ERRATUM: Page 73 is out of place. After p. 72 read p. 74; the paragraphs on p. 73 precede the first complete paragraph on p. 75 (i.e. should be read before "Solutions of reaction products....).

SOME STUDIES OF THE MECHANISMS OF SUBSTITUTION AND ELIMINATION REACTIONS.

A thesis submitted in part-fulfilment of the requirements of the Degree of Doctor of Philosophy in the University of Oxford by

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Pembroke College.

July, 1964.

ACKNOWLEDGEMENTS.

I am grateful to Professor Sir Ewart Jones, F.R.S. who granted permission for this work to be carried out in the Dyson Perrins Laboratory.

I am especially grateful to my supervisor, Dr. M.C. Whiting for his friendly help and encouragement.

The work was greatly assisted by the co-operation of Mr. A.E. Thompson who built and serviced the gas-liquid chromatographic apparatus.

A Research Studentship from the Department of Scientific and Industrial Research is gratefully acknowledged.

CONTENTS.

CONTENTS - PART II continued.

INTRODUCTION.

This thesis is in two parts. Part I describes attempts to separate completely by gas-liquid chromatography mixtures containing (i) the four trans-bicyclo[4,4,0]decanols and the two tertiary bicyclo[4,4,0]decanols and (ii) the six bicyclo[4,4,0]decenes. Part II describes the use of such methods for the analysis of the products of solvolytic displacement reactions of the trans-bicyclo[4,4,0]decanyl arylsulphonates and some related reactions.

Part I describes analytical methods to be used for the study of products from a variety of reactions in the system bicyclo[4,4,0]decane. This will enable the system to be compared with the systems t-butylcyclohexane[1,2], and octane[3,4]. A comparison should then be possible between conformational effects in the two "rigid" cyclohexane chair conformations and the conformations of a linear molecule.

Using analytical methods different to those described in the thesis, previous workers have studied some elimination reactions in the bicyclo[4,4,0]decanyl system[5,6,7]. Equilibrations of olefines have been studied too[8,9]. Part II describes the related acetolyses of sulphonates.

An appendix discusses the nuclear magnetic resonance spectra of some bicyclo[4,4,0]decanyl compounds.

Nomenclature.

The older names, decalins (bicyclo[4,4,0]decanes), octalins (bicyclo[4,4,0]decenes) and decalols (bicyclo[4,4,0]decanols) are only used as generic terms in certain discussions. The numbering of the bicyclo[4,4,0]decane skeleton is indicated in fig. 1. This nomenclature and numbering are in accordance with the von Baeyer system[10]. Unlike less systematic conventions, this terminology applies to all classes of compounds.

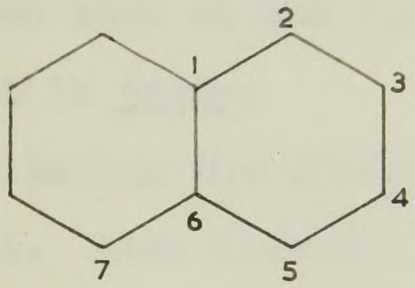


Fig. 1.

A problem arises in the description of the configuration of a substituent in the bicyclodecane skeleton. Some confusion exists in the literature because Hückel, who first succeeded in correlating the amines and alcohols in this system and in describing the stereochemistry at the ring-junction, was unable to define the stereochemistry of the substituent. He devised a system which used the Roman numerals, I and II, arbitrarily to describe the two members of each set[11]. For example, the two trans-bicyclo[4,4,0]decan-

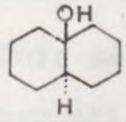
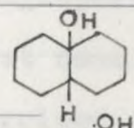
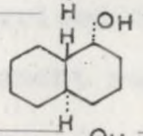
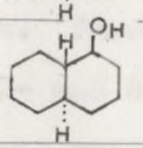
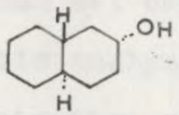
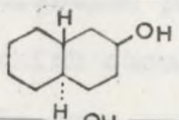
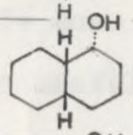
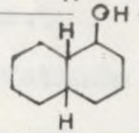
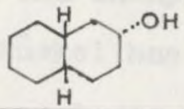
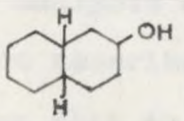
3-ols were described as trans-2-dekalol-I and trans-2-dekalol-II. Note that in all the earlier literature the positions 1, 2, 3 and 6 (fig. 1) were designated 9, 1 or α, 2 or β, and 10, respectively.

Dauben succeeded in correlating correctly the stereochemistries of a range of decalyl compounds[12]. His convention for describing their stereochemistries will be used in this thesis. The name is prefaced by a double prefix (e.g. trans-cis-). The first part refers to the stereochemistry of the ring-junction; the second part to that of the substituent. If this is on the same side of its ring as the carbon atom at the nearest ring junction it is cis. Otherwise it is trans.

To help in following the literature the conventions are summarised in table 1. Also included is the convention to be found in recent papers by Hückel[13]. This convention should be self-explanatory from the table. It should be noticed that the carbon atom 9 is the key to the convention and that it is always designated 9^c.

For the purposes of some discussions in the thesis the old uses of α and β (above) are employed.

Table 1.

	M.p (°C)	Hückel Early Work.	Hückel Recent Work.	Dauben	This Thesis
	53	-	trans-Dekalol-(9)	-	trans-Bicyclo[4,4,0]-decan-1-ol
	62	-	cis-Dekalol-(9)	-	cis-Bicyclo[4,4,0]-dean-1-ol
	49	trans-1-Dekalol-I	Dekalol 1^c 9^c 10^t	trans-cis-α-Decalol	trans-cis-Bicyclo[4,4,0]-decan-2-ol
	63	trans-1-Dekalol-II	Dekalol 1^t 9^c 10^t	trans-trans-α-Decalol	trans-trans-Bicyclo[4,4,0]-decan-2-ol
	75	trans-2-Dekalol-II	Dekalol 2^c 9^c 10^t	trans-cis-β-Decalol	trans-cis-Bicyclo[4,4,0]-decan-3-ol
	53	trans-2-Dekalol-I	Dekalol 2^t 9^c 10^t	trans-trans-β-Decalol	trans-trans-Bicyclo[4,4,0]-decan-3-ol
	93	cis-1-Dekalol-I	Dekalol 1^c 9^c 10^c	cis-cis-α-Decalol	cis-cis-Bicyclo[4,4,0]-decan-2-ol
	55	cis-1-Dekalol-II	Dekalol 1^t 9^c 10^c	cis-trans-α-Decalol	cis-trans-Bicyclo[4,4,0]-decan-2-ol
	105	cis-2-Dekalol-I	Dekalol 2^c 9^c 10^c	cis-cis-β-Decalol	cis-cis-Bicyclo[4,4,0]-decan-3-ol
	18	cis-2-Dekalol-II	Dekalol 2^t 9^c 10^c	cis-trans-β-Decalol	cis-trans-Bicyclo[4,4,0]-decan-3-ol

Nomenclature of Decalols.

PART I.

THE ANALYTICAL METHODS.

Introduction.

This section describes the devising of gas-liquid chromatographic analyses of two sets of compounds. The first set consists of those decalols reasonably to be expected to be derived from the substitution products of solvolytic displacement reactions of compounds with the trans-decalin skeleton. These decalols are the four trans-bicyclo[4,4,0]-decan- 2- and 3- ols, and the two bicyclo[4,4,0]decan-1-ols. The second set consists of the six octalins. Although such a complete analysis should not be necessary for analysing the elimination products of the type of reaction mentioned above, which should only give rise to trans-bicyclo[4,4,0]dec-2- and 3- enes and bicyclo[4,4,0]dec- 1,2- and 1,6- enes, it would be useful for a study of the equilibrations of the octalins.

Methods of performing the reactions and of working them up and analysing the two sets of products are described.

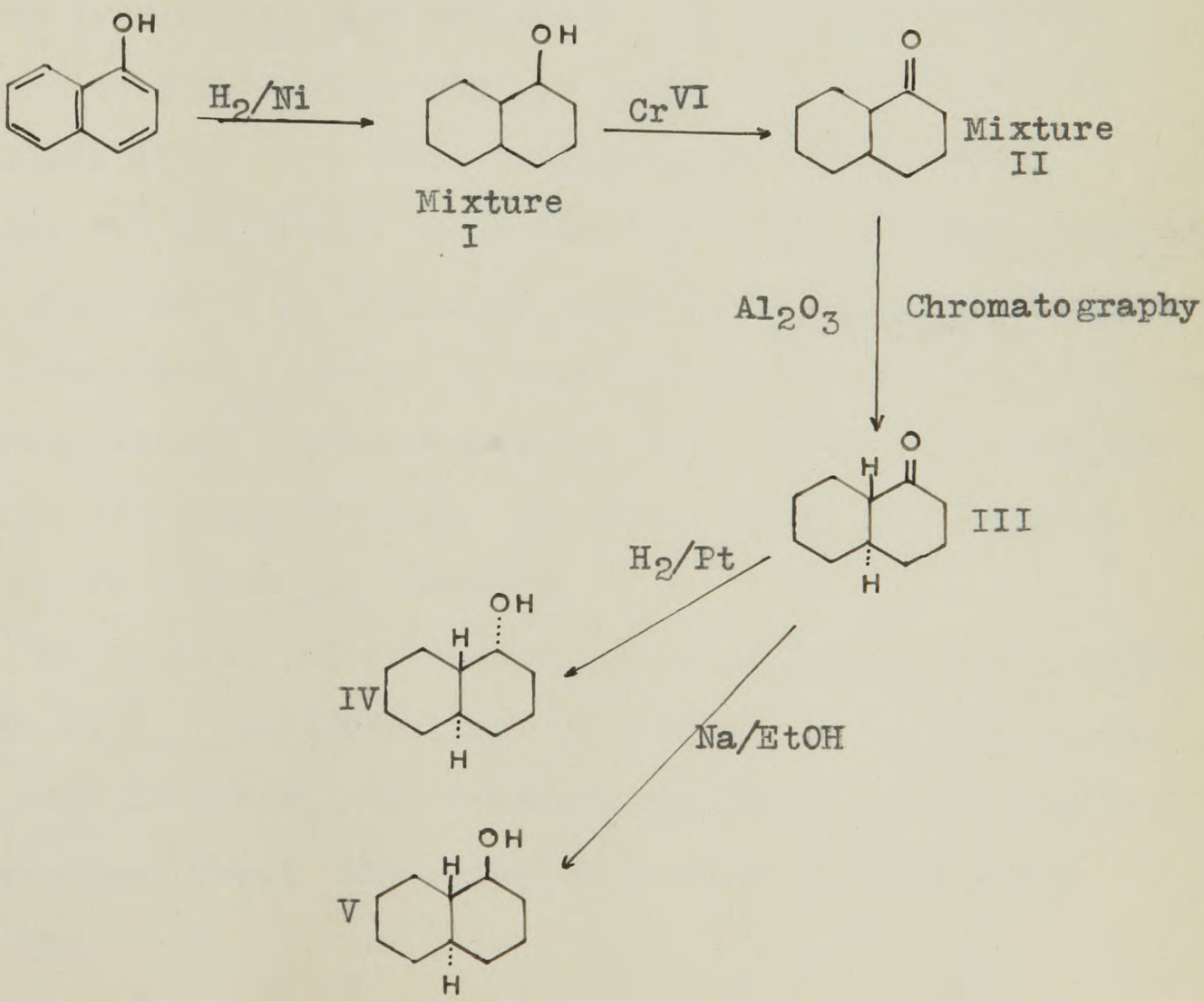
Hückel has described the partial gas-liquid chromatographic analysis of decalols using as stationary phase a substance described as "K+K"[14]. Insufficient details are given for this to form the basis of any further investigation of the problem. Hückel has also attempted the analysis of the

octalins using as stationary phase a mixture of silicone oil and "Carbowax", a polymer of ethylene oxide[15]. The relative quantities of these two substances are not mentioned. The column temperature (160°) was high in order to analyse other constituents on the same column; this must have made separation of C_{10} olefins very difficult. Powell and Whiting[16] and Oberhänsli[17] have made considerable progress with this problem. Their results are summarised and discussed on p.26.

Preparations of Secondary Decalols.

The two trans-bicyclo[4,4,0]decan-3-ols were obtained by the alumina chromatography of commercial "decahydro-β-naphthol". The trans-trans isomer is eluted first, followed by cis material. The trans-cis isomer is eluted last.

The two trans-bicyclo[4,4,0]decan-2-ols were obtained by the sequence following. The author did not prepare the trans-cis isomer as a sample prepared previously by Dr. R.G. Smith was available.



Following Powell's experience the naphthol was purified of catalyst poisons[7]. W-7 Raney Nickel[18] was used as catalyst and the hydrogenation was performed at 150° and ca. 100 atmospheres. Powell converted the mixture II to III by isomerisation with alkali. The present author's experience was that II consisted largely of III. The pure isomer was obtained by alumina chromatography. The epimers IV and V must be freed of traces of each other by alumina chromatography.

Bicyclo[4,4,0]decan-1-ols.

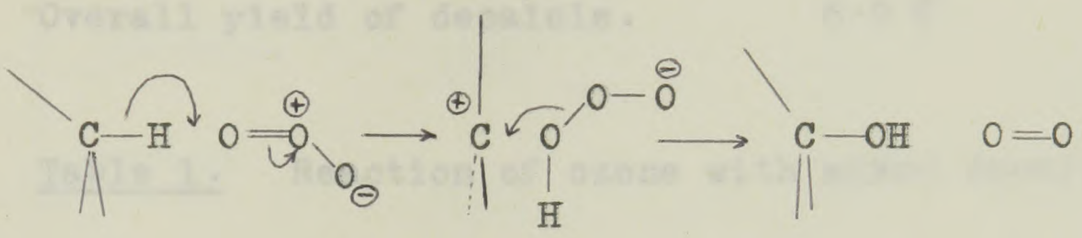
Durland and Adkins described the preparation of the two tertiary decalols by the oxidation of the corresponding decalins with ozone[19]. Hückel obtained the cis isomer in this way from a mixture of the decalins[20]. The present author obtained both alcohols from the reaction of ozone with mixed decalins. The alcohols were separated by alumina chromatography.

Details of the results of this preparative experiment are given in table 1, p. 9A. The reaction of ozone with the separate isomers was also examined. The product-analysis (by gas-liquid chromatography) is given in table 2, p. 9A. No decalols other than those mentioned in table 2 were detected. An additional oxidation with ozone of trans-decalin in the presence of an equimolar quantity of trans-cis-bicyclo-[4,4,0]decan-3-ol resulted in a greatly increased amount of trans-bicyclo[4,4,0]decan-3-one but the product contained no unchanged secondary decalol. It seems likely that ketones in table 2 were formed via decalols.

The results can be summarised as follows. Ozone reacts with decalin in all three types of position; the cis isomer is the more reactive; the tertiary position is more reactive than secondary ones; the reaction involves almost total retention.

The conventional interpretation of these oxidations is

that the process is a free radical one[21]. Certainly the medium (solution in carbon tetrachloride) is very non-polar. An alternative which would explain the retention of configuration more readily is that the reaction goes through an ion-pair which collapses.



The bridgehead hydrogens are more accessible in cis-decalin (they are equatorial to one ring, axial to the other) than in trans-decalin (they are axial to both rings).

A similar mechanism has been propounded for the oxidation of decalin by hydrogen peroxide in strongly acidic solutions[22]. The relative rates for the oxidations of the decalins and other pairs of alkanes are compared with Roček's figures for oxidation with chromium trioxide[23]. From this comparison Alder[22] deduces that the attack is primarily in the tertiary position and he compares the steric requirements of the two nucleophiles. The situation is rather complicated however; Roček's ionic mechanism for the oxidations with chromium trioxide has been disputed[24].

Proportions of decalins in starting material.	43·5 % trans	56·5 % cis
Proportions of isomers in recovered decalin.	86·8 % trans	13·2 % cis
Proportions of isomers in tertiary decalols.	16·1 % trans	83·9 % cis
Overall yield of decalols.	6·9 %	

Table 1. Reaction of ozone with mixed decalins.

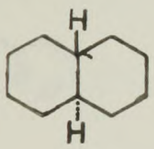
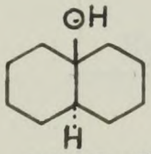
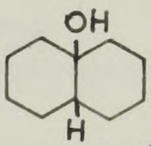
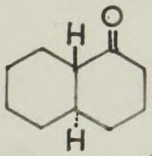
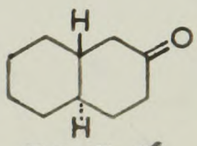
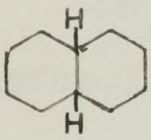
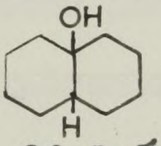
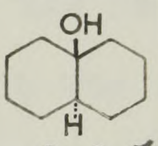
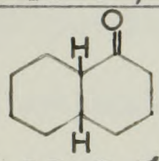
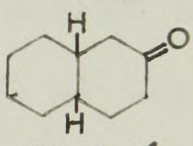
Starting Material	Alcohols		Ketones		A	B
	 98·2 %	 1·8 %	 43·5 %	 56·5 %	1·65	13
	 96·1 %	 3·9 %	 13·2 %	 86·8 %	2·5	20

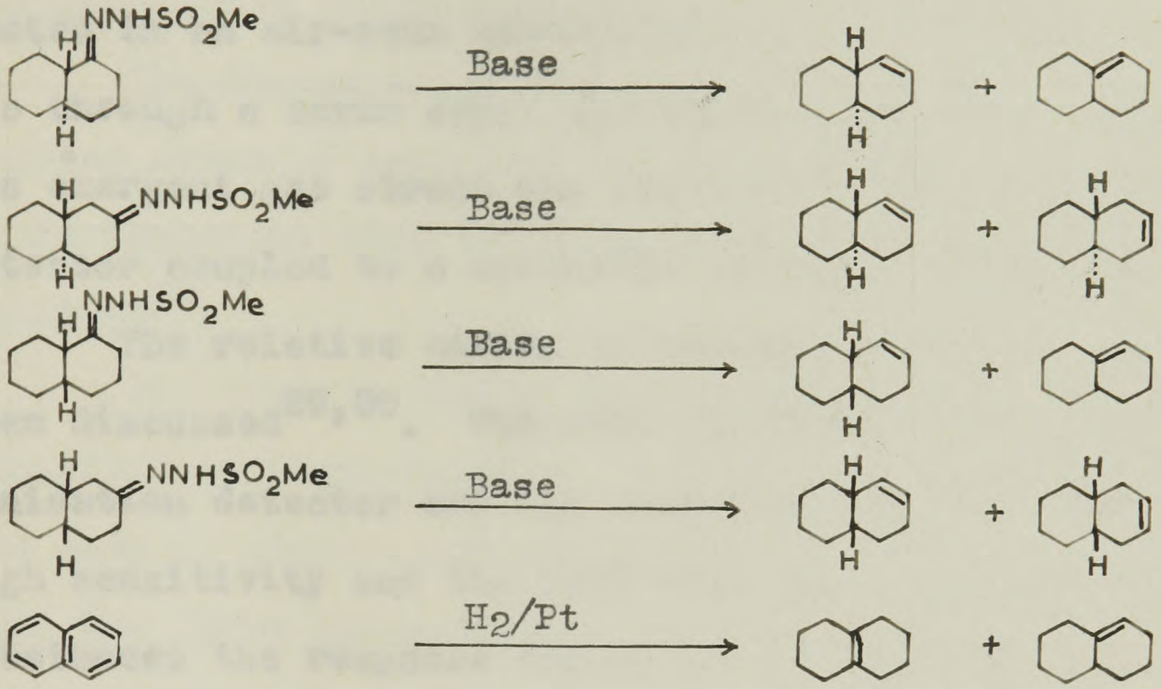
Table 2. Reaction of ozone with decalins.

A = ratio of alcohols/ketones.

B = ratio of attack (tertiary centres/secondary centres).

Preparation of Octalins.

The octalins required for gas-liquid chromatography were obtained as binary mixtures from the materials summarised below.



The base used for the decompositions of the methanesulphonylhydrazones was a solution of the sodium salt of acetamide in molten acetamide. The use of amides rather than glycols for this reaction (Bamford and Stevens' reaction) is due to Powell and Whiting[25]. It gives unrearranged products[7].

The olefines prepared from naphthalene were kindly supplied by Dr. P. Oberhänsli. More recently a method of preparing pure bicyclo[4,4,0]dec-1,6-ene from this mixture has been described[26].

Apparatus and General Technique.

The apparatus used for gas-liquid chromatography was built in this department and has been described in detail elsewhere[27]. The columns were coiled copper tubes and were heated in an air-oven controlled by a thermostat. Injection was through a serum cap. The carrier gas was nitrogen and the emergent gas stream was fed into a flame ionisation detector coupled to a specially designed amplifier[28].

The relative merits of various detection systems have been discussed[29,30]. The main virtues of the flame ionisation detector are its sturdy and simple lay-out, its high sensitivity and the fact that for injections of different substances the response varies in a moderately predictable way. Isomers give roughly equivalent responses. This "linearity" of the detector to different sample types has been extensively discussed[31,32]. The two most fruitful approaches have been to examine the linearity of response as a valve analogy[33], and from an examination of the mechanism of combustion. The current which causes the measured signal appears to be carried by particles which are formed by the re-polymerisation of cracked fragments of organic molecules[34,35,36]. Detector response is not necessarily linear for a mixture of isomers although Ettre claims ~~that~~ the assumption that it is safe for compounds higher than C_7[37].

TO BE

A test for linearity with a mixture of decalols showed a variation of the same order as the experimental error in the measurement of the peaks. The same test was not possible with the octalins because binary mixtures were used for gas-liquid chromatography.

The linearity of this type of detector for different samples sizes of the same substance is well established[31,32,33]. It is important that the flow-rate of the combustion gas is constant[38].

The general design of the detector is similar to that described by Ongkiehong[38]. A difference is that our gauzes are made of copper, not platinum. The gauze is mounted so that the flame burns through it and the insulator carrying the probe to the amplifier is mounted below the burner. These modifications are designed to reduce noise due to the sooting-up of the gauze and probe. Ongkiehong channels the air round the flame with a cone[38]. We force it through a sintered steel disc recommended by Desty[39]. The alternative method of using a bed of stone granules (mentioned by Clarke[27]) has been abandoned. Another modification since Dr. Clarke's account is that electrical noise picked up by the co-axial cable which connects the amplifier to the probe has been effectively reduced by incorporating an appropriate capacitance in parallel with the earthed screening round the cable. The time constant of the cable is thus increased.

In all cases the mixture to be analysed was dissolved in an appropriate solvent and these solutions were injected on to the column by the established method with a small hypodermic syringe and a serum cap[40]. Bayer claims that provided the tip of the needle reaches the top of the column-packing no pre-heating of the sample is required[41]. The author found that this was true for the octalins but that broad, ill-resolved peaks result from such injections of mixtures of the less volatile decalols unless the column is at a temperature of at least 140°. Inlet heating was therefore required because the analyses of the decalols were performed at temperatures less than this (p.23A). Pre-heating of samples for gas-liquid chromatography has been used for some time[42]. Our apparatus was originally fitted with bulky electric inlet heaters. When mixtures of decalols were injected through such heaters spurious peaks were obtained at short retention times and the decalol peaks were not quantitative. It was deduced that the decalols were partly dehydrated by the hot metal surface. These old heaters were replaced with gas-heated devices with a small dead space. A small jet played on to a copper tube which was lined with a narrow bore glass tube. The temperature in the small tube is ca. 150°. Such heaters give quantitative results with decalols and give with octalins peaks which are marginally sharper than those obtained without inlet heaters.

Measurement of Peaks.

For accurate work the ratios of the quantities of analysed substances were measured as the areas of the corresponding peaks with a planimeter. Janák finds that the use of a planimeter is less accurate than geometric construction methods[43]. However claims for accuracy in the use of the planimeter in this laboratory exceed those of Janák[44]. In some recent work areas have been measured on an integrating recorder. Details are given on p. 92.

The more approximate method involving use of the product (peak height x retention time) was employed for less accurate work. The occasions are indicated in the Experimental Section. Considerable claims have been made for the accuracy of the method[45].

Behaviour of Columns - General.

The position of a peak in chromatogram will be referred to by its "retention time", t_R, the time which elapsed between injection and the elution of the peak's maximum.

In order to identify a peak on a column of a given stationary phase by a number independant of column length, nature of carrier gas, flow rate and minor temperature fluctuations, the function "relative retention time", $t_{rel.}$, is used.

$t_{rel.} = t_R/t_s$, where t_s is the value of t_R for a standard substance.

Although various attempts have been made to choose universal standards, or to represent retention times by a universally applicable function of some kind[46], the relative retention times of peaks on those columns primarily designed for the analysis of mixtures of decalols are referred to octan-1-ol; those of peaks on columns primarily designed for the analysis of mixtures of octalins are referred to trans-bicyclo[4,4,0]decane. The same substances are used in the author's modification of the use of internal standards described by Ray[47] (see p. 25).

The "number of theoretical plates" or the "platage", N, of a gas-liquid chromatography column is the number of

hypothetical equilibrations undergone by the solute along the column. The concept derives from the view of the chromatographic process as being a complete equilibration of solute between liquid and vapour phases, followed by complete removal of the vapour and re-equilibration of its "solute component" with fresh liquid. The solute remaining in solution is re-equilibrated with fresh gas. N is the number of such processes. In this thesis theoretical platage invariably refers to N' (equation 1 and fig. 1).

$$N' = 16t_R^2/x^2 \qquad \ldots\ldots\ldots\ldots \quad 1$$

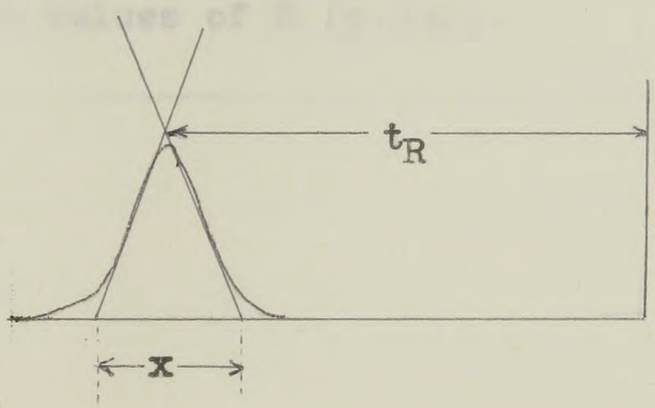


Fig. 1.

In fact $N = N'$ only in the limiting case of the injection of an infinitely small amount of a substance with an ideal solution isotherm[48].

The "height equivalent per theoretical plate" or "HETP", H, is obtained by dividing the length of the column by the number of plates.

For any two peaks the "resolution", R, is a figure such that the maxima are separated by 4R standard deviations[49].

