesulphenyl nitrate failed to react with p-benzoquinone.