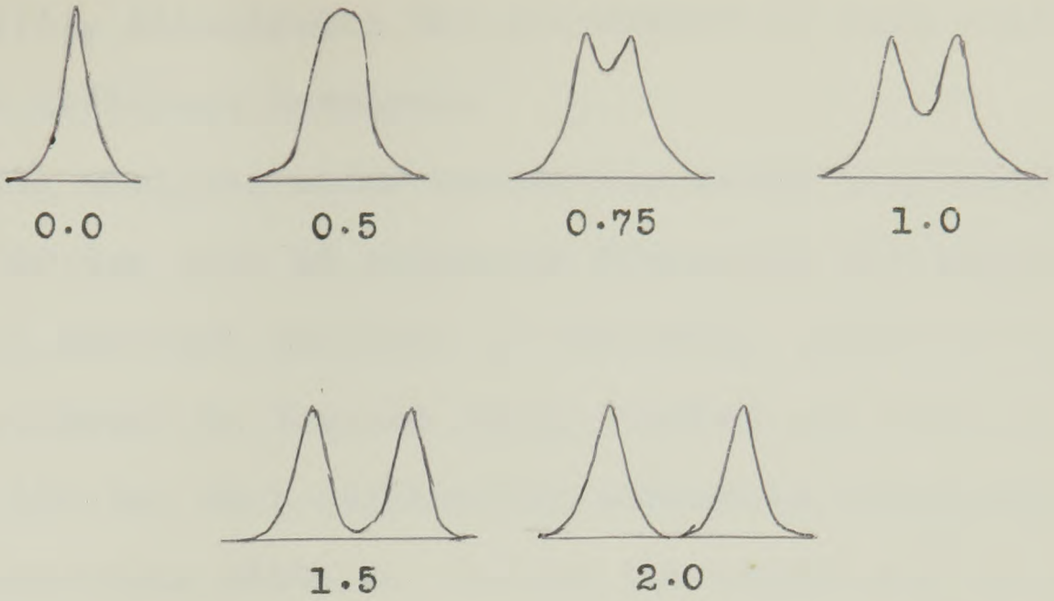


Fig. 2. General appearance of two peaks of equal size with different resolutions. The figures are values of R (p.16).

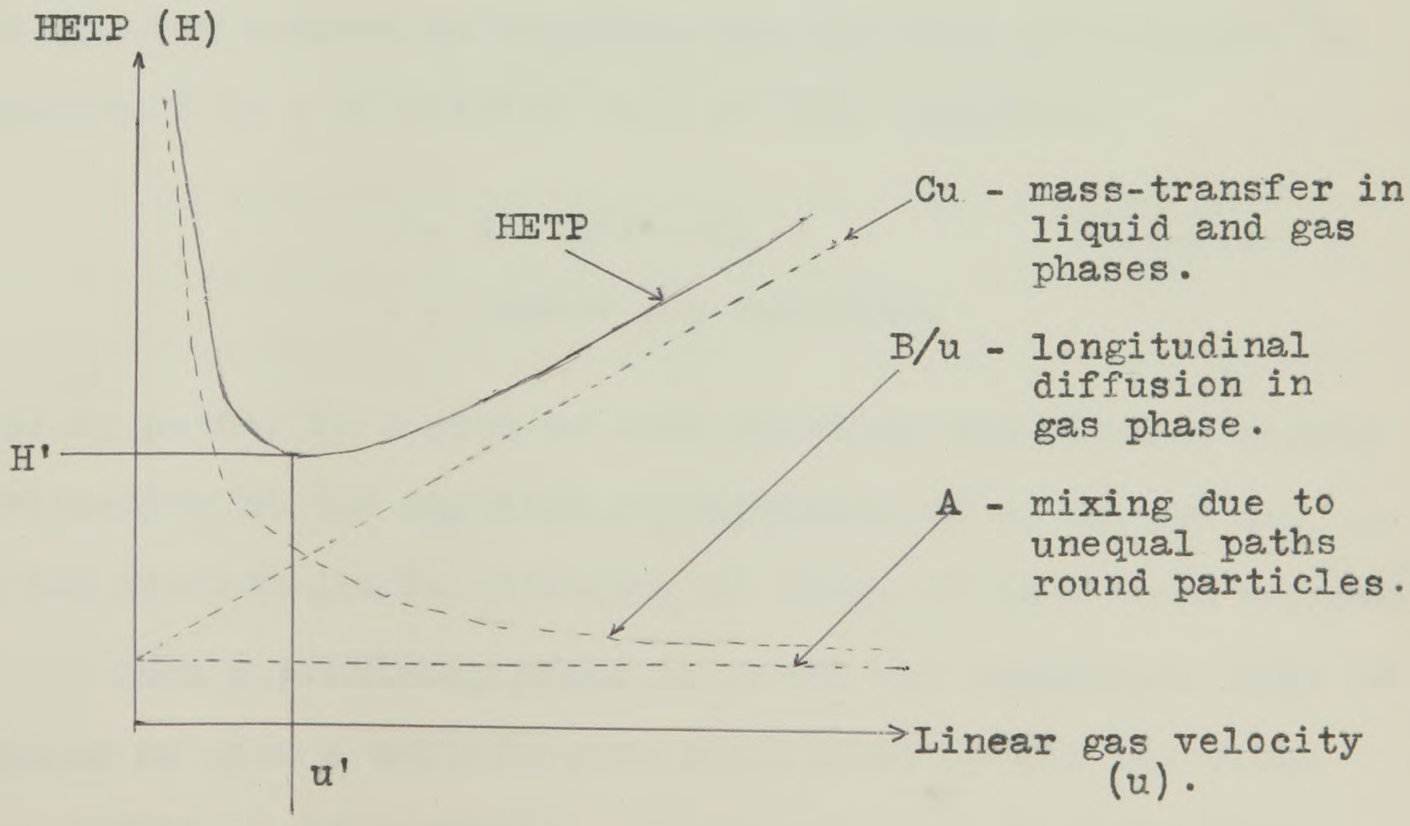


Fig. 3. Graphical representation of equation 2 (p.17).

Fig. 2, p.16A, illustrates the appearance of some pairs of peaks with different R-values.

Total analyses under reasonably rapid conditions were required for two sets of compounds (decalols and octalins). The general approach consists of measuring values of $t_{rel.}$ for each compound in the set being studied and then of injecting the two most difficultly separable components as a roughly equi-molar mixture. Unless the components of such a mixture at least begin to separate (R = 0.5; fig. 2, p.16A) on a 2 m. column in which the stationary phase constitutes 15% of the packing material, operated at a flow rate of u' (fig. 3, p.16A) at the given temperature, then satisfactory separation at that temperature would take too long.

From a "rate theory" of gas-liquid chromatography[50], van Deemter deduced an equation for the HETP of a column[51]. Equation 2 is a simplified form of this equation.

$$H = A + B/u + Cu \qquad \ldots\ldots\ldots 2$$

u = linear gas velocity.

Fig. 3, p.16A, is a plot of this equation and gives a simple explanation of the physical significance of A, B, and C. If the carrier gas is nitrogen, u' (fig. 3) is 3 to 6 cm./sec.[52]

Once a promising phase is found the conditions must be altered to give a satisfactory resolution of the two peaks most difficult to separate. The meaning of "satisfactory

resolution" depends on the nature of the analysis. The most exacting requirement is that two adjacent components should be present in very different amounts when large attenuation ratios are required. A resolution of R = 1.0 is required in every case.

The number of theoretical plates increases with column length. The exact relationship depends on the variation of inlet pressure and hence of rate of gas-flow. The number of plates required for a given resolution, R_{12}, between two components, 1 and 2, is given by equation 3[53].

$$N = [4(1 + 1/k).R_{12}/(\alpha_1/\alpha_2 - 1)]^2 \quad \ldots\ldots\ldots \quad 3$$

where $k = \frac{\text{Quantity of vapour in solution in the liquid}}{\text{Quantity of vapour in gas-phase}}$

and $\alpha = \frac{\text{Concentration of vapour in the liquid}}{\text{Concentration of vapour in gas-phase}}$

From equation 3 we see that for a low platage requirement for a given phase, k should be large; i.e. the stationary phase should be a good solvent for the components of the mixture and the phase should form a high proportion of the composition of the packing material. A limitation is that both techniques lead to increased values of t_R. These points are exemplified by the comparison of the cyanoethyl phases (table 8, p.27D; table 9, p.28B).

Choice of Stationary Phase.

With conventional, packed columns the platage which can be achieved is limited by the need for reasonable retention times. A "selective" phase is required. An unselective or "boiling point" phase is one in which the retention time is related to the boiling point, T_b, by an equation such as 4.

$$\ln t_R = x.T_b + y \qquad \ldots\ldots\ldots 4$$

where x and y are constants.

It is important to remember that deviation from the equation represents a deviation from ideal partition isotherms in the chromatographic process. The most important factor which leads to these deviations is the interaction of permanent dipoles in the solute and in the phase. Dispersion forces and induced dipoles are also important. Purnell has estimated the order of magnitude of these effects in certain cases[54]. As dispersion forces can account for ca. 90% of the deviation, variations in the chemical nature of the phase will not necessarily have a large predictable effect.

Bayer has described selectivity in terms of the difference between retention times of members of different homologous series corrected to the same boiling point. Another classification regards phases as being non-polar (or unselective), donor or acceptor. A "donor phase" is rich in electrons, an "acceptor phase" is deficient in electrons.

Both methods of classification have been described quantitatively[55,56] but they are only discussed qualitatively in this thesis.

Gas-liquid Chromatography of the tertiary and trans- Decalols.

The first attempt at a complete analysis of these alcohols was on polyethylene oxide, which has been successfully used as stationary phase in previous separations of alcohols[57]. Previous work in this laboratory[27,58] had suggested that a sample of this polymer designated "CEO-100" was very suitable. CEO is a crystalline polymer with a sharp melting point. Columns with stationary phases which are solid at room temperature are probably more closely packed and give lower values of H (p.16) than ones with stationary phases liquid at room temperature. CEO is supposed to have glyceryl end groups, i.e. to have the structure following.

$$\begin{array}{l} CH_2\text{-}(O\text{-}CH_2CH_2)_x\text{-}OH \\ | \\ CH\text{-}(O\text{-}CH_2CH_2)_y\text{-}OH \\ | \\ CH_2\text{-}(O\text{-}CH_2CH_2)_z\text{-}OH \end{array}$$

Complete separation of these decalols on CEO is possible but results in a chromatogram which takes almost six hours (see fig. 4, p.21A). As can be seen from the figure the peaks "slope backwards". Although a recent mathematical analysis of the shapes of peaks implies that this type of chromatogram is to be expected[59], it is less accurately measured in the partly resolved regions.

In an attempt to find a faster method of analysis a phase was sought which would resolve trans-trans-bicyclo[4,4,0]-

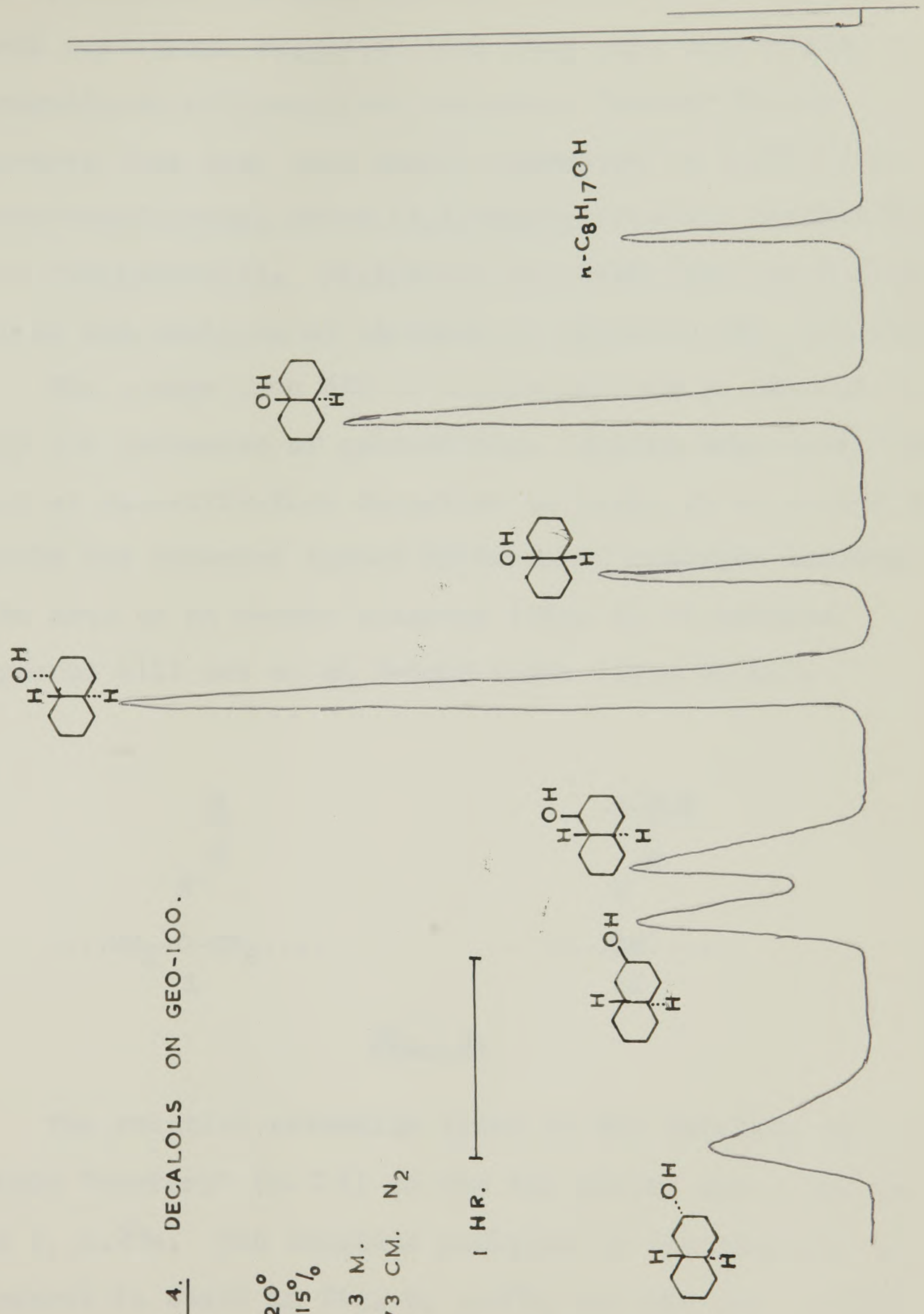


FIG. 4. DECALOLS ON GEO-100.

decan- 2- and 3- ols more easily. Experiments employing various conditions suggested that they were completely inseparable on polypropylene adipate. However it was discovered that they were easily separated on 2,2',3,3'-tetrahydroxydipropyl ether (1,1'-oxydiglycerol, hereinafter called "diglycerol"). Diglycerol has been used as stationary phase in the analysis of mixtures of alcohols for some time[60].

The change from GEO to diglycerol was an attempt to modify the mechanism of selectivity. Rather than using the method of classification described on p.19, it is easier to describe the intended change in terms of hydrogen bonding. If GEO acts as an H-bond acceptor (fig. 5, i) perhaps diglycerol will act as an H-bond donor (fig. 5, ii).

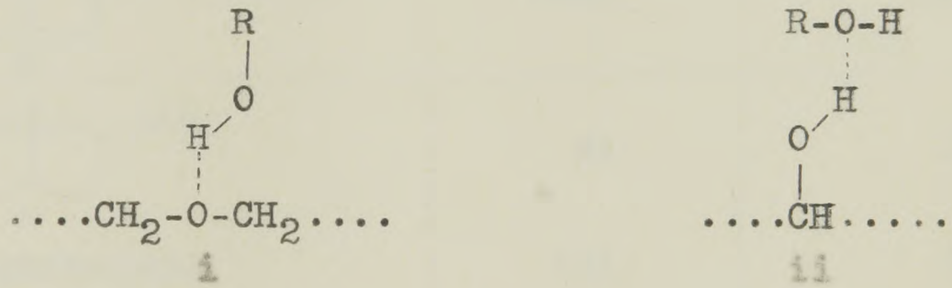
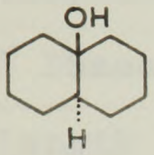
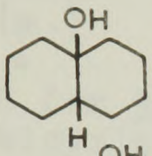
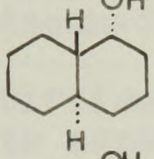
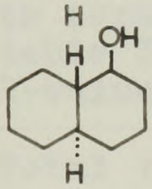
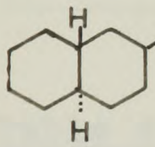
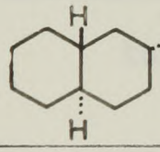
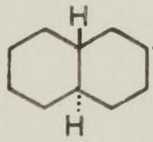


Fig. 5.

The relative retention times of the decalols and possible "markers" (p.24) on the two phases are given in table 3, p.23A. The complete analysis of the decalols on diglycerol is shown in fig. 6, p.23C, and the two methods are compared in table 4, p.23B.

From table 4 we see that diglycerol is the more satisfactory phase although it gives higher HETP's. GEO has been regarded as a possible alternative which could be used if it was suspected that an unknown product was contributing to a peak on a diglycerol chromatogram.

Diglycerol columns have a limited lifetime and it is wise to replace them after 20 to 30 hours of running time.

Phase Temperature	GEO-100 120°	Diglycerol 100°
$n\text{-}C_8H_{17}OH$	100	100
	175	135
	292	342
 1	258	316
	422	520
 2	445	482
	523	773
	91	36
Naphthalene	231	85
2-Methylnaphthalene	382	-
p-Dichlorobenzene	74	-
$Me[O(CH_2)_2]_2O\text{-}Me$	-	65
$Me[O(CH_2)_2]_3O\text{-}Me$	-	525

Relative retention times of decalols etc.

Table 3.

Phase	GE0-100	Diglycerol
Temperature	120°	100°
% Phase	15	15
Length of column (m.)	3	4
H for trans-cis-bicyclo[4,4,0]-decan-3-ol (mm.)	0·7	1·0
Difficult pair(s) to separate (see table 3): approx. R-values.	(2) 1·0	(1) 1·0 (2) 1·2
Total time (hr.)	5·8	3·5

Table 4. A comparison of the two methods for the total analysis of the tertiary and trans decalols.

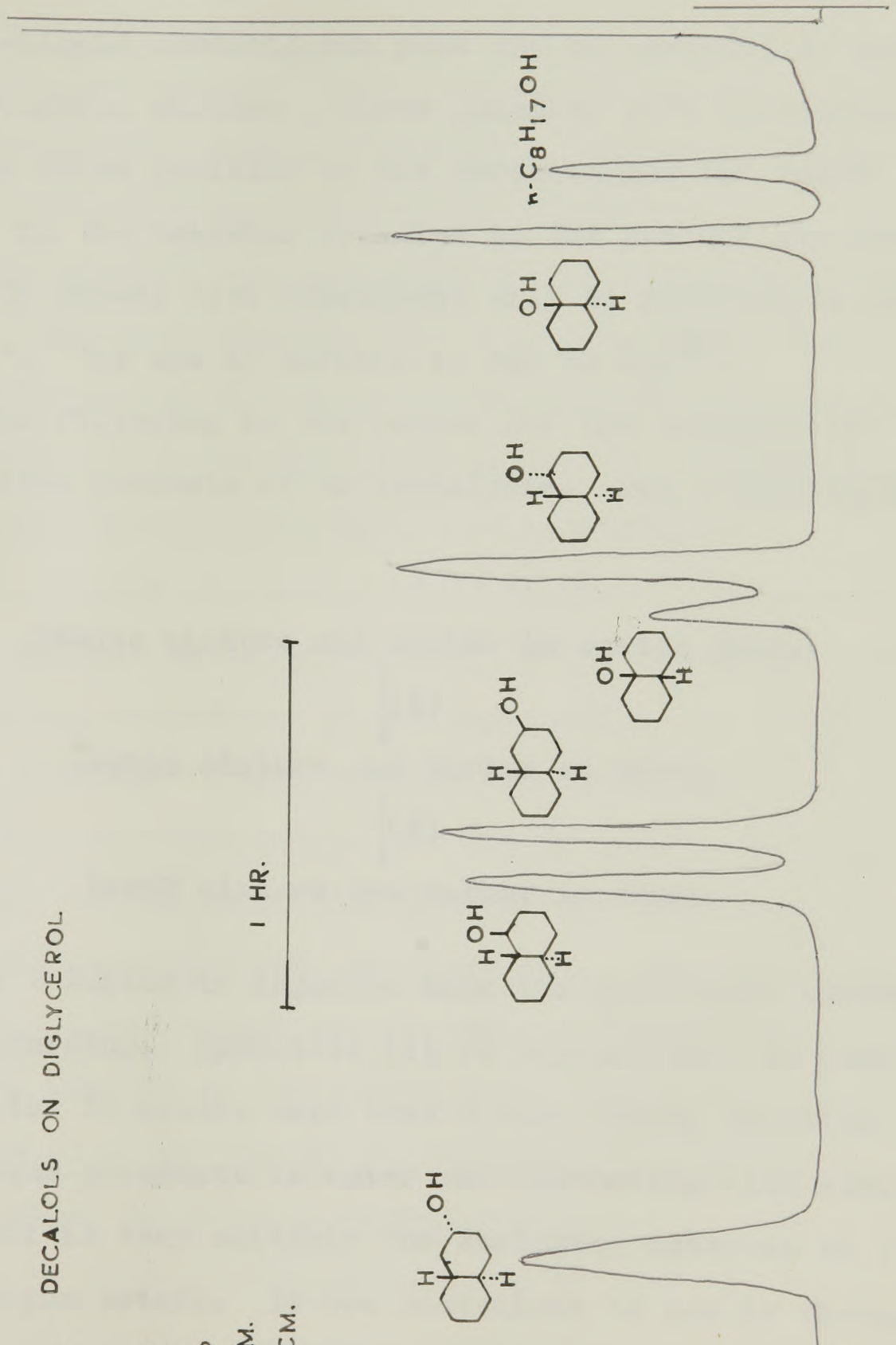


FIG. 6. DECALOLS ON DIGLYCEROL

The Analysis of the Substitution Products from the Reactions.

The absolute yield of a reaction product identified as a gas-liquid chromatogram peak can be assessed by including in the reaction mixture a known quantity of a non-participating substance whose position on the chromatogram and whose response in the detector relative to the product are both known. In future such substances will be referred to as "markers". The use of markers is due to Ray[47].

The following is the scheme for the analysis of substitution products of an acetolysis. Dec = bicyclo[4,4,0]-decanyl.

DecOAc mixture and marker in acetic acid.

↓ (1)

DecOAc mixture and marker in ether

↓ (2)

DecOH mixture and marker in ether.

The final solution is injected into the gas-liquid chromatography apparatus. Operation (1) is accomplished by pouring the solution in acetic acid into a very strong solution of tripotassium phosphate in water and extracting with ether. This alkali is very suitable for isolating acetates as it does not hydrolyse esters. It was convenient to use it throughout. Operation (2) is accomplished with lithium aluminium hydride. Details are given in the Experimental Section (p.95) but it

may be stated here that the addition of the hydride (in ethereal solution) and the destroying of excess must be performed in the absence of air and/or base. If such precautions are omitted axial isomers are partly converted to their equatorial epimers. Possibly a Ponndorf-Oppenauer equilibrium is set up with a trace of ketone.

The reaction was performed in the presence of two markers. The first marker to be eluted was used to adjust the setting of the attenuator on the recorder so that the sizes of the peaks corresponding to the second marker and the decalols would be guaranteed to be on-scale.

The choice of markers was made from those given in table 3, p.23A. There is a danger of the sulphonates reacting with aromatic compounds. p-Dichlorobenzene was chosen as a possible solution to this problem but it was not used on the grounds that it might damage the copper gauze. The acyclic ethers were abandoned on the grounds that they might not be transferred quantitatively in stage (1). This left trans-cis-bicyclo[4,4,0]decan-3-yl methyl ether as first marker and octan-1-yl acetate as the second one. The second marker is hydrolysed in stage (2) and is analysed as octan-1-ol.

A blank experiment established that the markers are unchanged by heating with acetic acid to 100° for 14 hr. Less than 0.1% of decalyl compounds (other than the ether) are formed.

Gas-Liquid Chromatography of the Octalins.

The following abbreviations for the names of octalins are used in tables and figures throughout this section.

trans-bicyclo[4,4,0]decane	tD
cis-bicyclo[4,4,0]decane	cD
trans-bicyclo[4,4,0]dec-2-ene	tα
trans-bicyclo[4,4,0]dec-3-ene	tβ
cis-bicyclo[4,4,0]dec-2-ene	cα
cis-bicyclo[4,4,0]dec-3-ene	cα
bicyclo[4,4,0]dec-1,2-ene	1,2
bicyclo[4,4,0]dec-1,6-ene	1,6

The relative retention times of octalins on a variety of columns were measured by Powell and Whiting and by Oberhänsli[16,17]. These results are summarised in table 5, p.26A. The outstanding problem is seen to be the separation of cα and 1,2 on a column which resolves the two trans-octalins satisfactorily. The "silver solumns" are alleged to give poor resolution generally[17]. The column Z2 (table 5) was abandoned because the methyl ester was eventually hydrolysed to 3,5-dinitrobenzoic acid, which isomerises olefines[17]. Nevertheless the nitro-eutectics are the most promising phases.

The operating conditions for some new phases were optimised by injecting a mixture of two easily separated octalins (1,2 and 1,6) into short columns (2 m., 15%). Some

S.P.	L	L	S	DNP	BDP	TCP	Ag^a	Ag^b	Ag^c	E1	E2	E3
T°C	120	65	100	100	90	100	40	50	55	40	85	90
tD	100	100	100	100	100	100	100	100	100	100	100	100
cD	125	139	130	130	144	144	155	-	-	159	145	-
tα	105	106	102	110	132	133	155	-	-	229	190	-
tβ	111	117	107	110	137	140	177	1175	1092	273	210	176
cα	120	129	119	127	160	159	210	1101	1094	280	212	188
cβ	125	140	126	136	179	178	235	1259	1211	336	245	197
1,2	117	129	119	127	161	157	200	518	556	246	186	163
1,6	124	148	135	145	192	182	240	256	294	225	165	136
Ref.	16	17	16	16	16	16	16	17	17	17	17	17

Table 5. Previous attempts at the separation of the octalins.

L = Apiezon-L hydrocarbon vacuum grease; S = squalane;

DNP = dinonyl phthallate; BDP = benzyl diphenyl (mixture);

TCP = tricresyl phosphate;

Ag^a = silver nitrate dissolved in polyethylene glycol;

Ag^b = silver nitrate dissolved in dipropylene glycol;

Ag^c = silver nitrate dissolved in dipropylene glycol and tetrahydrothiophen-1,1-dioxide;

E1 = ternary eutectic of 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene and m-dinitrobenzene;

E2 = ternary eutectic of 1,3,5-trinitrobenzene, 3,5-dinitrobenzonitrile and methyl 3,5-dinitrobenzoate;

E3 = ternary eutectic of 1,3,5-trinitrobenzene, 3,5-dinitrobenzonitrile and 1,3,7-trinitrofluorenone.

of the results for important phases are summarised in table 6, p.27A. In this survey GPO-C (a liquid similar to GEO, p. 21, but with groups $-CH(CH_3)CH_2-$ in place of $-CH_2CH_2-$) was rejected as it did not separate these two isomers. A silicone oil (MS 704), supposed to contain phenyl groups, retained decalins and octalins very strongly and was operated at 150°.

The relative retention times of various new phases are summarised on table 7, p.27B.

Tetrahydrothiophen-1,1-dioxide ("sulpholane") separates octenes quite well[27] and 2,5-dimethylsulpholane has been used for C_2 - C_5 olefines[61]. 3-Ethoxycarbonylsulpholane is chemically similar but has a higher working-temperature. Although it is not satisfactory for the complete analysis of the octalins it may be a useful phase for the analysis of mixtures of other olefines with higher boiling points.

Following Knight's analysis of the hexenes[62], β,β'-oxydipropionitrile was examined. From table 7, p.27B, it is seen that the phase offers little hope of a total analysis. The remaining columns mentioned in the table show the effect of modifying this phase, either by introducing an aliphatic chain into the molecule, or by dissolving a silver salt in it, or both. The trends are summarised in fig. 7, p.27C, in terms of $\log_{10} t_{rel.}$

Silver salts have been used previously to modify the selectivity of cyanide phases[63,64]. From the present results

Phase	Temp. °C	Pressure cm.	t_R's (min.)		N (1,6)	R (approx.)
			1,2	1,6		
SE	80	20	46	54		1·2
	90	18·5	33	38		1·2
	100	20·5	25·5	29	2080	1·0
	100	72	7	8		1·0
ODP	40	18	64·5	74·5	1730	1·5
	40	30	42·4	49	1320	1·2
CEE	42	22·5	43	50	1240	1·2
	42	47	20·5	24	695	1·0
	42	63	15	17·5	420	0·9
	50	70	10	11		0·7
	55	20·5	18	21	626	0·8

Table 6. The results of injecting a mixture of (1,2) and (1,6) into 15 %, 2 m. columns under various conditions.

SE = sulpholane ester, i.e. 3-ethoxycarbonyl-tetrahydrothiophen-1,1-dioxide;

ODP = β,β'-oxydipropionitrile;

CEE = 1,2-bis(2'-cyanoethoxy)ethane.

S.P.	MS 704	SE	ODP	Ag ODP 10%	CEE	Ag CEE 1%	Ag CEE 1%	CEPr	CEPe
T°C	150	100	40	40	50	50	50	50	50
tD	100	100	100	100	100	100	100	100	100
cD	140	139	152	155	160	159	161	158	158
tα	119	183	216	314	211	216	240	193	184
tβ	123	195	236	383	230	232	255	211	201
cα	139	220	276	300	268	273	285	246	234
cβ	149	263	324	382	312	316	334	285	270
1,2	140	220	250	343	254	255	264	234	220
1,6	163	257	273	301	288	292	290	272	258

Relative retention times of decalins and octalins.

Table 7.

SE, ODP and CEE - see table 6, p.27A.

CEPr = 1,3-bis(2'-cyanoethoxy)propane;

CEPe = 1,5-bis(2'-cyanoethoxy)pentane;

Ag/ODP/10% = 10 % (w/w) solution of $AgNO_3$ in ODP, likewise Ag/CEE/1% etc.

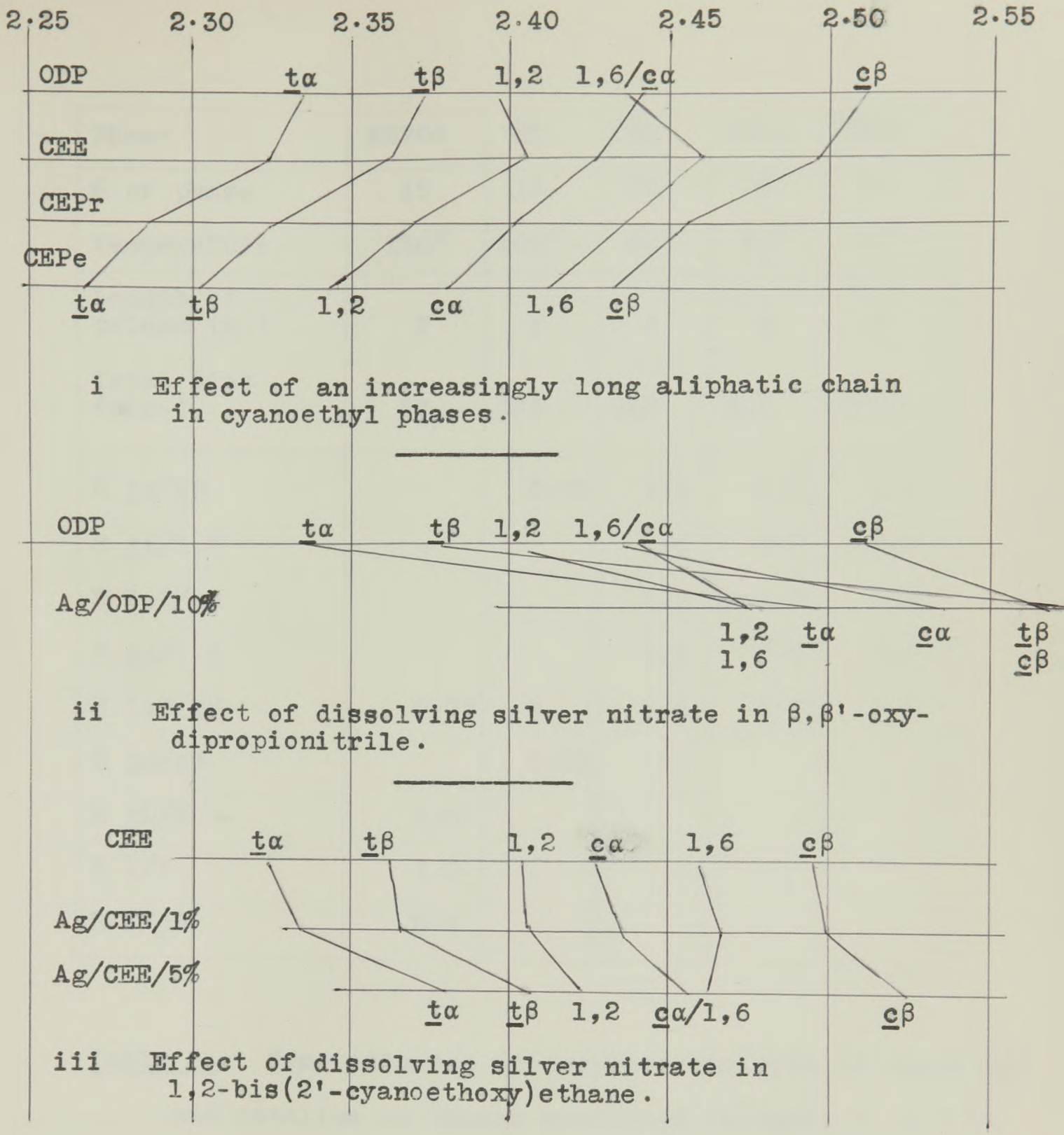


Fig. 7. See p.27 for explanation.

Vertical lines are values of $\log_{10} t_{rel.}$ 1 As usual, $t_{rel.}$(tD) = 100. The abbreviations for the phases are as in tables 6 and 7, pp.27A and 27B.

Phase	MS704	SE	CEE	CEPr	CEPe
% of phase	15	15	15	15	15
Temperature	150°	100°	50°	50°	50°
Length of column (m.)	2	6	6	4	4
Total time (min.)	57	135	240	300	360
R tα/tβ		0·75	1·4	1·2	1.2
R tβ/1,2			1·4	3·0	2·0
R 1,2/cα			1·2	1·2	0·9
R cα/1,6			1·4	3·0	2·0
R 1,6/cβ	0·75	z	1·4	0·75	0·5
R cα/cβ		0·75			
R tD/X	1·5				
R X/Y	1·0				
R Y/cβ	0·9				

Table 8. Some attempts at complete analysis of decalins and octalins on phases mentioned in table 7, p.27a.

z = almost unresolved;

X = totally unresolved mixture of cD, cα and 1,2;

Y = toatally unresolved mixture of tα and tβ.

(fig. 7) it was decided that a total analysis of the octalins should be possible without resorting to the less stable silver columns.

Attempts at complete analysis of the octalins are summarised in table 8, p.27D. 1,2-Bis(2'-cyanoethoxy)ethane was selected as the most suitable phase. The appearance of the successful chromatograph is shown in fig. 8, p.28A. Since this conclusion was reached, the phase has been recommended for a variety of separations but not for those involving mixtures of isomeric olefines[65].

Table 9, p.28B, shows the effect of varying conditions on the phase. The effect of treating the prepared packing material <u>in situ</u> in the column with hexamethyldisilazane is seen. The use of this material is supposed to improve the performance of columns[66,67]. It reacts with any hydroxyl groups in the support material by the reaction following.

$$-OH + Me_3Si-NH-SiMe_3 \longrightarrow -OSiMe_3 + NH_2-SiMe_3$$

The use of the material seems hardly worthwhile in this case. Perhaps its use is better reserved for "thin" phases (1% or less).

From table 9 we see that columns IA and IIC are comparable. Both sets of conditions were employed.

When operated at 50° no deterioration of 1,2-bis(2'-cyanoethoxy)ethane columns is observed.

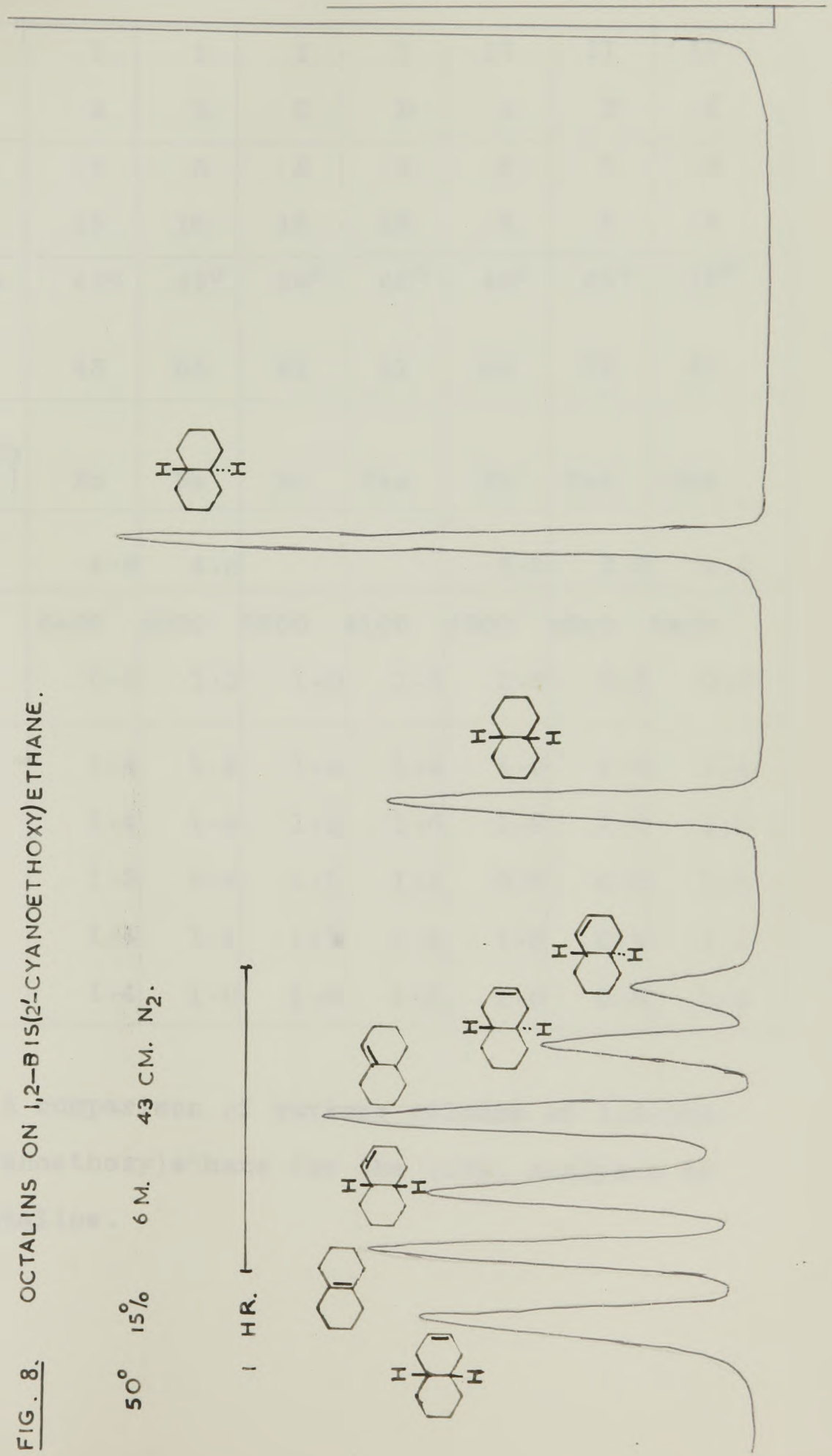


FIG. 8. OCTALINS ON 1,2-BIS(2'-CYANOETHOXY)ETHANE.

Column	I	I	I	I	II	II	II
Conditions	A	B	C	D	A	B	C
Length (m.)	6	6	6	6	8	8	8
% Phase	15	15	15	15	5	5	5
Temperature	49°	49°	59°	49°	49°	49°	49°
Pressure (cm.)	43	63	41	41	85	76	41
Whether treated with HMDS (p. 28)	No	No	No	Yes	No	Yes	Yes
Total time (hr.)	4·6	4·0			2·5	2·5	4·3
N (c2)	6400	4000	5800	4100	3300	2500	9400
H (c2) mm.	0·9	1·5	1·0	1·5	2·5	3·3	0·9
R tα/tβ	1·4	1·2	1·4	1·4	1·0	1·0	1·4
R tβ/1,2	1·4	1·4	1·3	1·6	1·2	1·0	1·5
R 1,2/cα	1·2	0·9	1·1	1·3	0·8	0·8	1·2
R cα/1,6	1·4	1·1	1·3	1·4	1·0	0·9	1·4
R 1,6/cβ	1·4	1·0	1·4	1·5	1·9	0·8	1·4

Table 9. A comparison of various columns of 1,2-bis-(2'-cyanoethoxy)ethane for the total analysis of the octalins.

The Analysis of the Elimination Products from the Reactions.

The two markers (p.25) employed were trans and cis-decalins. The reaction products in solution in acetic acid were partitioned between light petroleum and water and the decalins and octalins were separated as a single alumina chromatographic fraction. The eluent was concentrated under conditions which would minimise loss of decalins and octalins. Analysis by gas-liquid chromatography was accomplished using as stationary phase 1,2-bis(2'-cyanoethoxy)ethane under conditions IA or IIC (table 9, p.28B).

PART II.

CARBONIUM IONS AND ION-MULTIPLETS.

Introduction.

If trans-decalin and t-butylcyclohexane are both rigid cyclohexane systems we should expect the rates and Arrhenius parameters for comparable reactions in the two systems to be the same. These data are summarised in table 1, p.30A.

The results for the α-substituted compounds presumably reflect the effect of the vicinal carbon atom. Later in this thesis (p. 58) this effect is compared for various cases. The rates for the β-decalyl compounds are lower than those for the corresponding t-butylcyclohexyl compounds. It was this unexpected observation which prompted the present work.

Before these results and those of the author can be discussed it is necessary to fill in the background. The exact significance of the word "rigid" in descriptions of cyclohexyl compounds will be discussed (p. 31); then the nature of the solvolytic displacement reaction will be considered (p.39).

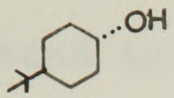
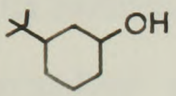
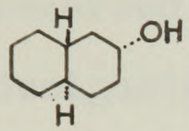
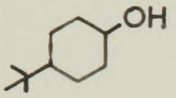
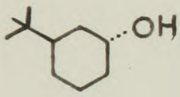
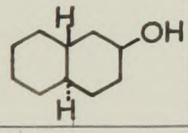
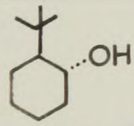
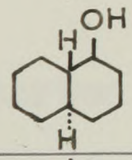
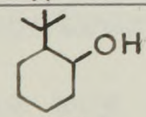
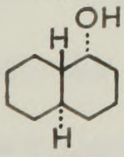
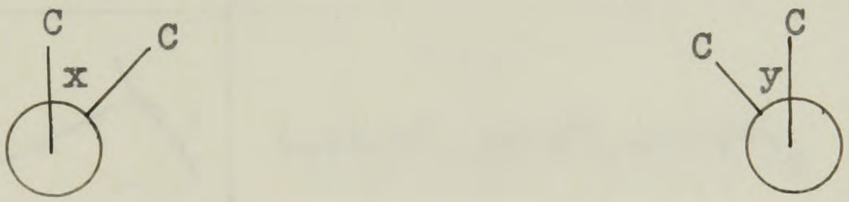
	Conformation of OH	Ref.	$10^5 . k_{75}$ mole.sec^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
	e	1	3·75	28·1	1·7
	e	1	3·33	27·5	-0·5
	e	68	1·99	28·5	-0·6
	a	1	10·2	26·7	-1·8
	a	1	10·9	26·6	-0·6
	a	68	6·19	27·8	-1·8
	e	69	331	25·2	2·4
	e	68	1·05	29·2	-2·2
	a	69	575	23·8	-0·5
	a	68	54·9	25·3	-2·2

Table 1. Figures for the acetolyses of toluene-p-sulphonates of the alcohols shown.

Conformational Analysis of Cyclohexene and Related Compounds.

The conformations of cyclic compounds are usefully described by the convention of Klyne and Prelog[70]. Each bond in turn is viewed in its Newman projection and the dihedral angle, τ, is measured. The values of τ (equal in number to the number of atoms composing the ring) are recorded in order round the ring. The way in which τ is designated is illustrated in fig. 1.



$\tau = x$ $\tau = -y$

Fig. 1.

If the tetrahedral arrangement of the bonds around each carbon atom is regarded as invariable, it is possible to construct a model of the cyclohexane molecule in two ways. One way results in a rigid conformation which is Sachse's "chair form"[71]. The designation of the chair in terms of τ-values is $(+60^{\circ}, -60^{\circ})_3$. The other way results in a flexible form with an infinite number of conformations. Those conformations with highest symmetry are detailed in table 2, p.32. The variable, θ, has values $(x + 2\pi n)$ where n has values, 0, 1, 2..., for identical conformations[72].

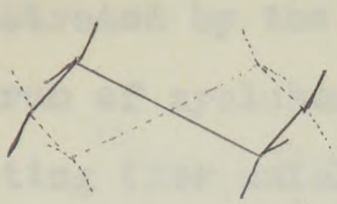
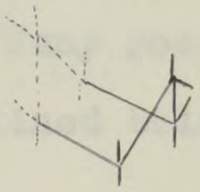
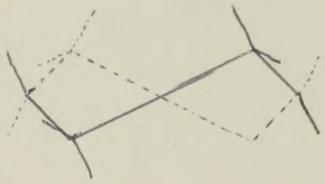
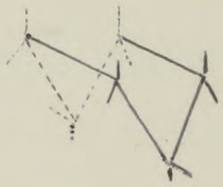
θ	Appearance	τ-designation.	Description.
0		$(+33\cdot2^{o},+33\cdot2^{o},-70\cdot6^{o})_2$	Twist[73] Stretch[72] Croisée[14]
$\pi/2$		$(+60^{o},-60^{o},0^{o})_2$	Boat
π		$(-33\cdot2^{o},-33\cdot2^{o},+70\cdot6^{o})_2$	Twist etc.
$3\pi/2$		$(+60^{o},-60^{o},0^{o})_2$	Boat

Table 2. The flexible form of cyclohexane. The values of τ for the twist conformations are due to Hendrickson[74]. Note that the two twist forms are enantiomers; the boats are identical.

So far the valency angles round carbon have been regarded as tetrahedral. A distortion takes place when the chair conformation is converted into a flexible form and vice versa. Such transformations take place when one chair

changes to another for the flexible form is an intermediate in such processes. That these transformations occur readily is demonstrated by the fact that the proton magnetic resonance spectrum of cyclohexane has only one line. The expected splitting (for axial and equatorial hydrogens) is observed at low temperatures[75].

Many possibilities exist for the transformation which is outlined below.

CHAIR
⇅
Transition State
⇅
FLEXIBLE FORM
(Intermediate)
⇅
Transition State
⇅
CHAIR

Not only is the flexible form made of many conformations but two transition states are possible. Transition state (1) has five carbon atoms in one plane (it can be regarded as half way between a chair and a boat); transition state (2) has four atoms in one plane. Hendrickson has estimated the energy differences theoretically[76]. They are given in fig. 2, p. 34.

Recent values of the Arrhenius parameters for the

transformation of one chair into another, calculated from the proton magnetic resonance spectrum of undecadeuterocyclohexene, suggest Hendrickson's values (fig. 2) are high[75].

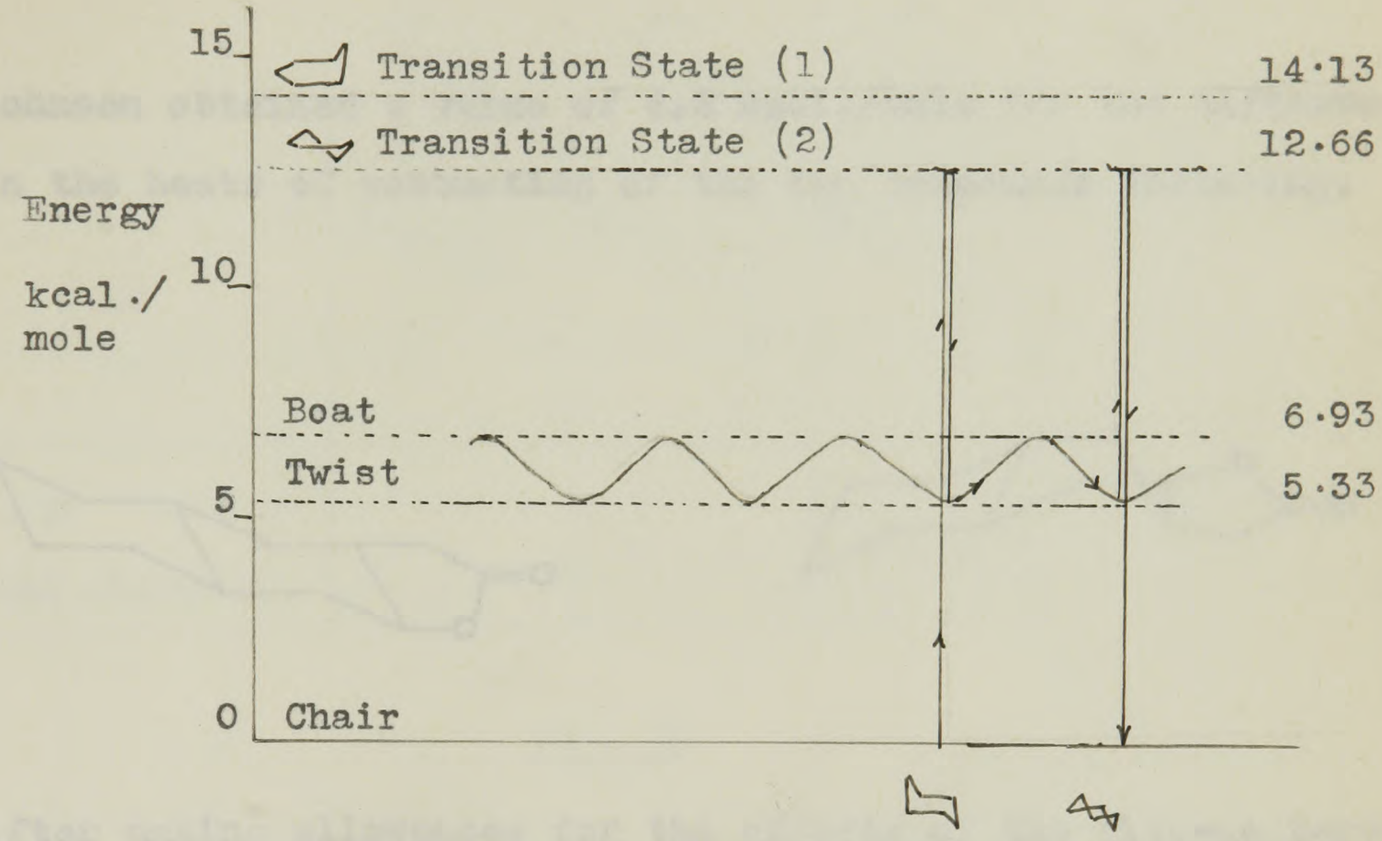
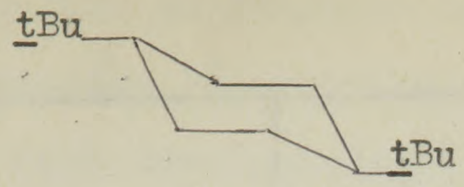
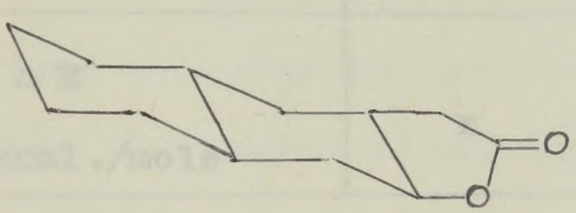


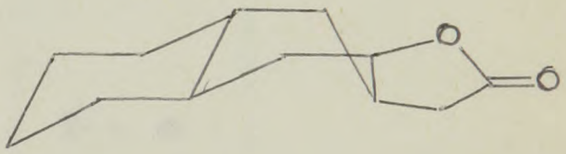
Fig. 2. Energy levels in cyclohexane calculated from theory[76]. The arrows indicate the most likely transformation. Experimental value of $\Delta H^{\ddagger}$ is 10.9 ± 0.6[75].

Earlier experiments appeared to be in agreement with Hendrickson's figures for the energy difference between the chair conformation and the flexible form. Allinger obtained a value of 5.5 kcal./mole from the vapour-phase equilibration of the two compounds following[77].



Johnson obtained a value of 4.3 kcal./mole for the difference in the heats of combustion of the two compounds following.





After making allowances for the effects of the five-membered ring, Johnson obtained a corrected value of 5.9 kcal./mole.[73] Kenner has critically appraised these two pieces of work[78].

Winstein estimated the energy difference between the two chair forms of t-butylcyclohexane to be ca. 5 kcal./mole[1]. For a substituted t-butylcyclohexane the difference is altered as seen from fig. 3, p. 36.

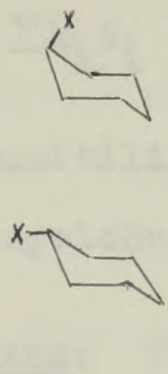
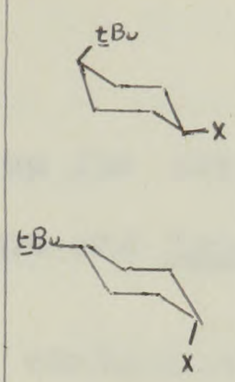
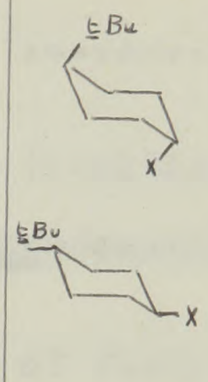
			
Δ E kcal./mole	x	5 - x	5 + x

Fig. 3.

With trans-decalyl compounds the corresponding difference corresponds to the breaking of a C-C bond (ca. 80 kcal.). However in discussing the conformational behaviour of a compound it is important to take into account all the possible conformations, not only the chairs. Hückel has emphasised this point[14,79,80].

Winstein suggested equation 1 would represent the rate of reaction of a cyclohexyl compound[1].

$$k = N_a k_a + N_e k_e \quad \text{.....} \quad 1$$

The subscripts stand for axial and equatorial. N is the mole

fraction of reactant in which the substituent is in the situation in question. Hückel's suggestion is that equation 2 is more appropriate.

$$k = \sum k_i N_i \qquad \text{.....} \quad 2$$

The range of possibilities for the flexible form of the systems t-butylcyclohexane and trans-decalin is given below.

t-Butylcyclohexane: The continuum of flexible forms lies in a range whose twist conformations are given in fig. 4. The last conformation shown in fig. 4 involves interactions of the same order of magnitude as the axial chair conformation.

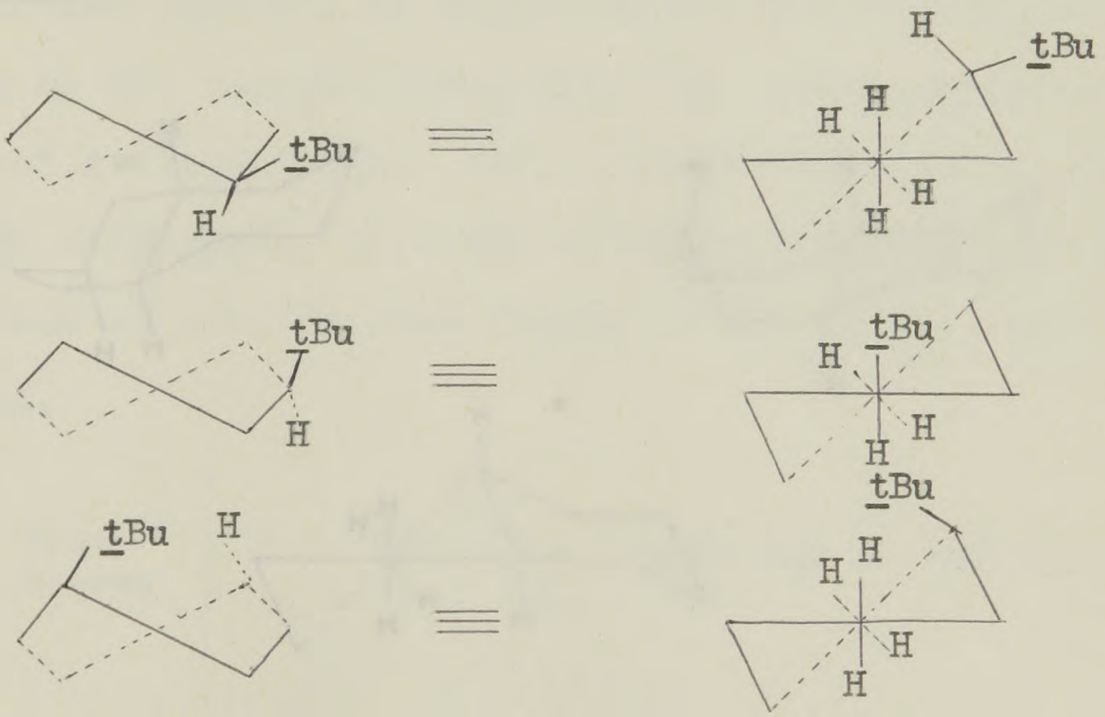
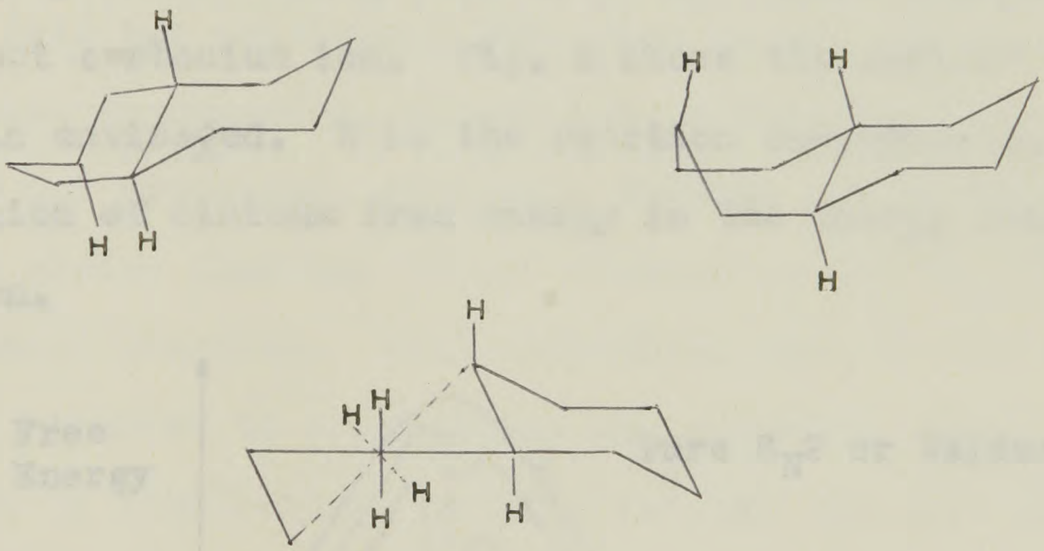


Fig. 4.

trans-Decalin: In fig. 5 one ring is drawn as a chair. Clearly it too can be flexible. Note that the boats are

probably more unfavourable than the boats in cyclohexane because the repulsion between the two hydrogens marked is less easily relieved by distortion of the ring. The twist conformation is probably less favourable too. The dihedral angle at the ring-junction is ideally 60° for the "chair ring" and 70.6° for the "twist ring". The conflict is possibly not serious but the parallel conflict (between 70.6° and 33.?°) probably eliminates the twist-twist conformation as a serious possibility. It is safe to say that we expect the flexible form to be less important when considering equations such as 2 (p. 37) and their application to <u>trans</u>-decalyl compounds.



<u>Fig. 5.</u>

The Solvolytic Displacement Reaction.

Solvolyses of secondary arylsulphonates lie in the "borderline region" of mechanism[81] between the S_N1 and S_N2 mechanisms[82]. Ingold's original work on these two types has been well summarised[83]. This section deals with concepts relevant to the understanding of the borderline region. The subject is yet controversial.

Doering and Zeiss emphasised that S_N2 reactions may go through an intermediate[84]. The region of the transition state will be partly stabilised if the electronic arrangement favours the formation of an electron-deficient intermediate. The notation ($\frac{1}{2}p$-sp^3) is suggested to describe the partial bonding by the incoming base with the vacant p-orbital of the incipient carbonium ion. Fig. 6 shows the sort of continuum which is envisaged. R is the reaction co-ordinate, the projection of minimum free energy in the energy surface of the reaction.

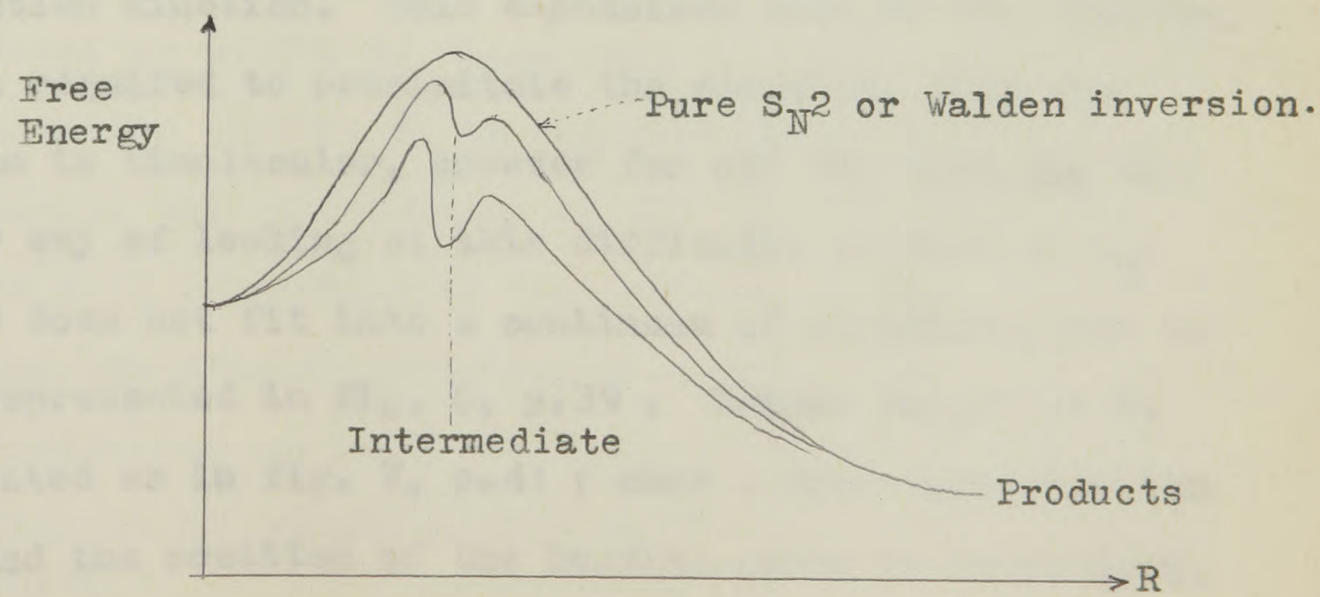


Fig. 6.

The intermediate is stabilised if the p-orbital at the reaction-centre is filled internally; the reaction then approaches S_N1 character.

The idea has been extended by Robertson who suggests the notation S_N12 to describe the intermediate cases[85]. Swain and, occasionally, Winstein and Streitwieser have been attracted by the idea that one mechanism should encompass all these reactions[86,87,88]. Ingold has gone so far as to suggest an all embracing kinetic expression for the reaction based on the idea that the formation of the carbonium ion intermediate is governed by the volume (characteristic for each reaction) within which a base molecule will precipitate the departure of the leaving group[87].

Gold has criticised this view on the grounds that the expression degenerates, either into a formula for concurrent S_N1 and S_N2 processes, or into a formula for an S_N1 process[90]. He also claims that the theory undermines the whole basis of reaction kinetics. Gold emphasises that if the entering base is required to precipitate the reaction, then the reaction is bimolecular, however far off the base may be. Another way of looking at this difficulty is that an S_N1 process does not fit into a continuum of reactions such as those represented in fig. 6, p.39 . Rather should it be represented as in fig. 7, p.41 ; once a free carbonium ion is formed the position of the leaving group is randomised.

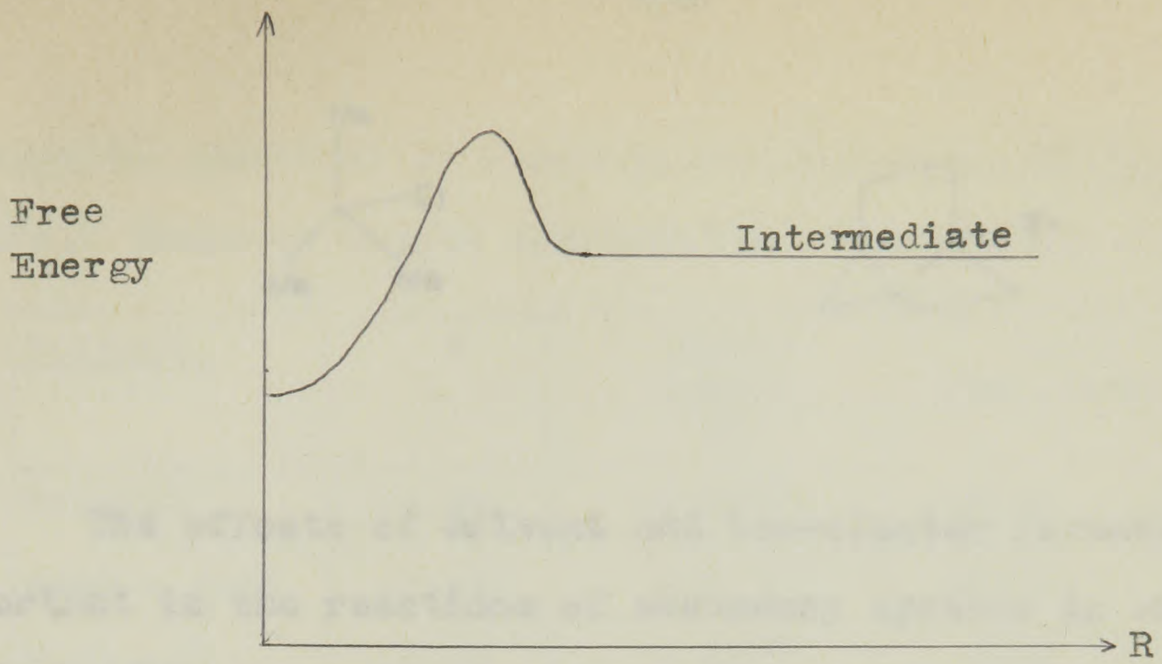
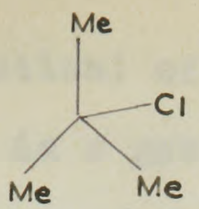
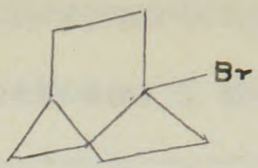


Fig. 7.

Brown has discussed the comparative rates by considering the increase or decrease in strain when a change of hybridisation (sp^3 to sp^2) occurs[91,92]. Woodward thinks that Brown's and Doering's hypotheses amount to the same thing[93]. If there is a lot of crowding in the original compound then the transition state will lie closer to the sp^3 hybridisation and the vacant p-orbital will become more readily available for stabilisation, either internally or from the base. Brown refers to such crowding as B-strain[94]. The concept is useful in discussing tertiary reaction centres. Rear-solvation appears to be unimportant in such systems. For example, the reactivities of the two compounds shown below have the same dependence on the polarity of the solvent (i.e. they have the same mY correlations - see below) even though the reactivities are very different owing to the difficulty of forming an sp^2 configuration in the bicyclo[2,2,2]octyl system[95,96].





The effects of solvent and ion-cluster formation are important in the reactions of secondary systems in solvents of low polarity such as acetic acid (the solvent used in the present work). Grunwald and Winstein classified solvents according to their Y-values (equation 3)[97,87].

$$Y = \log \frac{\text{Rate of solvolysis of t-butyl chloride in solvent}}{\text{Rate of solvolysis of t-BuCl in 80\% aq. EtOH}} \quad \ldots\ldots 3$$

Winstein showed that plots of ($\log k/k_{EtOH}$) vs. Y are linear for a variety of sulphonates[97]. Winstein further generalised solvolysis rates (equation 4).

$$d \log k = m\, dY + (\partial \log k/\partial N)_Y\, dN \quad \ldots\ldots 4$$

The first term on the right-hand side of equation 4 represents the solvation contribution and the second term represents the C-bond formation contribution.

Y-values for solvents of importance to this discussion are listed in table 3, p.43. Also given are dipole moments and Kosower's Z-values[98]. Z is the energy (measured spectrographically) for the charge-transfer reaction (in the

solvent in question) of N-methyl-4-methoxycarbonylpyridinium iodide. There is a good correlation between Z and Y.

Solvent.	Y	Dipole Moment (D)	Z kcal./mole
Ethanol	-2·03	1.70[99]	79·6
Acetic Acid	-1·64	1.4 [100]	79·2
Methanol	-1·09	1·69[99]	83·6
80 % Ethanol	0·00		84·8
Formic Acid	2.08	1·2 [100]	
Water	3·56	1·84[101]	94·6

Table 3. Hückel quotes 1.75 D as the dipole moment of acetic acid[102].

Solvents with high positive Y-values solvate carbonium ions well. It can be seen from table 3 and the foregoing discussion that carbonium ions formed in acetic acid are unlikely to receive much stabilisation from solvation. The dielectric constant of acetic acid is also low. One can therefore envisage the carbonium ions to be surrounded by a constantly changing cluster of ions. This is very important for we must consider a theory in which a specific cluster with unfavourable entropy requirements is invoked.

Winstein has deduced that there are two types of ion-pair[103,104]. He designated them "intimate" and "solvent-separated".

His evidence is based on the "special salt effect", which is the inhibition of ion-pair return by anion-exchange. The work has been done with systems in which achimeric assistance and the formation of non-classical carbonium ions are important.

In the case of a simple S_N1 solvolysis in which the intermediate is an ion-pair Winstein would represent the course shown in fig. 8.

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{Intimate}}{R^{\oplus}\,X^{\ominus}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{Solvent separated}}{R^{\oplus}//X^{\ominus}} \underset{k^{-3}}{\overset{k_3}{\rightleftharpoons}} \text{Free ions}$$

Fig. 8.

Return to starting material and solvolysis are possible from any position in the sequence.

For the solvolysis of secondary arylsulphonates Streitwieser has elaborated Winstein's view[81]. He found evidence for sulphonate-exchange in the acetolysis of octan-2-yl sulphonates and postulated that the reaction proceeded through an ion-quadruplet (fig. 9).

$$R^{\oplus}(OX)^{\ominus} \longrightarrow M^{\oplus}(OY)^{\ominus}R^{\oplus}(OX)^{\ominus} \rightleftharpoons (OY)^{\ominus}(R)^{\oplus}(OX)^{\ominus}(M)^{\oplus} \longrightarrow (OY)^{\ominus}R^{\oplus}$$

This scheme is a reaction of intimate ion-pairs. It is the process mentioned earlier (p.43) with unfavourable entropy requirements. It is discussed further on p.55 .

Acetolyses of Decalyl Toluene-p-sulphonates.

Let us return to the difference in rates for the acetolyses of the two sets of compounds mentioned in table 1, p.30A. In table 4 the rates are compared on the assumption that the lower rate for the decalyl compounds is due to a higher activation energy.

$$\log k = (\text{const.}) - E^{\ddagger}/RT$$

$$\log (k_t/k_\beta) = (E^{\ddagger}_\beta - E^{\ddagger}_t)/RT \quad \ldots\ldots\ldots 5$$

The subscripts in equation 5 refer to trans-β-decalyl (β) and to 4-t-butylcyclohexyl (t). In table 4 the values of $(E^{\ddagger}_\beta - E^{\ddagger}_t)$ are based on the substitution of values of k (from table 1, p.30A) in equation 5.

	Equatorial	Axial
(k_t/k_β)	1.89	1.68
$(E^{\ddagger}_\beta - E^{\ddagger}_t)$	436 cal.	356 cal.

Table 4.

If these figures are compared with the experimentally determined values of $\Delta H^{\ddagger}$ (table 1, p.30A) it is seen that they are within experimental scatter.

A possible explanation of a larger activation energy of trans-decalyl compounds is that a greater strain is imposed on a fused cyclohexane ring by introduction of an sp^2 centre

than is imposed by the same introduction into a non-fused ring.

Another general comparison between these two systems is summarised in table 5 which shows the ratios of elimination to substitution. All product-analyses of 4-t-butylcyclohexyl compounds are from a recent correction of Winstein's values[1] by Mr. N.C.G. Campbell of this laboratory[2].

	Equatorial	Axial
trans-β-decalyl	1.82	6.49
4-t-butylcyclohexyl	3.22	6.43

Table 5: Ratios of olefines/acetates.

A possible explanation of higher yields of olefine from the 4-t-butylcyclohexyl system is parallel to the previous argument. We can imagine the intermediate in an S_N1 reaction (or an S_N12 reaction involving solvent, p.40) to be the solvated ion-pair shown in fig. 10.

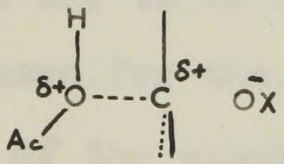


Fig. 10.

This solvated ion-pair can (i) collapse to acetate, (ii) eliminate, or (iii) return to sulphonate. It is possible

that route (ii) is more difficult for decalyl ion-pairs because of the strain imposed on the system by introducing two sp^2 centres; this would increase the relative importance of (iii) and decrease the titrimetric rate-constant. It should be born in mind that this is a possible cause of the rate-difference. It is separate from the other argument relating to the introduction of sp^2 centres for we are "on the other side" of the transition state. The lower yield of olefine (for the decalyl system) predicted by the second theory is not found in the axial case (table 5, p.47).

An explanation of the differences in olefine-yield and rates for the equatorial cases is that non-chair conformations may contribute significant terms to the generalised Winstein-Holness rate-equation (equation 2, p.37). It is hardly worth considering the non-chair conformations of the axial compounds as the functional group would be in a less reactive orientation and it is necessary for the substituent to be in a more reactive situation in these poorly populated, unfavourable states if the states are to be significant contributors to equation 2. The reason for the greater reactivity of the twist conformations of the equatorial compounds is that it is possible for the leaving group to adopt an orientation more reactive than equatorial and to leave behind a twist-ring with an sp^2 centre. There is abundant evidence that the preferred conformation of the di-sp^2 compound, cyclohexane-1,4-dione,

is twist[105], and optical rotary dispersion evidence suggests that the conformation may appreciably contribute to cyclohexanones[106]. Possible twist conformations for the two "equatorial" compounds under discussion are shown in fig. 11, p. 49. If the conformations of the parent hydrocarbons (fig. 4, p. 37; fig. 5, p. 38) are reconstructed with the sulphonate substituent, it will be found that the counterpart of conformation i (fig. 11) in the trans-cis-bicyclo[4,4,0]-decan-3-yl compounds would be of very high energy owing to a $33.2^{\circ}/60^{\circ}$ dihedral angle conflict at the ring-fusion. Similarly the conformation of trans-4-t-butylcyclohexyl compounds corresponding to ii involves the adoption of an orientation as unfavourable as axial by the t-butyl group.

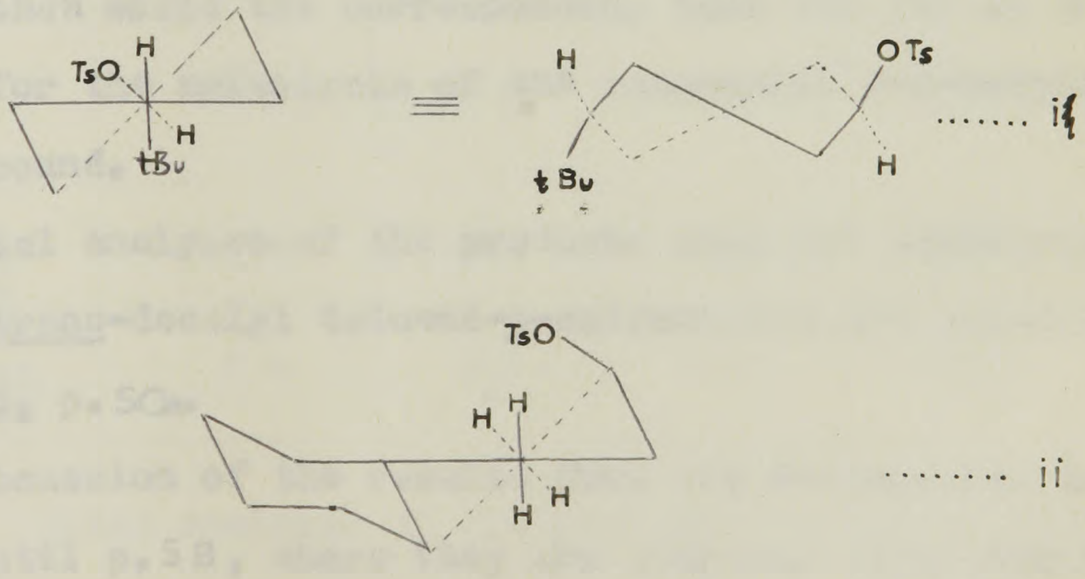


Fig. 11.

Hückel was the first to point out the possibility of (ii)[14].

From the previous discussion it will be obvious that this approach is only useful if (i) is more effective in altering equation 2 than is (ii). If it is assumed that the energy contributions of the twist forms and the two types of non-equatorial twist-orientations are equal in the two cases we are left with an unfavourable factor in (ii). This is the dihedral angle conflict at the ring-fusion (p. 38). In fact there is probably another unfavourable factor in (ii). The two non-equatorial orientations are very different. The OTs group in (ii) is "pseudo-axial"; in (i) it is much less hindered. Dr. Whiting has suggested that "isoclinic" would be a possible designation of this orientation. Thus if the rates are similar, conformation (ii) will contribute to a less significant term ($N_i k_i$) in the form of equation 2 (p. 37) appropriate to the solvolysis of the equatorial decalyl compound than would the corresponding term for (i) in the equation for the solvolysis of the equatorial 4-t-butylcyclohexyl compound.

Total analyses of the products from the acetolyses of the four trans-decalyl toluene-p-sulphonates are summarised in table 6, p. 50A.

Discussion of the results from the α-compounds is delayed until p. 58, where they are compared with some results of Wuckel, except for one point. It is clear that some of the products from the α-equatorial compound were formed via

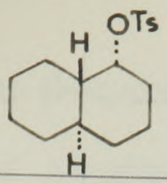
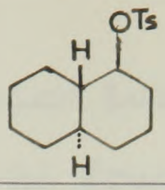
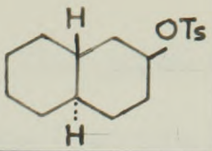
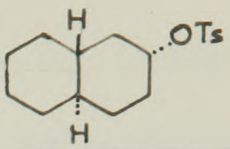
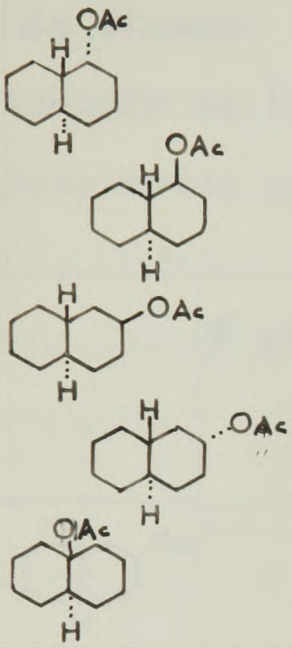
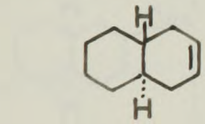
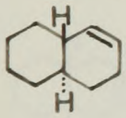
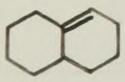
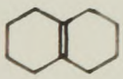
				
Conformation of OTs	a	e	a	e
	1·10	31·35	0·36(5)	
	0·68	15·25	0·02	
		0·41	4·03	33·3
		0·52	7·80	2·17
	7·45	0·35	0·09(5)	
		3·82	59·1	40·2
	1·26	10·6	26·1	23·7
	32·4	27·6	0·60	0·09
	57·6	10·1	0·55	0·47
Alcohols / Olefines	0·1	0·9	0·15	0·55
Retention / Inversion	1·6	0·5	0·5	0·07

Table 6. Total analyses of the products of the acetolyses of trans-decalyl toluene-p-sulphonates. These are averaged and normalised results. See Experimental Section, table 1, p.97A.

rearrangement to a β-carbonium ion. The yields of these products from this source and from the β-axial sulphonate are compared in table 7, p. 51. The resemblance, seen from this figure, suggests that rearrangement leads to the β-axial ion-pair as intermediate, i.e. that the toluene-p-sulphonate group moves over the same face of the molecule.

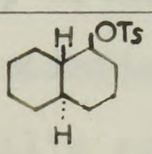
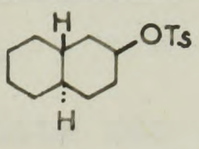
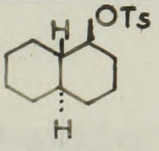
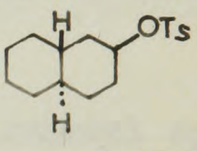
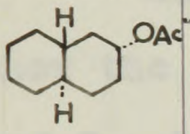
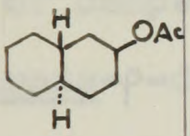
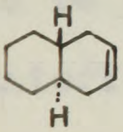
	% yields from table 4.		Relative yields.	
				
	0·52	7·80	1	1
	0·41	4·03	0·8	0·5
	3·82	59·1	7.4	7·5

Table 7.

The trans-decalyl system is degenerate in the sense that if a rearrangement of the type referred to above should occur from one β-position to the other (i.e. from C^3 to C^4) the resulting acetate formed via rearrangement would be indistinguishable from unrearranged, retained material. This ambiguity would be removed if the work was repeated with resolved material.

The first work in this field (solvolysis of conformationally homogeneous sulphonate-esters) was by Nace, who studied the alcoholysis-products of cholestanyl (equatorial) and epicholestanyl (axial) toluene-p-sulphonates[107]. Using classical techniques of analysis (product-isolation) Nace claimed 100% inversion. He established that the rate was independant of lyate-ion concentration, although this concentration does affect the amount of elimination.

Campbell's results for the 4-t-butylcyclohexyl system show the same very small extent of retention[2]. These results (of Campbell) are compared with those of the author (for the trans-β-decalyl system) in figs. 12 and 13, p. 52A. It is to be assumed that the bulk of the apparently retained material in the decalyl case is really rearranged to the other β-position. If this assumption is made it is clear that rearrangement to the other β-position is more favourable than rearrangement to the α-position. In the case of the β-axial compound the rearranged material seems to be largely derived from a 1,3-shift to the tertiary centre (fig. 14, p. 52A). Presumably any α-equatorial ion-pair returns to the unreactive α-equatorial sulphonate. Rearrangement of the β-equatorial compound to the α-axial ion-pair would give, largely, the observed mixture of bridgehead olefines (table 6, p.50A, also p.59).

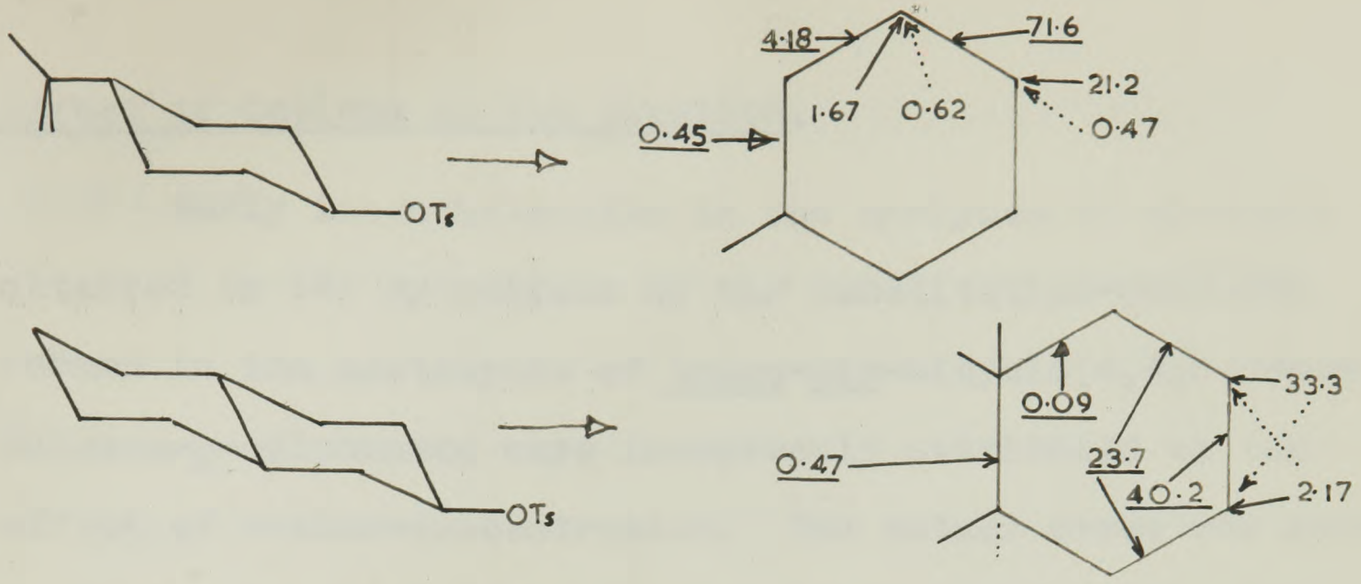


Fig. 12. Acetolyses of equatorial toluene-p-sulphonates at 100°. Underlined figures refer to yields of olefines; the others refer to yields of acetates.

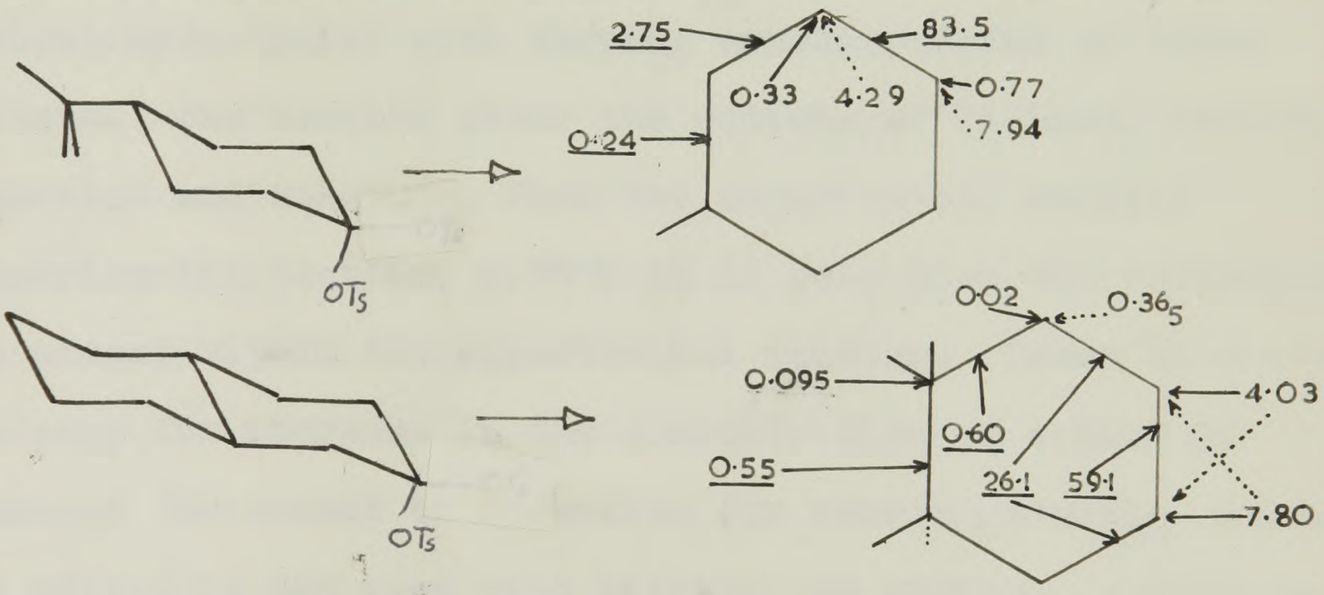


Fig. 13. Acetolyses of axial toluene-p-sulphonates at 100°.

Fig. 14. 1,3 shift of axial trans-β-decalyl toluene-p-sulphonates.

Effect of Cations on the Reaction.

Early inconsistencies in the analyses of alcohols obtained by the hydrolysis of the substitution-products formed in the acetolysis of trans-cis-bicyclo[4,4,0]decan-3-yl toluene-p-sulphonate were incorrectly attributed to the effect of cation-concentration. The actual error was later corrected (p. 25) and no results obtained prior to this correction are included in this thesis. A by-product was a survey of analyses of acetates from this reaction (analysed without hydrolysis) with varying concentrations of metal acetate. The results cover the cations of lithium, sodium, potassium and caesium. From the experimental results (Experimental Section, p.99B) it is seen that the variations are almost within the experimental scatter. There is a slight tendency for increase in the concentration of cation to increase the amount of retention (or rearrangement); moreover the effect is not seen with lithium and sodium. A similar experiment with the axial epimer (trans-trans-bicyclo-[4,4,0]-decan-3-ol) showed a slight drift in the opposite direction with potassium. The effect was sufficiently small to allow a direct comparison between results with different bases to be made. The slight effect which was observed is discussed on p. 56.

The Effects of the Nature of the Leaving Group and the Temperature.

In order to compare these results with others in different systems the effect of substituting nitrobenzene-p-sulphonate for toluene-p-sulphonate was examined with the two trans-β-decalyl systems. The new type of sulphonate is much more reactive and affords the possibility of performing the same reaction at 100° and at 25°. The normalised results are summarised in table 8, p.54A, which also contains data from table 6, p.50A. It must be emphasised that the results for this new class are less satisfactory than previous ones as the experimental total yields, prior to normalisation, are in the range 80 - 95%, whereas previous ranges were 95 - 105% (see Experimental Section tables 1 and 3, pp. 97A and 99A).

It is probably fair to say that there is no significant change in the products obtained when the leaving group is changed. In both cases the lowering of the temperature results in reduced amounts of elimination and rearrangement. Both these generalisations are true for the 4-t-butylcyclohexyl and 4-octyl systems[2,109].

The effects following the lowering of temperature presumably reflect that the activation energies for elimination and rearrangement are less easily surmounted at lower temperatures.

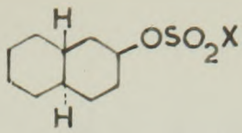
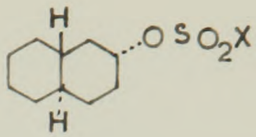
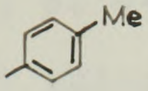
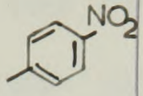
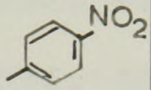
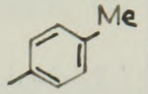
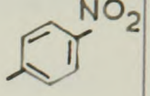
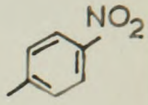
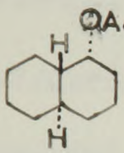
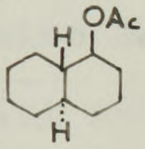
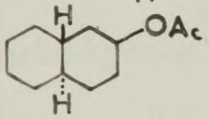
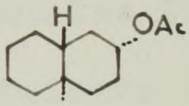
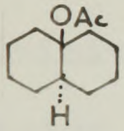
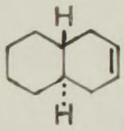
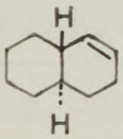
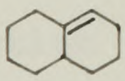
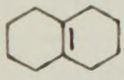
Reactant						
X						
Temperature (°)	100	100	25	100	100	25
	0.36_5	0.36				
	0.02					
	4.03	3.60	4.03	33.3	27.9	32.4
	7.80	9.13	11.07	2.17	1.50	2.90
	0.09_5	0.20				
	59.1	56.8	58.9	40.2	43.0	41.2
	26.1	28.55	26.3	23.7	24.3	22.1
	0.60	0.56	0.82	0.09	0.37	0.38
	0.55	0.82	0.30	0.47	0.90	0.94
Alcohols / Olefines	0.15	0.15	0.18	0.55	0.42	0.54
Retention / Inversion	0.5	0.4	0.4	0.07	0.07	0.09

Table 8.

Exchange of Sulphonate.

Streitwieser has postulated a reaction of intimate ion-pairs (fig. 9, p. 44) the overall effect of which would be the exchange of sulphonate groups, apparently with inversion, during the course of the solvolysis[81]. After establishing that the reaction in question (acetolysis of octan-2-yl arylsulphonates) proceeded with almost complete inversion although there was appreciable racemisation of starting material, Streitwieser studied the kinetics of the acetolyses of octan-2-yl n-butyl and benzyl nitrobenzene-p-sulphonates in the presence of lithium toluene-p-sulphonate. Streitwieser found that the first order rate-constant diminished during the first part of the reaction and became steady at a lower figure between 10 and 20 half-lives. The evidence was interpreted as exchange with dissolved sulphonate anions. The rate-reduction was attributed to the formation of the less reactive alkyl toluene-p-sulphonate. A possible objection to this argument is that there is such a difference in reactivities between these two groups of compounds that the introduced anions are preferentially displacing the groups on the reactant.

The following series of experiments was designed to test the theory for the trans-β-decalyl compounds. As the method used was not a kinetic one, it was possible to choose two sulphonate groups of comparable reactivity, viz.

toluene-p-sulphonate (-OTs) and naphthalene-β-sulphonate (-Oβs), and in this way to overcome the objection to Streitwieser's deduction, mentioned at the end of the previous paragraph.

In the following discussion the two trans-β-decalyl radicals are referred to as aDec (axial) and eDec (equatorial). Solvolyses were carried out at 100° of aDecOTs and eDecOTs in the presence of equivalent quantities of potassium acetate (as usual) and KOβs. Cyclohexane-extracts of the solutions were examined in an ultraviolet spectrophotometer, to detect any DecOβs and to assess the percentage reaction. The results are summarised in table 9, p.56A. The reaction sequences are so complicated that the results cannot be discussed quantitatively. However from table 9, it can be seen that up to 0.5% of the products could be due to the "epimeric ion-pair" formed via sulphonate-exchange. The situation is summarised in fig. 15, p.56A.

Fig. 15 suggests that the effect is likely to be insignificant. If a similar calculation is done with Campbell's results[2] (fig. 12 and 13, p.52A) it is found that of the 0.47% of retained material from the equatorial sulphonate up to 0.04% could be due to exchange, and of the 0.77% from the axial epimer up to 0.1% could be due to exchange.

Variation of ratios of (retention/inversion) with cation-concentration (p.53) does not appear to simply be

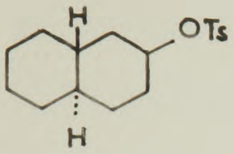
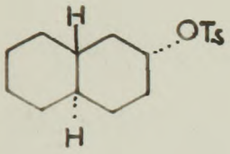
Starting Material	% of Reaction	% of DecOβs in Sulphonate	Contribution of DecOβs to Product-formation
	78·6	2·48	0·5
	91·9	6·08	0·5
	97·8	7·32	0·15
	40·3	0·68	0·2
	63·0	0·86	0·35
	77·5	0·83	0·2

Table 9. Sulphonate-exchange. Figures in the last column are arrived at by multiplying the percentage of DecOβs by the proportion of unreacted sulphonate.

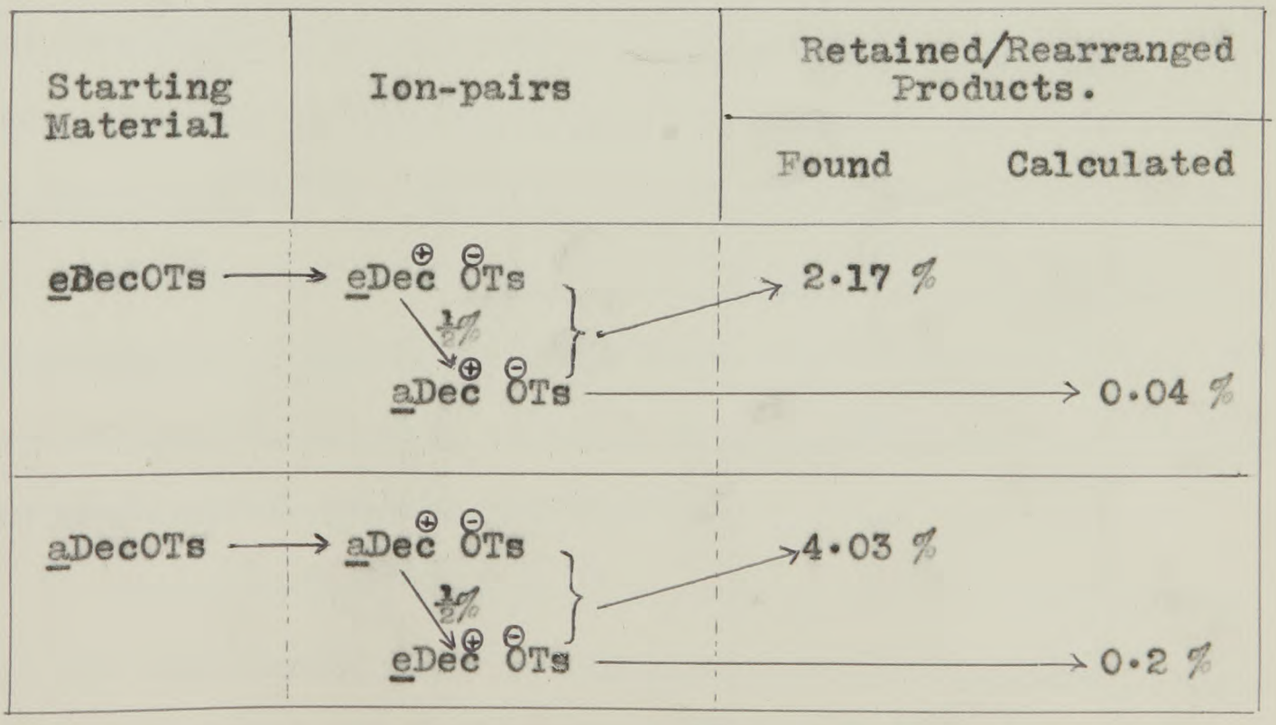


Fig. 15. Possible contribution of sulphonate-exchange to "retained/rearranged" products.

explained by sulphonate-exchange. Presumably the effect is so small that it is masked by other effects.

Solvolytic Displacements in Cyclohexyl Systems in which there is a Vicinal Carbon Atom.

Hückel has done a lot of work in such systems in order to review critically the use of conformational analysis to rationalise solvolytic displacement reactions. Although the present author would share some of Hückel's doubts about the validity of such reasoning, it seems that Hückel's results are considerably confused by this vicinal effect. Indeed some very recent work has effectively disposed of one of his arguments. Restricting himself to these α-compounds Hückel discovered that the difference in rates between cis- and trans- alkylcyclopentyl sulphonate-esters was as great as that between the cyclohexyl analogues. From this he reasoned that the difference in reactivities of cis- and trans- t-butylcyclohexyl compounds was not due to characteristic reactivities of equatorial and axial substituents, because these two types of orientation cannot exist in cyclopentane[5b,80]. Lillien and Khaleeluddin have shown the rates of acetolysis of cis- and trans- 3-t-butylcyclopentyl toluene-p-sulphonates are the same and thus establish the fundamental difference between cyclopentyl and cyclohexyl compounds which Hückel denies[114].

Nevertheless Hückel has done a lot of interesting work with his compounds and the results are here compared with the present ones (for the trans-α-decalyl compounds).

CIS (APPROXIMATELY AXIAL) COMPOUNDS: Hückel has conveniently collected some rate-constants for the methanolyses at 30° of toluene-p-sulphonates of some of these compounds[110]. It is striking that the reaction-rates are of the same order of magnitude when the vicinal atom is part of a methyl or methylene group, but much higher when it is part of a bigger group (see table 10).

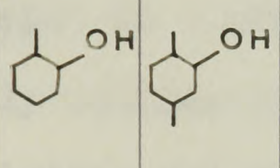
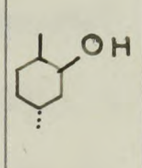
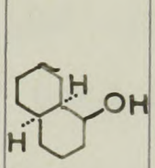
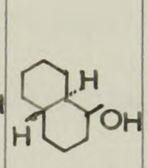
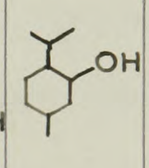
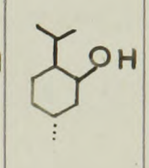
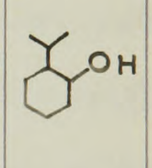
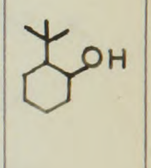
									
$k_{30} \cdot 10^6$	2·26	1·23	2·58	3·0	1·39	37	6·8	6·2	28·4

Table 10. Rates of methanolysis of toluene-p-sulphonates.

The differences are large enough to emphasise that there are many factors affecting the rates, in particular they are sensitive to B-strain (p.41). It is probable that the speed of the reactions relative to the trans-epimers (conveniently seen from table 1, p.30A) is due to hydrogen-participation, fig. 16.

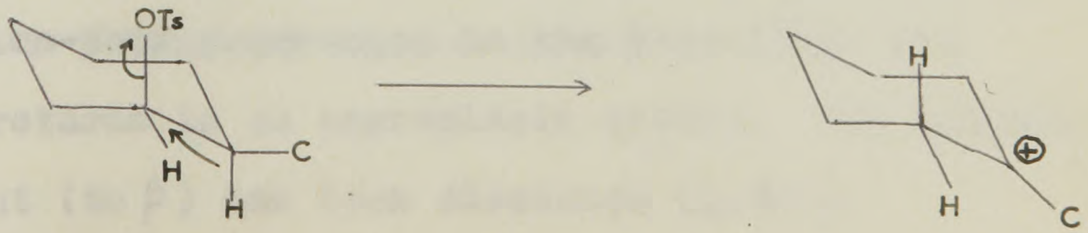


Fig. 16.

Hückel analysed products from some of these reactions[111]. The general impression is of a high yield of olefine and such substitution-products as are formed are tertiary. Product-analyses of some decalyl compounds by Hückel and the present author are compared in table 11, p.60A. Clearly the tertiary decalyl carbonium ion is sensitive to solvation. The resemblance of the relative olefine-yields from the cis tertiary decalol with those from the trans-α-decalol (in acetic acid) is a support for the rule postulated on p.51. Presumably methanolysis of this tertiary derivative would show a similar pattern to that of column 2. If the trans tertiary decalol could be converted into a similar derivative which was then methanolysed it would resemble column 1.

TRANS (APPROXIMATELY EQUATORIAL COMPOUNDS): Hückel has again surveyed a range of compounds[111,112]. The kinetics can be summarised by saying that in those compounds in which a large vicinal group (t-butyl, i-propyl, cyclohexyl) contributes to B-strain, then the reaction is faster than for cyclohexyl sulphonates; otherwise it is slower.

The charge-separation is difficult for these slower reactions, i.e. the transition state is close to sp^2. As can be seen for the trans-decalyl compound in this class (table 6, p.50A) the ion-pair rearranges to the β-position and presumably returns to an appreciable extent. The pattern of rearrangement (to β) has been discussed (p.51).

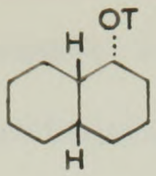
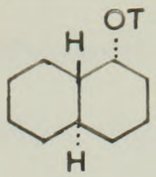
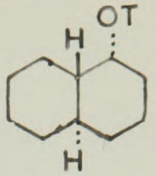
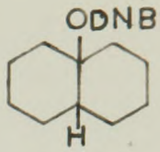
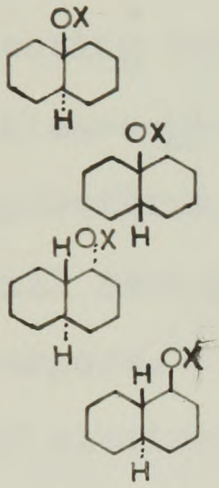
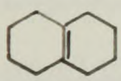
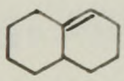
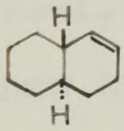
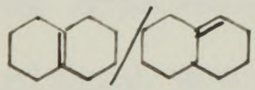
	1	2	3	4
Reference	Hückel[111]		The thesis.	
				
Solvent Base	MeOH $CaCO_3$	MeOH $CaCO_3$	HOAc KOAc	HOAc KOAc
	10	22 2	7·45 1·10 0·68	0·24
	8	18	57·6	42·4
	82	57	32·4	27·2
		1	1·26	
	0·1	0·32	1·78	1·56

Table 11. DNB = 3,5-dinitrobenzoate. The yields in column 4 are not normalised; their low total (70·2 %) could be due to the formation of the less reactive secondary decalyl dinitrobenzoates.

Another Route to trans-β-Decalyl Carbonium Ions.

The present work originated as an attempt to discover a base, not containing metal cations, which would inhibit the isomerisation and acetylation of octalins. It dated from the time when it was thought that the cation had an effect on the reaction (p.53). The results (table 12, p. 61A) of heating solutions of trans-bicyclo[4,4,0]dec-3-ene in 0.5 M toluene-p-sulphonic acid with different quantities of tetrahydrofuran at 100° for 15 hr. demonstrate that tetrahydrofuran will accomplish this, but not sufficiently for the present purpose. Tetrahydrofuran is seen to reduce the isomerisation of olefines known to occur with solutions of toluene-p-sulphonic acid in acetic acid[113]. The equilibrium mixture of octalins obtained from acid-catalysed isomerisation consists of ca. 90% bicyclo[4,4,0]dec-1,6-ene, ca. 9% bicyclo[4,4,0]-dec-1,2-ene and ca. 1% "the rest"[3]. The figures in table 12 show that, in the absence of tetrahydrofuran, this equilibrium was approached. The drift of the results suggest that the primary product of the addition of acetic acid, at least in the presence of tetrahydrofuran, is the axial epimer. The reaction is clearly worth further study.

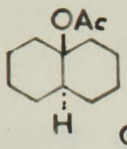
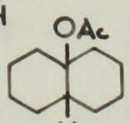
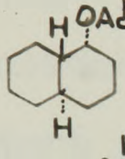
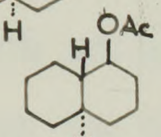
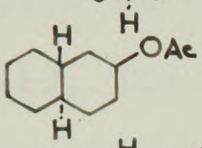
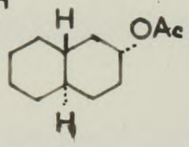
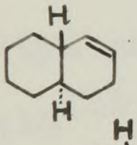
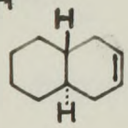
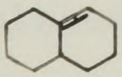
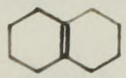
Ratio of THF:TsOH	0	1:1	5:1
% of THF	0	0·8	4
	0·10	0·06	0·03
	0·97	0·00	0·09(5)
	0·87	0·82	0·22(5)
	0·59		
	29·9	42·6	21·5
	21·9	12·2	3·78
Other "acetate"	0·07		
	2·15	4·95	10·2
	3·64	8·20	48·2
	1·86	1·64	1·36
	10·73	13·42	1·59
Total acetate	54·2	55·7	25·6
Total olefine	18·3	28·2	60·2
TOTAL	72·5	83·9	85·8

Table 12. See p. 61 for explanation.

APPENDIX.

NUCLEAR MAGNETIC RESONANCE SPECTRA.

The resonance due to the proton *gem* to oxygen in a number of decalyl compounds, DecOX, was examined and the results are summarised in table 1, p.65A. The table will be considered from the point of view of the effect of (i) the nature of X; (ii) the equatorial or axial character of the proton on the position and width of the resonance-band; and (iii), for the alcohols, an assessment of Eliel's generalisation[115].

The nature of X (in DecOX).

Shoolery describes the replacement of hydrogen by acetyl as resulting in a shift of *ca.* 45 c.p.s. to lower field[119]. In the present case shifts of 63 were obtained (both from 3 and 11, and 4 and 12; all in table 1). Replacement of hydrogen by methyl results in a shift in the opposite direction (29 c.p.s. for 3 and 13; 31 c.p.s. for 4 and 14). The effect of the substitution is greater if the proton *gem* to oxygen is axial than if it is equatorial.

Effect of equatorial or axial character of the proton.

The results correlate quite well with others designed to test the difference of τ-values for axial and equatorial protons in comparable cyclohexane chair-compounds.

Jackman[116] has used some theoretical calculations by Bothner-By and Naar-Colin[117] of magnetic susceptibilities in C-C bonds to calculate the expected difference ($\tau_a - \tau_e$). He quotes 0.40 p.p.m. The results for various cases are shown in the table. The origin of the difference can be seen qualitatively in fig. 1. The diamagnetic anisotropy of the C^2-C^3 bond has a different long-range shielding effect for the protons, owing to the different distances from the centre of the bond to the protons. These differences do not occur with bonds from C^1. The bond C^5-C^6 has to be taken into account; it is similarly situated to C^2-C^3. Jackman neglects the very long-range effects from the C^4 bonds.

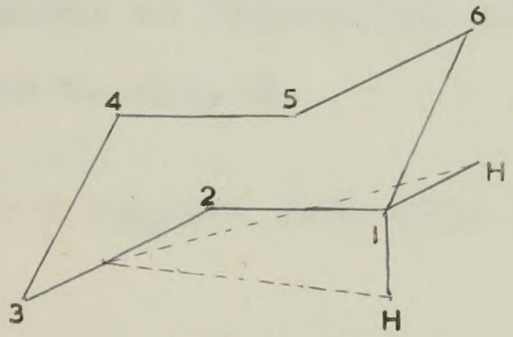


Fig. 1.

The effect of the equatorial or axial character of the proton gem to oxygen on the width of its resonance ("width" is defined in fig. 2) has been noted before[118].

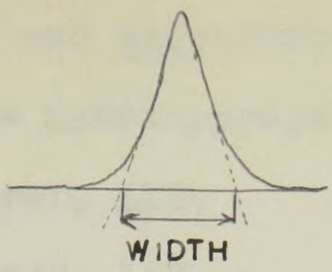


Fig. 2.

Position of the resonance for alcohols.

Eliel has claimed that for cyclohexanols the position of the "carbinol proton" (i.e. the one *gem* to O) is given by the formula following[115].

Frequency downfield from TMS at 60 Mc./sec. = 240 - 20n, where n is the number of "syn-axial protons"; the syn-axial situation is shown in fig. 3.

The data in table 1 suggest that this rule is poorly observed in the decalols.

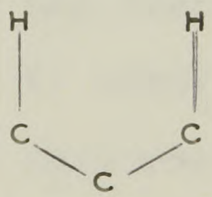


Fig. 3.

Key to table 1.

(a) Values for the position, calculated from ref. 115.

(b) These samples were kindly supplied by Mr.N.C.C. Campbell.

(d) Androsterone and epiandrosterone.

(e) 11α- and 11β- hydroxyprogesterones.

(e) Values from ref. 115.

(f) Values from ref. 118.

(g) Values from ref. 119.

The methylene resonance.

The nuclear magnetic resonance spectrum of cis-decalin shows a narrow band. The different environments of the protons are "smoothed out" owing to the flexing of the molecule. In the rigid trans-decalin molecule the band is broad and there are two main features, probably due to the equatorial and axial protons. As can be seen from fig. 4, p.66A, the same general effect is observable with some decalols.

In figs. 5 and 6, pp.66A&B, a number of spectra of trans-decalyl derivatives are reproduced and it can be seen that when the substituent is axial the methylene region is narrower and the two main features of the region are less prominent than in the cases where the substituent is equatorial. Perhaps the generalisation has some limited application in identifying decalyl compounds.

A possible explanation of the effect is that the axial substituent distorts the protons in the ring and reduces the difference between equatorial and axial positions.

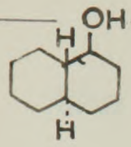
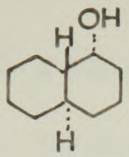
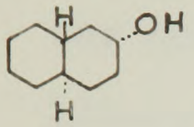
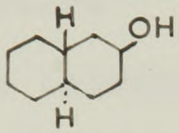
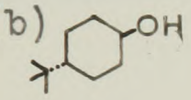
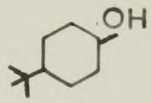
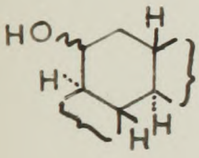
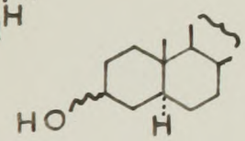
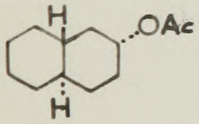
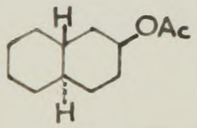
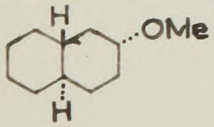
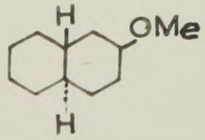
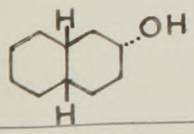
	No.	X	c.p.s.	(a)	Line-Width	τ	$(\tau_a - \tau_e)$
	1	a	183	180	40	6·95	0·63
	2	e	221	240	15	6·32	
	3	a	216	200	45	6·41	0·55
	4	e	242	240	19	5·86	
(b) 	5	a	202 202(e)	200	36 22(f)	6·63	0·39
(b) 	6	e	237 236(e)	240	18 7(f)	6·04	
 (c)	7,8						0·43(g)
 (d)	9,10						0·54(g)
	11	a	279		41	5·34	0·42
	12	e	305		19	4·92	
	13	a	187		39	6·88	
	14	e	211		15	6·49	
	15	eea	213		42	6·45	

Table 1. See p.64 for key. X = conformation of H gem to O.

In figs. 4, 5 and 6, x indicates the resonance due to the proton gem to oxygen and the formula ROD indicates that the CH resonance has been suppressed by recording the spectrum in the presence of deuterium oxide. With the exception of the decalins (fig. 4) whose spectra are reproduced from the literature[120], all the spectra were recorded in solution in carbon tetrachloride and tetramethylsilane (TMS) was used as internal standard.

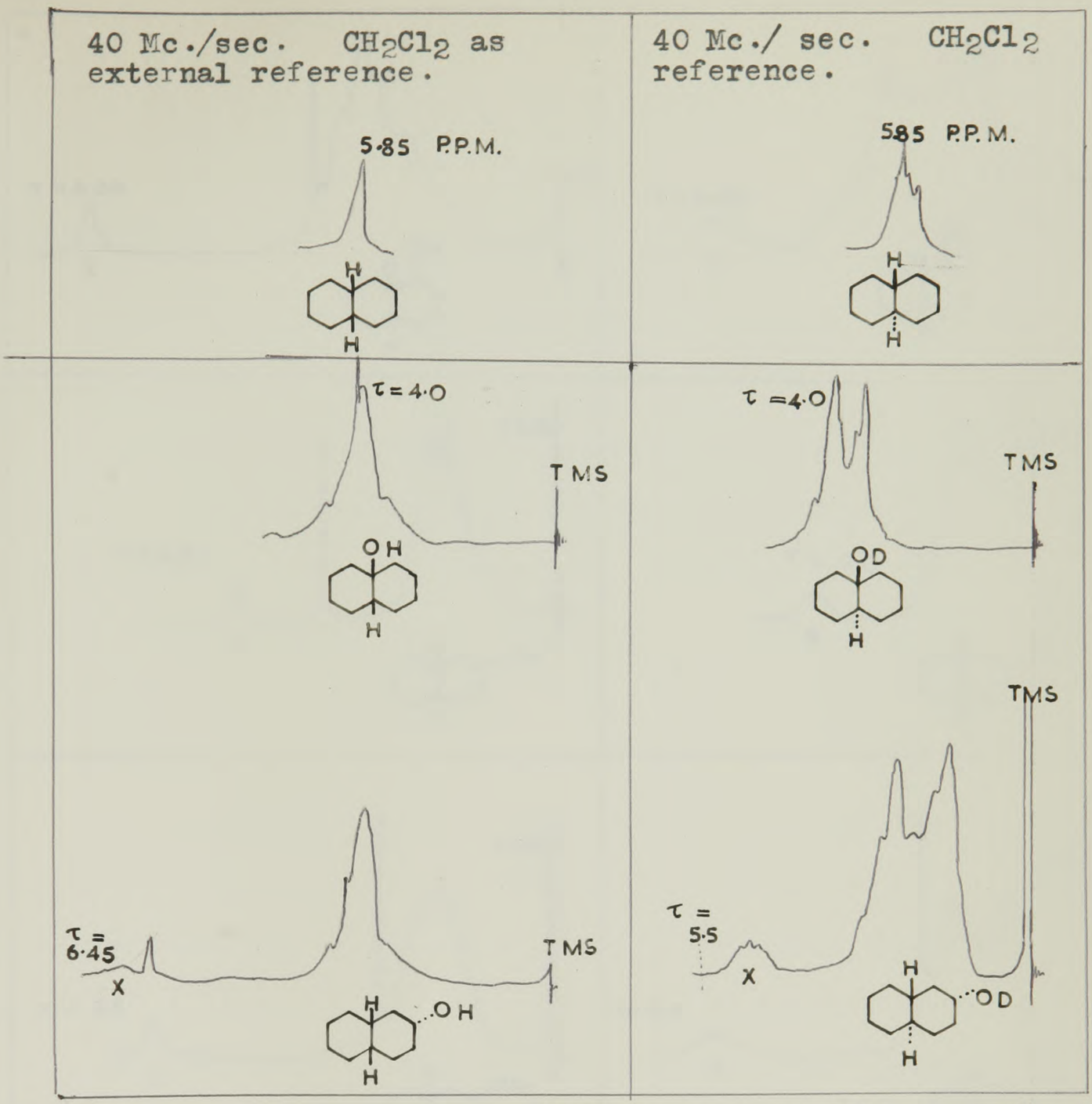

40 Mc./sec. CH_2Cl_2 as external reference.
5·85 P.P.M.
H
H
τ = 4·0
TMS
OH
H
τ = 6·45
X
TMS
H
OH
H
40 Mc./ sec. CH_2Cl_2 reference.
5·85 P.P.M.
H
H
τ = 4·0
TMS
OD
H
TMS
τ = 5·5
X
H
OD
H

Fig. 4.

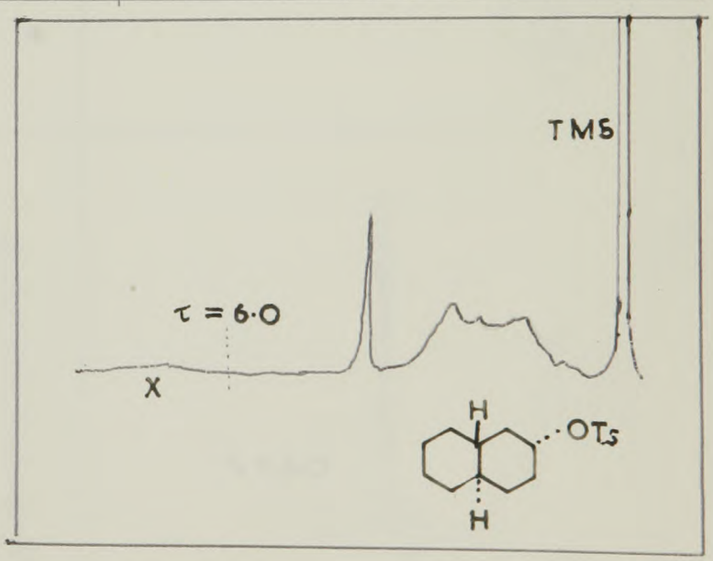

TMS
τ = 6·0
X
H
OTs
H

Fig. 5.

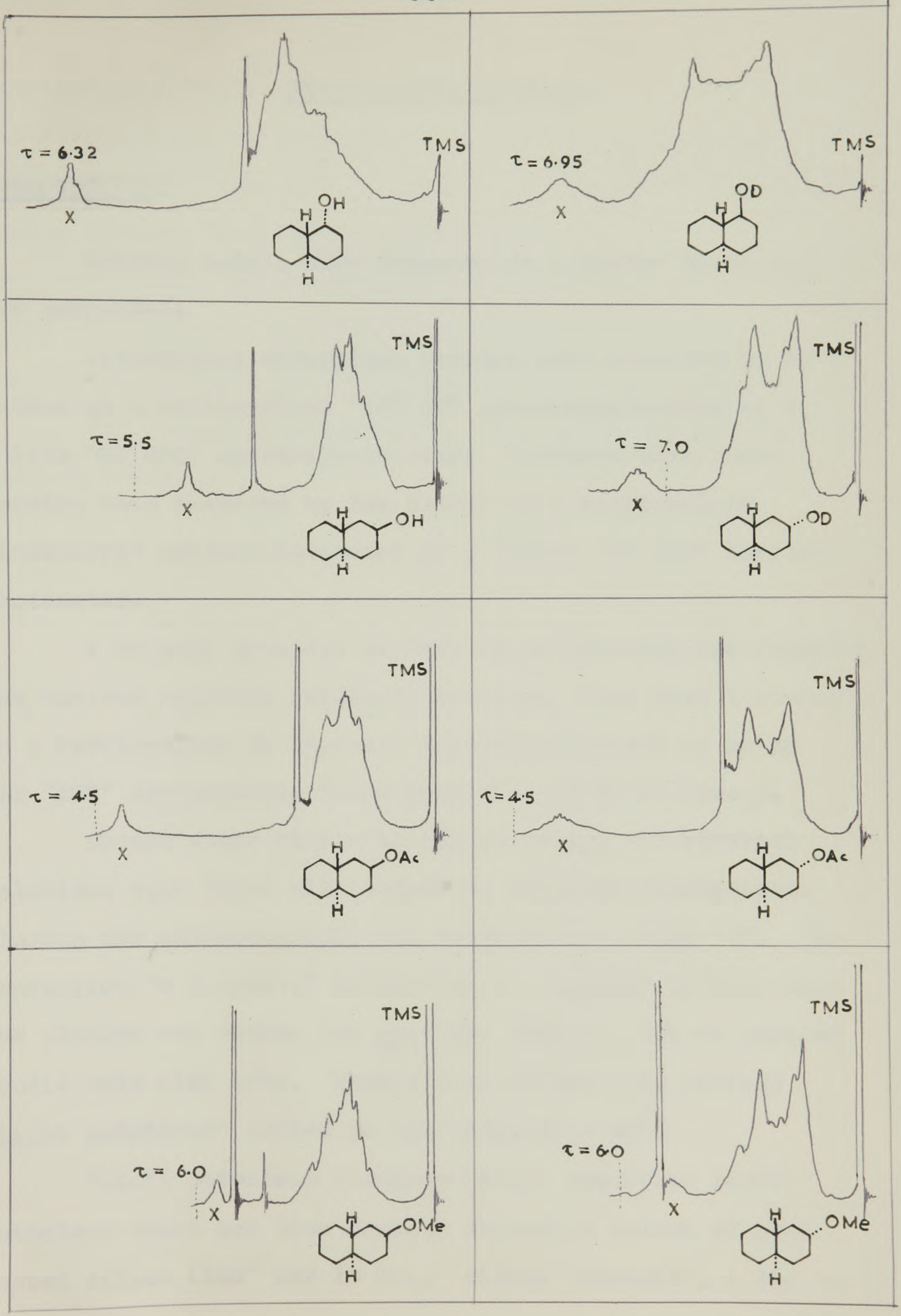

τ = 6·32
X
TMS
OH
H
H
τ = 6·95
X
TMS
OD
H
H
τ = 5·5
X
TMS
OH
H
H
τ = 7·0
X
TMS
OD
H
H
τ = 4·5
X
TMS
OAc
H
H
τ = 4·5
X
TMS
OAc
H
H
τ = 6·0
X
TMS
OMe
H
H
τ = 6·0
X
TMS
OMe
H
H

FIG. 6.

EXPERIMENTAL SECTION.

INTRODUCTION.

Melting points were recorded on a Kofler block and are corrected.

Ultraviolet absorption spectra were recorded by the author on a Perkin-Elmer "137 UV" spectrophotometer or a Unicam "SP 800" spectrophotometer; infrared absorption spectra were recorded by the author on a Perkin-Elmer "Infracord" spectrophotometer or a Unicam "SP 200" spectrophotometer.

I am very grateful to Mrs. R. B. Richards who recorded the nuclear magnetic resonance spectra. They were recorded on a Perkin-Elmer 60 Mc./sec. spectrophotometer or on an AEI "RS2" spectrometer (also operating at 60 Mc./sec.).

Except where stated to the contrary, all ethereal solutions were dried with magnesium sulphate monohydrate. Alumina for chromatography was Peter Spence Grade "H". The expression "x % deact." (referring to alumina) implies that the alumina was shaken for ca. ½ hr. with x % v/w of aqueous acetic acid (10% v/v). Except when differently defined "light petroleum" boiled in the range 30 - 40°.

"Light petroleum (benzene-free)" describes light petroleum which has been drained through a column of pre-heated silica (180° for 15 hr.; either "Sorbsil", 2 lb. or

Harrington, 1 kg.). The absence of benzene in the eluate was demonstrated by recording the ultraviolet spectrum in an uncompensated 1 cm. cell. A column of the above type will remove benzene from 6 l. of petroleum.

Pyridine was Harringtons' and was dried by boiling under reflux over potassium hydroxide pellets for 6 hr.; it was distilled and kept over potassium hydroxide pellets.

The author is indebted to Drs. Weiler and Strauss for microanalyses.

PREPARATIONS.

trans-cis- and trans-trans- Bicyclo[4,4,0]decan-3-ols.

"Decahydro-β-naphthol" (semi-solid, Lights', 100 g.) was dissolved in light petroleum (250 ml.) giving a solution which deposited crystals when cooled to -10°. Two recrystallisations from the same solvent yielded trans-cis-bicyclo[4,4,0]decan-3-ol, m.p. 75° (Dauben et al. quote[12] m.p. 75°). Such material was free of other decalols according to such gas-liquid chromatographic criteria as are mentioned in other parts of this thesis; the yield varied from 40 to 60 g. and depended on the original sample.

Residues from the above crystallisations (37.5 g.) were chromatographed on alumina (10% deact., 3 kg.). Elution with light petroleum (boiling range 40 - 60°) afforded crystals (2.12 g.) which on recrystallisation from the same solvent yielded trans-trans-bicyclo[4,4,0]decan-3-ol (1.94 g.), m.p. 53 - 53.5° (Dauben et al. quote[12] m.p. 53°). The purity was established by the same method as was used for the epimer (above).

Infrared absorbtion spectra of solutions of these two alcohols in carbon tetrachloride were recorded and the bands in the region 920 - 1100 $cm.^{-1}$ were used to follow the rest of the chromatogram. Such bands were, for the trans-cis isomer: 935w, 970w, 1030m, 1050m, 1070m; for the trans-trans

isomer: 925w, 950m, 975w, 1010m, 1030m.

Returning to the chromatogram, further elution with light petroleum afforded a crude liquid sample (7.64 g.) which, after re-chromatography under the same conditions on alumina (750 g.) and recrystallisation of the product afforded more of the trans-trans isomer (3.00 g.), m.p. 52.5°. Further elution of the first column yielded, with light petroleum, unidentified material (22.5 g., ? cis-decalols), and with ether and light petroleum (1:1 v/v) a semi-solid (20.0 g.) which, after two recrystallisations, yielded the trans-cis isomer (13.2 g.), m.p. 75°.

Hydrogenation of α-naphthol.

"W-7" Raney Nickel[19] was prepared by adding nickel-aluminium alloy (ca. 1:1, 125 g.) to a solution of sodium hydroxide (160 g.) in water (600 ml.) at such a rate that the temperature was maintained at 50°. After addition the temperature was maintained by external heating for 1 hr. The whole process was accompanied by vigorous stirring. The resulting nickel was very pyrophoric. It was washed (3 times with water, 3 times with 95% ethanol, 3 times with water, 3 times with 95% ethanol, 3 times with absolute ethanol) by stirring with liquid and centrifuging. The product was stored under ethanol and used within 48 hr.

α-Naphthol (B.D.H.) was distilled at 76 cm. A solution

of the distillate (60 g.) in ethanol (200 ml.) was boiled under reflux with W-7 nickel (20 ml. sludge) for 16 hr. The ethanol and naphthol were boiled out and the latter was recrystallised from light petroleum (boiling range 60 - 80°). Only the first crop (30 g.) was taken.

W-7 nickel (25 ml. sludge) was suspended in a solution of α-naphthol (29.3 g.) in ethanol (50 ml.) and was shaken in a high-pressure hydrogenator (50 atmos., 20°). The furnace was set to 150°. This temperature was reached after 40 min. when the pressure was 60 atmos. The process was stopped after 4 hr. when the pressure was 40 atmos.

The product (27 g.) was distilled through a Vigreaux column (30 cm.) to yield decalin (4.0 g.), b.p. 21°/0.1 mm. and decalols (19.5 g.), b.p. 62 - 70°/0.1 mm.

trans-Bicyclo[4,4,0]decan-2-one.

Following the method of Brown[121] the above mixture of decalols was oxidised to ketone. A solution of the decalols (19.5 g.) in ether (150 ml.) was boiled under reflux and was stirred mechanically. To this solution, was added over a period of 1 hr. one of potassium dichromate (200 g.) and sulphuric acid (100 ml.) in water (100 ml.). After further stirring (15 min.) product was obtained in the usual way. Chromatography of the product on alumina (5% deact., 1 kg.) and elution with light petroleum afforded crystalline ketone

(11.65 g.), m.p. 29°. Recrystallisation of a sample (300 mg.) from light petroleum yielded trans-bicyclo[4,4,0]decan-2-one (270 mg.), m.p. 33° (Hückel and Brinkmann found[122] m.p. 33°).

trans-trans-Bicyclo[4,4,0]decan-2-ol.

trans-Bicyclo[4,4,0]decan-2-one (m.p. 29°, 11.35 g.) was dissolved in a mixture of water (30 ml.) and ethanol (90 ml.). Sodium (wire, 18 g.) was added with stirring, over a period of 1 hr., to the above solution. Water (500 ml.) and light petroleum (500 ml.) were added and the upper layer was worked up in the usual way. Chromatography of the product (9.19 g.) on alumina (10% deact., 900 g.) and elution with light petroleum afforded starting material (4.5 g.). Further elution afforded solid (4.65 g.) which, after recrystallisation from light petroleum, yielded trans-trans-bicyclo[4,4,0]decan-2-ol (4.27 g.), m.p. 63° (Dauben et al. quote [12] m.p. 63°).

Reaction of decalins with ozone.

For the preparative experiment, oxygen (ca. 12.1./hr.) containing ozone (ca. 1.5 mole O_3/l.) was bubbled through a stirred mixture of decalin (Harrington, 30 g.) and carbon tetrachloride (250 ml.) at 0° for 40 hr. As commercial decalin contains tetralin, there was a danger that the product might contain aromatic ozonides. Carbon tetrachloride (ca. 120 ml.) was removed at 21 - 25°/100 mm.

For the analytical experiment, decalin (free of aromatic compounds, see p.86) was separated into its isomers by gas-liquid chromatography (4.65 m. of 1" diameter column packed with 30% Apiezon-L on firebrick, 143°, inlet pressure of nitrogen 20 lb./sq."). I am grateful to Mr. C. Ball for performing this separation. By analytical gas-liquid chromatography (as in previous paragraph) each isomer was shown to contain less than 0.1% of the other.

In each case the decalin (trans 1.02 g.; cis 1.14 g.) was dissolved in carbon tetrachloride (25 ml.). Ozone (same concentration and flow rate as before) was bubbled through the solutions at 0° for 20 hr. The solutions were washed with aqueous hydrogen peroxide (6% w/v, 25 ml.), and with aqueous potassium hydrogen carbonate (concentrated, 25 ml.). The solutions were dried (magnesium sulphate) and were evaporated to ca. 5 ml. through a Dufton column (20 cm).

Analysis of the products was by gas-liquid chromatography (diglycerol-column, 2 m., 15%, conditions mentioned on p.96). Relative retention times of some possible products were previously measured and were found to be as follows.

trans-Bicyclo[4,4,0]decan-1-ol.....41

trans-Bicyclo[4,4,0]decan-2-one.....53

trans-Bicyclo[4,4,0]decan-3-one.....74

cis-Bicyclo[4,4,0]decan-1-ol.....100

cis-Bicyclo[4,4,0]decan-3-one.....55

The residue was stirred with aqueous hydrogen peroxide (2% w/v, 300 ml.) for 15 min. at 25°. Stirring was continued for 30 min. at 60°. Non-acidic products were obtained from this mixture in the usual way (*via* ether).

Distillation of the products through a Dufton column (20 cm.) afforded an oil (9.28 g.), b.p. 72 - 76°/0.07 mm., from which crystals separated after 20 hr. at 18°. The oil was drained off and recrystallisation from light petroleum yielded *cis*-bicyclo[4,4,0]decan-1-ol (501 mg.), m.p. 65 - 66° (Hückel *et al.* give[20] m.p. 62.5 - 63°). The residue was chromatographed on alumina (5% deact., 100 g.). Elution with light petroleum afforded ketonic material. Further elution afforded solids (420 mg.) which, after recrystallisation from light petroleum (benzene-free), yielded *trans*-bicyclo[4,4,0]decan-1-ol (370 mg.), m.p. 52.5 - 53° (Hückel *et al.* give[20] m.p. 53°). Further elution with light petroleum afforded more of the *cis* isomer (1.93 g.), m.p. 63°.

The assignments of these two isomers were confirmed by nuclear magnetic resonance (p. 66A). The gas-liquid chromatography (mentioned on p. 9A) of decalin involved in this reaction was accomplished on a column of Apiezon-L (15%, 50°). Identification of chromatogram-fractions was assisted by the infrared absorption spectra of the alcohols in solution in carbon tetrachloride. The bands in the

region 820 - 1050 cm.$^{-1}$ were, for the trans isomer: 835m, 860w, 910m, 960s, 970w, 1005w, 1045w, 1080m; and for the cis isomer: 825m, 845m, 860w, 890m, 930s, 945s, 985s, 1020m.

Solutions of reaction-products in carbon tetrachloride were injected into this column. The flame was not lit until the solvent had been eluted (ca. 5 min. after injection). The results are given on p. 9A. There were only four peaks in each case. There were no peaks in the secondary decalol region. The four peaks from the reaction of trans-decalin were identified by the retention time of the cis alcohol and the relative retention times of the remaining constituents. The peaks were similarly identified for the analysis of the products from the reaction of cis-decalin, except that an unidentified peak ($t_{rel.}$ = 30) was assumed to be due to cis-bicyclo[4,4,0]decan-2-one.

The further reaction mentioned on p. 8 , which demonstrated the oxidation of trans-cis-bicyclo[4,4,0]decan-3-ol under the conditions of the reaction, was performed exactly as the above "analytical runs" except that the decalol (1.54 g.) and trans-decalin (1.38 g.) were dissolved in carbon tetrachloride (50 ml.).

trans-cis-Bicyclo[4,4,0]decan-3-yl methyl ether.

This compound was required as a "marker" (p. 24). It

was prepared by adding an excess of methyl iodide to the decalyl alkoxide anion which was generated in dimethyl sulphoxide by the method of Price and Whiting[123].

Sodium hydride was added to crude dimethyl sulphoxide to make a mixture ca. 10% w/v. When evolution of hydrogen ceased, dimethyl sulphoxide was removed by distillation at 28°/0.1 mm. Sodium hydride was dissolved in dry dimethyl sulphoxide (the above distillate) to make a solution of the base, $CH_2=S(CH_3)-O^- Na^+$ (ca. M/5). The solution was titrated from an anaerobic burette[124] into a solution of trans-cis-bicyclo[4,4,0]decan-3-ol (20.34 g., 132mmole) in dry dimethyl sulphoxide (50 ml.) with triphenylmethane (previously dried at 0.05 mm.) as internal indicator. A fluffy white solid was deposited. Methyl iodide (redistilled, 20 ml.) was added. The solid immediately dissolved to give a yellow solution. The product was extracted with ether (4 x 200 ml.). Towards the end of the extraction the lower layer became viscous and was rendered limpid by the addition of water. Product (37.6 g.) was obtained in the usual way and was chromatographed on alumina (5% deact., 500 g.). Elution with light petroleum afforded material lacking the colour and unpleasant smell hitherto associated with the product of this reaction and which, on distillation, yielded trans-cis-bicyclo[4,4,0]decan-3-yl methyl ether (19.2 g., 114 mmole, 86.5%), b.p. 104 - 105°/20 mm., $n_D^{23.5}$ 1.4628

(Found: C, 78.3; H, 12.2. $C_{11}H_{20}O$ requires C, 78.5; H, 12.0%).

trans-trans-Bicyclo[4,4,0]decan-3-yl methyl ether.

An impure sample (300 mg.) containing a sulphur-compound of low molecular weight (Lassaigne test and a seriously asymmetric gas-liquid chromatography peak on diglycerol at lower retention time than the main peak), believed to be this compound, b.p. 95°/12 mm., was obtained by performing the previous experiment with a solution of trans-trans-bicyclo[4,4,0]decan-3-ol (0.49 g.) in dry dimethyl sulphoxide (4 ml.). The quantities of methyl iodide (0.5 ml.) and alumina (40 g.) were appropriately reduced. The sample was required for nuclear magnetic resonance studies (p.62). An unassigned resonance at τ = ca. 2.6 was assumed to be due to the impurity.

Octan-1-yl acetate.

Octan-1-ol (St. Just) was distilled through a Vigreaux column (30 cm.) and the fraction, b.p. 88°/12 mm., $n_D^{1.4275}$, was taken. Octan-1-ol (above, 28 g.), acetic anhydride (44 ml.) and pyridine (100 ml.) were kept at 18° for 15 hr. The product was worked up *via* light petroleum to yield, after distillation through the above column, octan-1-yl acetate (36 g., 97%), b.p. 89°/11 mm., n_D^{25} 1.4160 (Hatch and

Adkins give[125] b.p. 209 - 210°/76 cm., n_D^{25} 1.4157).

Toluene-p-sulphonates of decalols.

Equimolar proportions of the alcohol and toluene-p-sulphonyl chloride (recrystallised from light petroleum, boiling range 60 - 80°) were dissolved in pyridine (6 ml./ g. of alcohol) and kept at 18°. The products were worked up *via* ether in the usual way and were recrystallised from mixtures of benzene and light petroleum, boiling range 60 - 80°. The results are summarised below.

Yields of toluene-p-sulphonates of decalols:

Toluene-p-sulphonate	Reaction time (hr.)	Yield (%)	M.p. (°)	M.p. Moritani *et al.*[68]
trans-cis-Bicyclo[4,4,0]decan-2-yl	48	41	70-70.5	70-71
trans-trans-Bicyclo[4,4,0]decan-2-yl	24	74	97-98	97-98
trans-trans-Bicyclo[4,4,0]decan-3-yl	48	30	110	110-111
trans-cis-Bicyclo[4,4,0]decan-3-yl	24	69	62·5-63	62.5-63

1-Ethylcyclohexanol.

This compound was prepared as a readily available model for preparing possible derivatives of tertiary decalols. The Grignard reaction was performed in the usual way on a ½ mole scale. Ethyl bromide used for the reaction (13.4 g., 0.55 mole) was redistilled and the cyclohexanone (49.8 g., 0.50 mole) was purified *via* the bisulphite compound and distillation. Distillation of the product yielded 1-ethylcyclohexanol (54.1 g., 84%), b.p. 74.5°/20 mm., m.p. 29 - 30°. Recrystallisation of a sample from light petroleum (benzene-free) raised the m.p. to 33.5 - 34° (Found: C, 74.6; H, 12.5. Calc. for $C_8H_{16}O$: C, 74.9; H, 12.6%). Previous workers reported the substance to be a liquid[126].

1-Ethylcyclohexanyl 3,5-dinitrobenzoate.

3,5-Dinitrobenzoyl chloride (prepared in the usual way from the parent acid and phosphorus pentachloride and recrystallised from carbon tetrachloride, 1.00 g.) and 1-ethylcyclohexanol (0.55 g.) were dissolved in pyridine (25 ml.). The initial fine precipitate of N(3,5-dinitrobenzoyl) pyridinium chloride had been replaced after 14 hr. at 18° by a courser precipitate of pyridinium chloride. The product was worked up *via* ether in the usual way. Successive recrystallisations of the product from mixtures of light petroleum (boiling range 60 - 80°) and ethyl acetate until a

constant melting point was reached yielded 1-ethylcyclohexanyl 3,5-dinitrobenzoate (0.31 g.), m.p. 129 - 130° (Found: C, 55.7; H, 5.4. $C_{15}H_{18}O_6N_2$ requires C, 55.9; H, 5.6%).

cis-Bicyclo[4,4,0]decan-1-yl 3,5-dinitrobenzoate.

cis-Bicyclo[4,4,0]decan-1-ol (4.78 g.), 3,5-dinitrobenzoyl chloride (6.16 g.) and pyridine (25 ml.) stood at 18° for 60 hr., by which time the change in the nature of the precipitate (see previous section) had occurred. Work-up and repeated recrystallisation (as above) yielded cis-bicyclo [4,4,0]decan-1-yl 3,5-dinitrobenzoate (0.31 g.), m.p. 163° (Found: C, 58.2; H, 5.8. $C_{17}H_{20}O_6N_2$ requires C, 58.6; H, 5.8).

trans-cis-Bicyclo[4,4,0]decan-3-yl naphthalene-β-sulphonate.

trans-cis-Bicyclo[4,4,0]decan-3-ol (2.75 g.) and naphthalene-β-sulphonyl chloride (B.D.H., 4.06 g.) were dissolved in pyridine (20 ml.) and the solution was kept at 18° for 24 hr. The product was worked up *via* ether in the usual way. The ethereal solution was boiled with activated animal charcoal before the ether was removed and the product was recrystallised from benzene to constant melting point to yield trans-cis-bicyclo[4,4,0]decan-3-yl naphthalene-β-sulphonate (2.23 g.), m.p. 94 - 94.5° (Found: C, 69.7; H, 7.4. $C_{20}H_{24}O_3S$ requires C, 69.75; H, 7.0).

Nitrobenzene-p-sulphonyl chloride.

Meerwein's procedure was followed[127]. p-Nitraniline (35 g., 0.25 mole) was dissolved in hot concentrated hydrochloric acid (500 ml.) and the solution was cooled to 10°. A saturated aqueous solution of sodium nitrite (containing 17.25 g., 0.25 mole of the salt) was slowly added, with stirring, to the above solution. The resulting solution was added to a stirred solution of cupric chloride dihydrate (4.25 g., 0.25 mole) in acetic acid (200 ml.) which had been saturated with sulphur dioxide. The crystalline product was recrystallised from a mixture of benzene and light petroleum, boiling range 40 - 60°, to yield nitrobenzene-p-sulphonyl chloride (40 g., 70%), m.p. 79° (Meerwein *et al.* give[127] m.p. 79 - 80°).

trans-Bicyclo[4,4,0]decan-3-yl nitrobenzene-p-sulphonates.

Nitrobenzene-p-sulphonyl chloride (2.22 g., 10 mmole) and the appropriate alcohol (1.54 g., 10 mmole) dissolved in pyridine (10 ml.) were kept at 18° for 19 hr. The products were worked up *via* ether in the usual way. The results following are for samples of the nitrobenzene-p-sulphonates recrystallised from mixtures of benzene and light petroleum, boiling range 60 - 80°, to constant melting point. From the *trans*-*trans* alcohol was obtained trans-trans-bicyclo[4,4,0]decan-3-yl nitrobenzene-p-sulphonate (1.00 g., 30%),

m.p. 86.5° (Found: C, 57.8; H, 6.1. $C_{16}H_{21}O_5NS$ requires C, 57.6; H, 6.25%). From the trans-cis alcohol was obtained trans-cis-bicyclo[4,4,0]decan-3-yl nitrobenzene-p-sulphonate (1.29 g., 38%), m.p. 103.5° (Found: C, 57.7; H, 6.1 $C_{16}H_{21}O_5NS$ requires C, 57.6; H, 6.25%).

trans-cis-Bicyclo[4,4,0]decan-3-yl acetate.

A solution of trans-cis-bicyclo[4,4,0]decan-3-ol (6.00 g.) and sodium acetate (fused, 1.00 g.) in acetic anhydride (redistilled, 50 ml.) was boiled under reflux for 2 hr. The product was worked up via light petroleum in the usual way, giving after distillation trans-cis-bicyclo[4,4,0]-decan-3-yl acetate (1.02), b.p. 71°/0.2 mm., n_D^{20} 1.4702 Elsevier quotes[128] b.p. 118°/9 mm., $n_{He}^{16.8}$ 1.4720).

trans-Bicyclo[4,4,0]decan-3-one.

Following Brown's method[121] a solution of sodium dichromate dihydrate (100 g.) and sulphuric acid (75 ml.) in water (total volume 1 l.) was prepared. 50 ml. of this solution will oxidise 100 mmole of alcohol to ketone.

This solution (100 ml.) was added, over a period of 45 min., to a stirred solution of trans-cis-bicyclo[4,4,0]-decan-3-ol (30.8 g., 200 mmole) in ether (100 ml.) boiling under reflux. After a further 30 min. the product was worked up in the usual way to yield, after distillation through a

Vigreaux column (30 cm.), trans-bicyclo[4,4,0]decan-3-one (30.75 g., 90%) b.p. 105 - 110°/ 14 mm., n_D^{22} 1.4831 (Rao gives[129] b.p. 117°/15 mm., n_D^{22} 1.4834).

cis-Bicyclo[4,4,0]decan-2-one.

A solution of chromium trioxide (133.35 g.) and sulphuric acid (115 ml.) in water (total volume 500 ml.) was titrated into an ice-cold, stirred solution of cis-cis-bicyclo-[4,4,0]decan-2-ol (prepared by Dr. J. W. Powell; 1.54 g.) in acetone ("AnalaR", 17.5 ml.) until the solution was green. The product was worked up in the usual way but was not purified.

Methanesulphonylhydrazones of decalones.

cis-Bicyclo[4,4,0]decan-3-one methanesulphonylhydrazone had been prepared by Dr. Powell. The remaining three compounds were prepared by adding a solution of the ketone in ethanol to a hot solution of methanesulphonyl hydrazide (previously prepared by Dr. P. Oberhänsli) and allowing the solution to stand at 0° for 24 hr. The resulting crystals were collected and used for the preparations of olefines without further crystallisation. The results are summarised below.

Ketone	cis-2	trans-2	trans-3
Weight of ketone (g.)	1.44	1.47	2.50
Vol. of ethanol for ketone (ml.)	1.4	1.5	0.0
Weight of $MeSO_2NHNH_2$ (g.)	0.89	0.91	1.87
Weight of product (g.)	1.76	1.96	6.91
Yield (%)	89	96	75
M.p. (°)	177-178	184-185	123
Powell's[7] m.p.	165.5	180-182	123

Binary mixtures of octalins.

Sodium (0.15 g.) and acetamide (Harringtons', redistilled, b.p. 109°/17 mm., 5 g.) in a test tube with a "Quickfit" neck were heated in an oil bath to 100° at a pressure of 15 mm. When all the sodium had dissolved, air was admitted and the methanesulphonylhydrazone was added. A reflux air condenser was added and the temperature of the bath was increased to 160° and maintained at this until the evolution of nitrogen had ceased. The bath was cooled to 90° and water (5 ml.) was added. When the temperature of this aqueous solution had dropped to 25°, the octalins were extracted with light petroleum (benzene-free, 2 x 1.5 ml.).

Such solutions were used for gas-liquid chromatographic work. The octalins derived from each methanesulphonylhydrazone are summarised on p. 10.

trans-Bicyclo[4,4,0]dec-3-ene.

The octalin was prepared from the dibromide following Johnson's procedure[73]. trans-Bicyclo[4,4,0]dec-3-ene dibromide (m.p. 81 - 85°, prepared by Dr. P. Oberhänsli; 11.3 g.), zinc (powder, "AnalaR", 20 g.) and ethanol (90 ml.) were stirred for 1.5 hr. at 18° and for 2.5 hr. at 65°. The product was worked up *via* ether in the usual way except that the ethereal solution was finally washed with a saturated aqueous solution of calcium chloride and was dried over calcium chloride. Removal of ether through a Dufton column (20 cm.) and distillation of the residue afforded trans-bicyclo[4,4,0]-dec-3-ene (3.58 g.), b.p. 70 - 71°/20 mm., n_D^{25} 1.4794 (Johnson *et al.* give[73] b.p. 59°/8 mm., n_D^{25} 1.4796).

trans-Decalin.

trans-Bicyclo[4,4,0]decan-3-one (20.0 g.), triethylene glycol (100 ml.), "hydrazine hydrate" (10 ml.) and potassium hydroxide (13 g.) were boiled under reflux for 1 hr. The temperature of reflux was raised to 170°, the more volatile material being removed in a Dean-Stark apparatus. The boiling

under reflux was continued for 16 hr. The distillate in the Dean-Stark apparatus was added to the reaction mixture and the total was worked up *via* ether in the usual way. Chromatography of the product (18 g.) on alumina (500 g.) and elution with light petroleum afforded, after distillation through a Vigreaux column (30 cm.), *trans*-decalin (15.7 g.), b.p. 63 - 64°/11 mm.

Mixture of decalins for gas-liquid chromatography.

Commercial decalin (Harrington) was drained through a column of dry-packed silica ("Sorbsil", 0.5 lb.). The first 80 ml. were collected and showed no absorption at wavelengths higher than 240 m . (1 cm. uncompensated cell). Distillation of this material afforded decalins, b.p. 96 - 99°/30 cm. Gas-liquid chromatography on column "IA", p. 28B, indicated the material to free of less volatile hydrocarbons, to contain less than 0.01% of any octalins, and to be 42.4% *cis* (mean of 10 injections, range of results 41.5 - 43.1%).

GAS-LIQUID CHROMATOGRAPHY.

Packing of columns.

The columns were prepared by Mr. A. E. Thompson's staff. They consisted of copper tube (Yorkshire Imperial Metal Company, 3/16" O.D., 3.25 mm. bore) in 2 m. lengths with standard petrol couplings (1/8" gas thread) silver soldered on to their ends. Longer columns consist of such lengths bolted together.

The columns were cleaned internally with dilute chromic acid (prepared by mixing equal volumes of 20% w/v aqueous chromium trioxide and 20% v/v aqueous sulphuric acid) and, after thorough washing with water and acetone, they were dried by sucking air through them.

The support material, coated with stationary phase, was sieved to 60 mesh and was packed into the 2 m. lengths using a mechanically agitated hopper as described by Clarke[130].

Stationary phases.

"GEO-100", m.p. 61 - 62° and "GPO-6" (see pp. 21 and 27) were kindly supplied to Dr. M. C. Whiting by the Research Department of Messrs. Unilever, Ltd.

Polypropylene oxide ("Hexaplas") was kindly supplied by Imperial Chemical Industries.

The following phases were obtained comercially:

1,1-oxydiglycerol ("Diglycerol suitable for gas chromatography", May and Baker), silicone fluid MS 704 (Hopkin and Williams), β,β'-oxydipropionitrile (Applied Science Laboratories, Inc.), 8-ethoxycarbonyltetrahydrothiphen-1,1-dioxide (Whiffen), "Apiezon-L" (Shell).

All "silver phases" were prepared by dissolving silver nitrate ("AnalaR") in the phase before use.

The preparations of the remaining phases follow.

1,2-Bis(2'-cyanoethoxy)ethane.

Acrylonitrile (freshly distilled, 79.0 g., 1.49 mole) was added dropwise over a period of 2 hr. to a vigorously stirred mixture of glycol (37.34 g., 0.745 mole) and aqueous potassium hydroxide solution (40% w/v, 2.24 g.) maintained at 25 - 28°. The rate of addition was such that no separate layer of acrylonitrile was allowed to form. If this precaution is ignored the violently exothermic polymerisation of acrylonitrile may occur. After the addition, stirring was continued for 18 hr.

Water (50 ml.) was added, followed by aqueous hydrochloric acid (5 N) until the pH was below 2. The product was extracted with 1,2-dichloroethane (3 x 100 ml.). Removal of solvent and distillation through a Dufton column (20 cm.) yielded 1,2-bis(2'-cyanoethoxy)ethane (62.4 g., 50%), b.p. 150 - 152°/1 mm.(Bruson and Riener give[131] b.p.158°/2 mm.).

Absence of hydroxyl groups in the product was established by infrared spectroscopy.

1,3-Bis(2'-cyanoethoxy)propane.

Cyanoethylation of propane-1,3-diol (16.25 g.) with acrylonitrile (22.7 g.) in the presence of 40% aqueous potassium hydroxide (0.95 g.) followed by the work-up (both as for the previous experiment) yielded 1,3-bis(2'-cyanoethoxy) propane (16.75 g., 52%), b.p. 140 - 143°/0.2 mm. (Bruson and Riener give[131] b.p. 161°/1 mm.).

Absence of hydroxyl groups in the product was established by infrared spectroscopy.

1,5-Bis(2'-cyanoethoxy)pentane.

Cyanoethylation of pentane-1,5-diol (16.39 g.) with acrylonitrile (19.7 g.) in the presence of 40% aqueous potassium hydroxide (0.98 g.) followed by the work-up (both as before) yielded 1,5-bis(2'-cyanoethoxy)pentane (21.18 g., 76%), b.p. 160 - 165°/0.2 mm. (Bruson and Riener give[131] b.p. 185°/1 mm.).

Absence of hydroxyl groups in the product was established by infrared spectroscopy.

Coating support material with stationary phase.

The support material was May and Baker's "Embacel", an

acid-washed and graded kieselguhr of 60 - 100 mesh.

The stationary phase was dissolved in an appropriate solvent. These solvents were as follows.

For GPO-6, GEO-100 and diglycerol.....	Methanol
For all cyanoethyl phases, polypropylene adipate and 3-ethoxycarbonyltetrahydrothiphen-1,1-dioxide.....	Dichloromethane
Apiezon-L.....	Ether
MS 704.....	Light Petroleum.

The solution of the phase was added to a weighed quantity of Embacel. Note that a 15% phase refers to 15% of phase relative to the total quantity of phase and Embacel. When dissolving the phase, ca. 4 ml. of solvent should be allowed for each gramme of Embacel, to afford an even slurry. The solvent was removed immediately at 15 mm. The temperature was raised to 100° until the solid was sufficiently dry for the particles to cease to cohere. The drying was completed by drawing air over the material.

Injection.

Injection was effected by plunging the needle of a "Microliter Syringe" (supplied by the Hamilton Co.) through a serum cap. The inlet-heater consisted of a small jet of

burning gas emerging from a hypodermic needle playing on a short vertical length of brass tube with a "liner" consisting of a length of glass tube of appropriate width to give a tight fit.

Siliconisation of prepared packing material.

Hexamethyldisilazane (Lights, 50 µl.) was injected through an inlet heater on to the column (1,2-bis(2'-cyanoethoxy)ethane/Embacel, 5%, 8 m.). The column was at a temperature of 100° and carrier gas (nitrogen) at an inlet pressure of ca. 80 cm. flowed through for 12 hr.

For this experiment the outlet of the column was screwed on to a tube which led the gas away in order that the detector should not be contaminated with silicon compounds.

Such direct injections of hexamethyldisilazane has been recommended by Horning[67]. The effect in the present case can be judged from table 9 of Part I, p.28B.

Areas of Chromatograph Peaks.

The area of a peak is the area of the envelope formed by the curve and the extension of the base-line under the curve. These areas were measured with a planimeter (Stanley, Sliding Bar, Rule-Form). The planimeter was taken round each peak three times and the mean reading was used. For

incompletely resolved peaks, a perpendicular was dropped from the minimum to the base-line and the two areas so defined were regarded as the separate peaks. Columns used for the present work were sufficiently long for this latter procedure only to be required with minima very near the base-line for, although Pecsok claims the method to be applicable to very poorly resolved peaks[132], it is doubtful whether the approximation is justifiable for unsymmetrical peaks.

Some recent chromatograms were recorded on an integrating recorder (Model 213 Disc Integrator supplied by Disc Instruments, Inc. and fitted to a Sunvic Model 10S recorder). Yields estimated in this way are marked by "i" in tables 2 and 3, pp.98A and 99A.

Mr. R. M. Southam has recently shown the two methods to be of comparable accuracy.

ANALYSES OF PRODUCTS FROM ACETOLYSES AND RELATED REACTIONS.

Solutions of metal acetates in acetic acid.

Acetic acid was dried by distilling it through a Fenske column from a solution of acetic anhydride in commercial acetic acid (*ca.* 10% anhydride v/v).

Potassium and sodium acetate solutions were prepared by dissolving the requisite quantity of recently fused anhydrous acetate in the dried acetic acid.

Caesium acetate solutions were prepared by dissolving caesium carbonate dihydrate in the acid; the quantity of acetic anhydride required to destroy the water was added. Lithium acetate solutions were prepared in the same way from lithium acetate dihydrate. In these two cases the solutions were boiled under reflux for 1 hr. to ensure completion of the reaction of water with acetic anhydride.

Acetolyses of decalyl toluene-p-sulphonates - preliminary.

The quantitative reliability of the procedures described below was checked by the following observations.

As a result of a series of ten injections of a mixture of octan-1-ol and *trans*-*cis*-bicyclo[4,4,0]decan-3-ol, it was found that for calculations of weights of decalols based on chromatogram areas the ratio must be divided by 1.23. The

range of factors was 1.19 - 1.26.

After some inconsistencies found when a less rigorous method was used, it was found that, within the range of experimental error, the ratio of trans-cis to trans-trans isomers in the bicyclo[4,4,0]decan-3-yl case, measured as acetates and as alcohols, agreed, thus validating the procedure for converting acetates into alcohols. As mentioned on p.12 , it was established that the response of the detector to different alcohols was satisfactorily linear.

By obvious gas-liquid chromatographic methods, following isolation procedures described below, it was established that a sample of trans-bicyclo[4,4,0]dec-3-ene is not discernably rearranged (not more than 0.01%) when standing on alumina for 15 min. and that it is neither rearranged nor acetylated to more than the same extent when kept at 100° for 14 hr. in acetic acid.

Technique of an acetolysis: the acetolysis of decalyl toluene-p-sulphonates.

The decalyl arylsulphonate was dissolved in the appropriate acetic acid/metal acetate solution. The scale was 5 ml. or 10 ml. The ester was weighed out so that the metal acetate was in slight excess (10 - 20% excess). The appropriate markers were included (decalin for an octalin-analysis; trans-cis-bicyclo[4,4,0]decan-3-yl methyl ether

and octan-1-yl acetate for a decalol-analysis). The markers could not all be put in one solution for the method of working up solutions intended for olefine-analyses would leave in a compound (the decalyl methyl ether) of very long retention time on olefine-columns.

The solutions were sealed up in ampoules and these were placed in a water bath for the appropriate time. The temperature of those at 25° was maintained with a "Circotherm" heater/stirrer/contact-thermometer unit.

After the reaction those tubes containing solutions intended for alcohol-analysis were smashed and their contents were diluted with ether (peroxide-free, 5 ml.). This solution was added, with vigorous shaking, to a super-saturated aqueous solution of tripotassium phosphate (prepared by adding potassium hydroxide, 27.6 g., to a solution of dipotassium hydrogen orthophosphate, 90 g., in water, 60 ml.; 3 ml./ml. of acetic acid). The ethereal layer was removed by pipette. This solution was used directly for acetate-analysis in certain cases. For this purpose it was injected into a diglycerol-column (15%, 100°, 4 m., inlet pressure of nitrogen ca. 80 cm.). Otherwise the solution was cooled to -60° and rapidly filtered. In an atmosphere of nitrogen an ethereal solution of lithium aluminium hydride (prepared by distilling ether, previously dried over sodium, over lithium aluminium hydride, followed by stirring the suspension

for 5 hr. at *ca.* 18°) was added to the solution of acetates until hydrogen-evolution ceased. The resulting solution was poured, with shaking still under nitrogen, into a saturated aqueous solution of tartaric acid. The upper layer was removed and used for injection into a diglycerol-column (as above or 2 m. with inlet pressure of *ca.* 40 cm.).

Diglycerol-columns were discarded after *ca.* 30 hr. at 100°.

Those tubes containing solutions intended for olefine-analysis were smashed and the contents were poured into a mixture of light petroleum (benzene-free, 10 ml.) and water (50 ml.). The aqueous layer was discarded. The organic layer was washed with water (10 ml.) and a saturated aqueous solution of potassium hydrogen carbonate (10 ml.). It was then chromatographed on alumina (40 g.). It was rapidly eluted with light petroleum (benzene-free, 150 ml.) and evaporated to *ca.* 2 ml. through a Dufton column (20 cm.). The solution was used for injection into a column of 1,2-bis(2'-cyanoethoxy)ethane (conditions IA or IIC, table 9 of Part I, p.28B). Following recent improvements of the performance of the machines and a reduction in "dead space", conditions for operating "IA", p.28B, satisfactorily have been speeded up. It is now possible to use an inlet-pressure of 70 cm. and to complete a chromatogram (without *cis*-bicyclo-[4,4,0]dec-3-ene) in 3 hr.

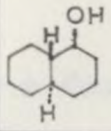
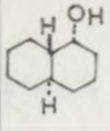
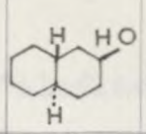
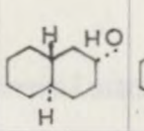
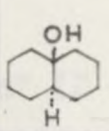
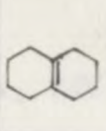
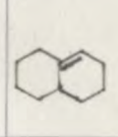
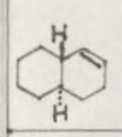
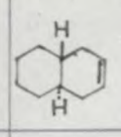
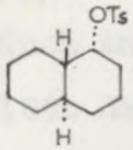
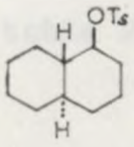
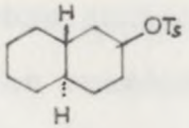
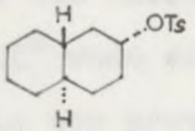
A 15% column of 1,2-bis(2'-cyanoethoxy)ethane has been in regular use at 50° for a year and is not deteriorating noticeably.

The results for the acetolyses of decalyl toluene-p-sulphonates are summarised in table 1, p.97A. The analyses on the same horizontal line in the table are for solutions (either of alcohols, acetates or olefines) obtained from the same reaction mixture. Results on different lines are from separate mixtures from independent reactions, except when otherwise indicated. This indication takes the form of brackets which join horizontal lines of analyses of solutions derived from the same reaction mixture.

Acetolysis of cis-bicyclo[4,4,0]decan-1-yl 3,5-dinitrobenzoate.

The kinetics of this reaction were unknown. A sample of the dinitrobenzoate (ca. 200 mg.) and a few drops of decalin were dissolved in the usual solution (0.15 M KOAc in HOAc; 10 ml.). This solution was divided and sealed in five ampoules (group 1). A similar solution was prepared containing octan-1-yl acetate and in which all the components were accurately weighed out. This solution was divided into two ampoules (group 2). All the ampoules were kept at 100°. Ampoules from group 1 were occasionally removed and the contents were worked up for olefine-analysis (pp.29 and 96). The resulting solutions (of decalins and octalins) were

Table 1.

Starting Material										TOTAL	TOTAL ALCOHOL	TOTAL OLEFINE	RETENTION / INVERSION
	0·64	1·04			7·06					94·7	8·74		1·64
						54·1	30·7	1·20				86·0	
N	0·68	1·10			7·45	57·1	32·4	1·26		100	9·22	90·8	1·64
	16·3	33·9	0·46	0·57	0·40						51·6		0·48
						10·6	29·0	11·2	4·02	106·5		54·8	
	15·8	32·1	0·41	0·53	0·345					104·0	49·2		0·49
N	15·25	31·35	0·41	0·52	0·35	10·1	27·6	10·6	3·82	100	47·9	52·1	0·485
	0·034	0·35	3·57	7·91	0·088						11·95		0·451
						0·54	0·59	25·5	57·6	96·18		84·2	
	<0·01	0·355	4·28	7·32	0·097					96·28	12·05		0·585 (A) 0·525
N	0·018	0·365	4·03	7·80	0·095	0·55	0·60	26·1	59·1	100	13·3	86·35	0·520
			33·2	2·31							35·5		0·0695
						0·47	0·09	24·1	41·1	101·3		65·8	
													(B) 0·0652 (A) 0·0635
						Not suspected		22·2	37·6	102·91		67·4	
N			33·3	2·17		0·47	0·09	23·7	40·2	100	35·5	64·5	0·0661

N = Results averaged and/or normalised.

A = Analysis of acetates without markers.

B = Analysis of alcohols without markers.

injected into a fast rough "olefine-column" (2 m., 15% β,β'-oxydipropionitrile, 50°, inlet-pressure ca. 40 cm.). Such analyses of group 1 ampoules removed on the 12th and 13th days showed an unchanged ratio of cis-decalin/octalins. Ampoules in group 2 were removed on the 13th day and were worked up and analysed in the usual way; the results are in table 2, p.98A.

Acetolyses of trans-β-decalyl nitrobenzene-p-sulphonates.

The products from these reactions at 100° and at 25° were analysed. The kinetics of the reactions were unknown. The reaction-times for the reactions at 100° were 1/5th of the times allowed for the toluene-p-sulphonates; comparison with the 2-octyl system suggested that this would be ample[109]. This allowance makes the assumption that the ρ-correlations are the same for the two systems; in fact an extra factor of 2 was allowed in the present case. The reaction-times at 25° were calculated by a method similar to the one described in the previous section ("Acetolysis of cis-bicyclo[4,4,0]-decan-1-yl 3,5-dinitrobenzoate", p.97). Solutions of the nitrobenzene-p-sulphonates and decalin in the potassium acetate/acetic acid solution were divided and sealed in many ampoules. The usual set of quantitative solutions (two for olefine-analysis, two for alcohol-analysis, one for acetate-

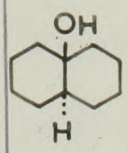
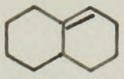
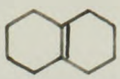
				Total
	0·24	25·7	41·4	67·3
		28·7	43·4	72·1
Average	0·24	27·2	42·4	69·8

Table 2. Yields of products from the acetolysis of cis-bicyclo[4,4,0]decan-1-ol.

Yields of olefine were measured with the integrator.

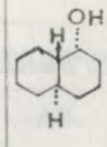
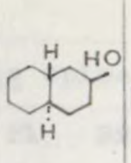
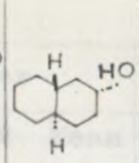
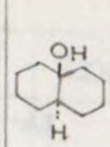
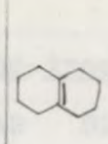
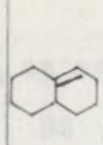
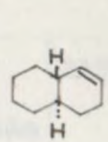
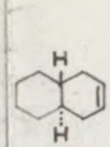
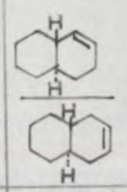
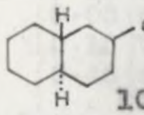
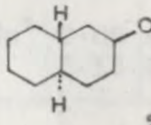
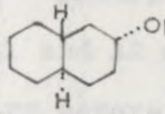
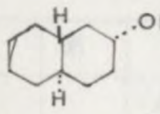
analysis, see p.95) was made up for each sulphonate. All the ampoules were kept at 25°. After 2 weeks, two of the "kinetic" ampoules containing trans-trans epimer were removed; one was heated to 100° for 1 hr. and both were worked up and analysed (for cis-decalin/octalins) as before (p.97). The results were the same (within 1%) and the other ampoules of trans-trans epimer were removed and the complete analyses were performed. The same procedure was adopted with the trans-cis epimer; in this case the total reaction-time was 8 weeks.

The results are summarised in table 3, p.99A. The same conventions apply as before (p.97). See p.92 for the significance of "i".

Effect of Cations.

The general method was as before. Markers were omitted and only acetate-analyses were performed. Each run (with different cations and/or concentrations) were duplicated. The planimetered areas from each trace were expressed as %'s of total acetate and these were averaged. The results are summarised in tables 4 and 5, p.99B. It can be seen that the variations are almost within experimental error.

Table 3.

									TOTAL	Total olefine	Total alcohol	Retention Inversion	
 100°	0·32	3·20	8·12	0·18	i 0·73	i 0·50	i 25·4	i 50·4	88·95	77·13	11·82	0·39	0 0·46 0·44
N	0·36	3·60	9·13	0·20	0·82	0·56	28·55	56·8	100	86·71	13·3		
 25°		3·29 3·53	8·72 10·0		0·25 i 0·25	i 0·70	i 20·6	i 49·8	86·6 85·3	71·34	12·01 13·53	0·40 0·35	
N		4·03	11·07		0·30	0·82	24·3	58·9	100	84·9	15·10	0·37	
 100°		26·1	1·40		i 0·97 i 0·84	i 0·38 i 0·35	i 24·2 i 24·6	40·9 i 40·9 i 40·2	93·85 93·49	66·35 65·99	27·50	0·054 0·079 A	
N		27·9	1.50		0·90	0·37	26·3	43·0	100	70·58	29·42	0·066	
 25°		27·6	2·47		i 1·00 i 0·59	i 0·37 i 0927	i 18·1 i 19·6	i 34·9 35·3	84·4 85·8	54·4 55 8	30·7	0·090	
N		32·4	2·90		0·94	0·38	22·1	41·2	100	64·7	35·3		

A = analysis of acetates without marker.

C = analysis of olefines without marker.

N = normalised and averaged results.

	M	trans-cis epimer					trans-trans epimer					RATIO
		A1	A2	B1	B2	Mean	A1	A2	B1	B2	Mean	
Li^+	0·01	6·65	5·62	5·86	5·67	5·95	93·4	94·4	94·2	94·2	94·1	0·063
	0·05	6·86	7·57	7.20	6·73	7.59	93·1	92·4	90·8	93·3	92·4	0·082
	0·15	7·85	6·42	6·64	7.30	7·05	92·1	93·6	93·4	92·6	92·9	0·076
	0·45	6·62	6·32	6·54	6·69	6.54	93·4	93·8	93·3	93·3	93·5	0·070
Na^+	0·05	7·01	7·55	8·19	6·72	7.42	92·8	92·3	91·7	93·2	92·5	0·080
	0·15	7·59	7·59	6·89	7·50	7.39	92·4	95·5	93·2	93·8	91·0	0·081
K^+	0·05	6·02	5·92	5·90	7·88	6.40	94·7	94·1	94·4	96·4	94·9	0·068
	0·15	7·05	6.89	7.76	8·06	7·69	92·2	92·2	93·0	92·0	92·4	0·083
Cs^+	0·05	6·08	6·18	6·78	7·24	6·57	93·8	93·7	93·4	92·8	93·4	0·070
	0·15	8·42	7·44	7·12	7·24	7·55	91·7	92·5	92·8	92·8	92·5	0·082

Table 4. Acetolysis of trans-cis-bicyclo[4,4,0]decan-3-yl toluene-p-sulphonate.

M = molarity of metal acetate.

A1 and A2 are separate injections of the same sample; A and B are separate solutions. The ratio is the ratio of (retention/inversion).

	M	trans-trans epimer					trans-cis epimer					RATIO
		A1	A2	B1	B2	Mean	A1	A2	B1	B2	Mean	
K^+	0·03	32·4	32·9	35·0	32·0	33·0	67·6	67·1	65·0	67·6	66·8	0·494
	0·15	31·6	30·8	31·9	31·7	31·5	68·4	69·2	68·1	68·3	68·5	0·463

Table 5. Acetolysis of trans-trans-bicyclo[4,4,0]decan-3-yl toluene-p-sulphonate.

The conventions are as in table 4.

Acetolyses of toluene-p-sulphonates in the presence of potassium naphthalene-β-sulphonate.

All spectra were recorded in solution in cyclohexane (B.D.H. "special for spectroscopy"). The spectra of trans-cis-bicyclo[4,4,0]decan-3-yl toluene-p-sulphonate and naphthalene-β-sulphonate are reproduced below, fig. 1.

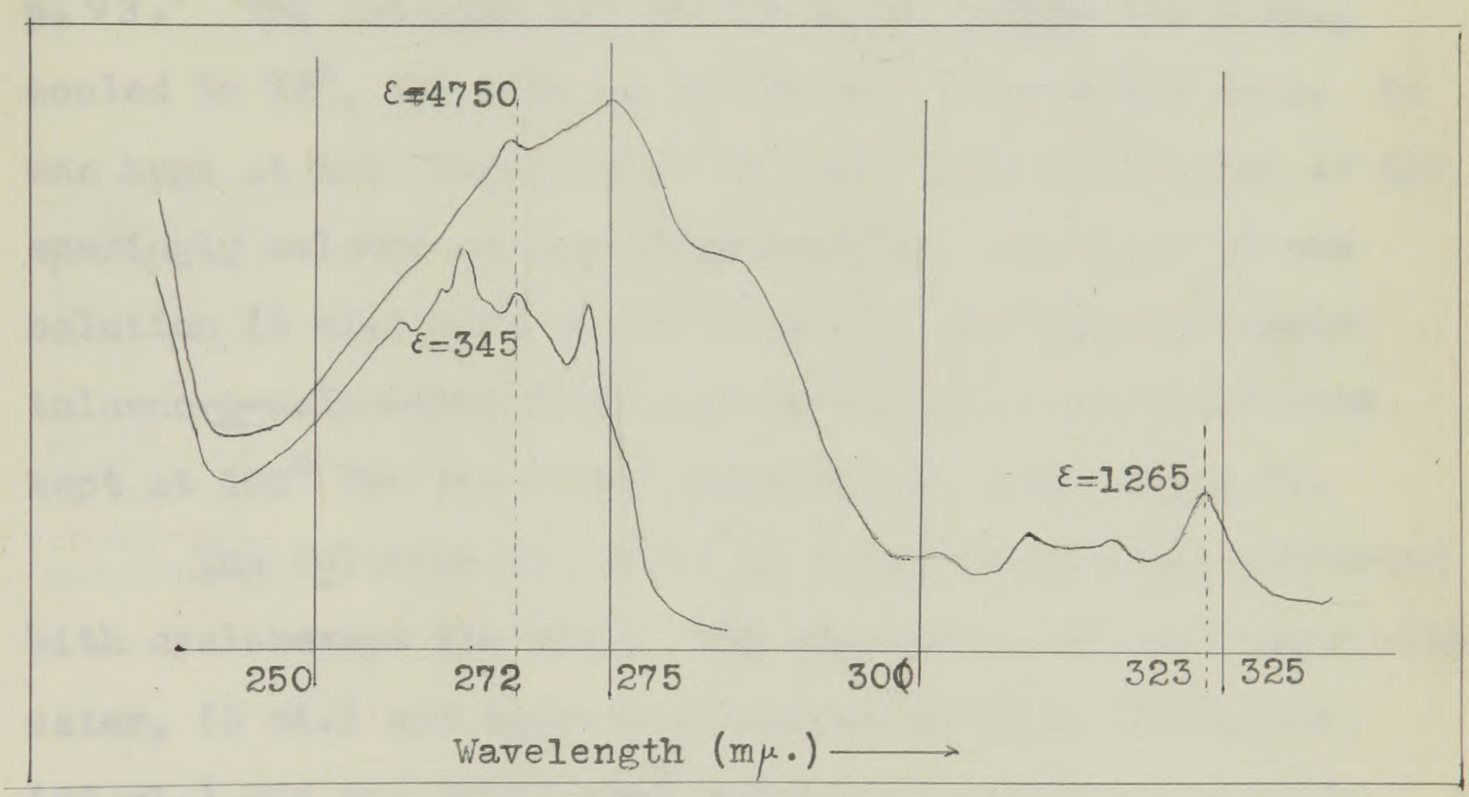


Fig. 1. The spectrum of the toluene-p-sulphonate (lower curve) is on 10 times the scale of the other.

Cyclohexane-extracts of available samples of naphthalene-β-sulphonic acid (B.D.H.) showed strong absorption at wavelengths above 250 mμ. The impurity was removed by extracting an aqueous solution of the sodium salt with ether and regenerating the acid in the usual way. Recrystallisation from aqueous hydrochloric acid (ca. 5 N) followed by drying

in vacuo over sodium hydroxide afforded naphthalene-β-sulphonic acid trihydrate, m.p. 83° (Witt gives[133] m.p. 83°).

Naphthalene-β-sulphonic acid trihydrate (3.39 g., 0.015 mole), potassium acetate (2.94 g., 0.30 mole) and acetic anhydride (4.68 g., 0.045 mole) were dissolved in acetic acid. All materials were of purities mentioned on p. 93. The solution was boiled under reflux for 2 hr., cooled to 75°, and made up to 100 ml. with acetic acid. It was kept at this temperature to avoid crystallisation of the sparingly soluble potassium sulphonate. Portions of the solution (5 ml.) were sealed with the appropriate decalyl toluene-*p*-sulphonate (150 mg.) in ampoules and these were kept at 100° for the times indicated in table 6, p.102.

The solution was added to water (5 ml.) and extracted with cyclohexane (10 ml.). The organic layer was washed with water, (5 ml.) and aqueous potassium hydrogen carbonate (25 ml.) and was dried over magnesium sulphate. A blank solution of potassium acetate and sulphonate was extracted in the same way and the extract was used in the compensating cell of the spectrophotometer. If the solution required dilution, the cyclohexane in the compensating cell was "diluted" to the same extent with fresh cyclohexane. From the peak at 323 mμ., the concentration of naphthalene-β-sulphonate was calculated. From this figure, the absorbance due to naphthalene-β-sulphonate at 272 mμ. was calculated.

From the difference between this and the experimental value the concentration of toluene-p-sulphonate was calculated. The ratio of naphthalene-β-sulphonate to toluene-p-sulphonate and the concentration of total sulphonate in the cyclohexane (and hence the % reaction) were calculated from these figures (see table 6).

	Time (min.)	% reaction	Ratio naphthalene-β-sulphonate to total sulphonate (%)
trans-trans-Bicyclo[4,4,0]-decan-3-yl toluene-p-sulphonate	10	78·6	2.48
	20	91·9	6·08
	40	97·8	7.32
trans-cis-Bicyclo[4,4,0]-decan-3-yl toluene-p-sulphonate	10	40.3	0·676
	20	63·0	0·863
	40	77.5	0.830

Table 6.

Toluene-p-sulphonic acid.

Water in excess of the stoichiometric composition was removed from toluene-p-sulphonic acid monohydrate by azeotropic distillation with toluene followed by recrystallisation from chloroform. The acid was dissolved in dry acetic acid, with the theoretical quantity of acetic anhydride to destroy the water, to make a solution M/2.

Tetrahydrofuran.

Commercial tetrahydrofuran (B.D.H. stabilised) was boiled under reflux over potassium hydroxide pellets for 15 hr. The liquid was transferred by distillation to second vessel and lithium aluminium hydride was carefully added until hydrogen-evolution ceased. It was then boiled under reflux for 8 hr. and transferred to a third vessel by distillation. It was used immediately.

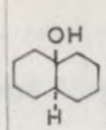
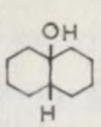
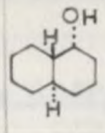
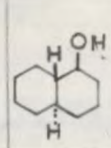
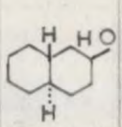
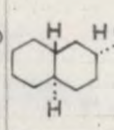
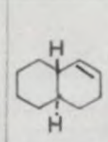
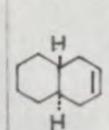
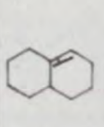
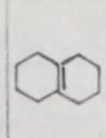
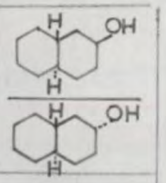
Reaction of trans-bicyclo[4,4,0]dec-3-ene with toluene-p-sulphonic acid in acetic acid; the effect of tetrahydrofuran on the reaction.

trans-Bicyclo[4,4,0]dec-3-ene (ca. 0.1 g.), decalin (ca. 0.1 g.) and octan-1-yl acetate (ca. 0.1 g.) were weighed out and the volume was made up to 25 ml. with a solution of toluene-p-sulphonic acid (M/2) in acetic acid. The solution was sealed in two ampoules. Two other pairs were prepared with 1 ml. and 5 ml. of tetrahydrofuran added.

The tubes were kept at 100° for 15 hr. The contents of each tube were divided into two parts, one of which was analysed for olefines, the other for acetates and alcohols.

The results are in table 7, p.103A. Other details were as before (p. 93).

Table 7.

Amount of THF							Other Alcohol	Total alcohols					Total olefines	TOTAL	
	0·14	1·19	1·01	0·84	31·6	23·1	0·08	57·95	2·15	3·64	1·86	10·73	18·38	76·3	1·37
NONE	0·06	0·70	0·86	0·34	27·4	20·8	0·06	50·215						68·8	1·32
	0·10	1·02	0·75	0·58	30·2	21·8	(a)	54·45						72·8	1·32
															1·27 A
Average	0·10	0·97	0·87	0·59	29·9	21·9	0·07	54·2						72·6	1·34
	0·05	0·00	0·86	0·00	43·3	11·7	0·00	55·9	4·94	8·20	1·64	13·42	28·21	84·1	3·72
Equimolar	0·07	0·00	0·80	0·00	40·8	13·7	0·00	55·4						83·5	2·98
to		0·00	0·805												
TsOH B															2·96 A
Average	0·06	0·00	0·82	0·00	42·6	12·2	0·00							83·8	3·22
5 x molar	0·03	0·10	0·22	0·00	21·4	3·61	0·00	25·26	10·12	48·2	1·36	1.59	60·19	85·7	4·76
XS over	0·03	0·09	0·23	0·00	21·5	3·95	0·00	25·88						86·1	5·45
TsOH															5·55 A
Average	0·03	0·095	0·225	0·00	21·45	3·78	0·00	25·6						85·9	5·25

A - Analysis of acetates without marker.

B - Partial analysis on short column to check the absence (less than 0·01 %) of cis-bicyclo[4,4,0]-decan-1-ol.

(a) - This peak is between trans-trans-bicyclo[4,4,0]-decan- 2- and 3- ols. It could not be seen in this analysis which was on a 2 m. column.

REFERENCES.

1. Winstein and Holness, J. Amer. Chem. Soc., 1955, 77, 5562.

2. Campbell, Part II Thesis, Oxford, 1964.

3. Clarke, Part II Thesis, Oxford, 1961; D. Phil. Thesis, Oxford, 1963; Carr, Clarke and Whiting, Proc. Chem. Soc., 1963, 333.

4. Southam, Part II Thesis, Oxford, 1963.

5. (a) Hückel, Tappe and Legutke, Annalen, 1940, 543, 206;
(b) Hückel, Bross, Fechtig, Feltkamp, Geiger, Hanack, Heinzel, Hubele, Kurz, Maier, Maucher, Naher, Neidlein and Rashingkar, Annalen, 1959, 624, 142.

6. Powell and Whiting, Tetrahedron, 1961, 12, 169.

7. Powell, D. Phil. Thesis, Oxford, 1960.

8. Powell and Whiting, Proc. Chem. Soc., 1960, 412.

9. Oberhänsli, D. Phil. Thesis, Oxford, 1962.

10. IUPAC - Nomencleture of Organic Chemistry, Butterworths, London, 1957, 32.

11. Hückel, Annalen, 1938, 533, 1.

12. Dauben, Tweit and Mannerskantz, J. Amer. Chem. Soc., 1954, 76, 4420.

13. Hückel, Maucher, Fechtig, Kurz, Heinzel and Hubele, Annalen, 1961, 645, 115.

14. Hückel and Rashingkar, Annalen, 1960, 637, 20.

15. Hückel et al., op. cit.[5b], p. 238.

16. Powell and Whiting, Tetrahedron, 1961, 12, 163.

17. Oberhänsli, op. cit.[9], p. 29.

18. Adkins and Billica, J. Amer. Chem. Soc., 1948, 70, 695.

19. Durland and Adkins, J. Amer. Chem. Soc., 1939, 61, 429.

20. Hückel et al., op. cit.[13], p. 144.

21. Schubert and Pease, J. Amer. Chem. Soc., 1956, 78, 5553.

22. Alder, D. Phil. Thesis, Oxford, 1962.

23. Mareš, Roček and Silner, Coll. Czech. Chem. Comm., 1961, 26, 2355; Mareš and Roček, ibid., 2370.

24. Wiberg and Eisenthal, Tetrahedron, 1964, 20, 1151.

25. Powell and Whiting, Tetrahedron, 1959, 7, 305.

26. Benkeser and Kaiser, J. Org. Chem., 1964, 29, 955.

27. Clarke, D. Phil. Thesis, Oxford, 1963.

28. Thompson, J. Chromatog., 1959, 2, 148.

29. Bayer, Gas Chromatography, Elsevier, London, 1961, 50.

30. Purnell, Gas Chromatography, Wiley, New York and London, 1962, 320.

31. McWilliam and Dewar, Gas Chromatography, 1958, Butterworth, London, Ed. Desty, 144.

32. Condon, Scholly and Averill, Gas Chromatography 1960, Butterworth, London, Ed. Scott, 30.

33. Middlehurst and Kennet, J. Chromatog., 1963, 10, 294.

34. Sternberg, Gallaway and Jones, Gas Chromatography, Academic Press, New York, Ed. Brenner, Callen and Weiss, 1962, 245.

35. Calcote and King, 5th Symposium on Combustion, Reinhold, New York, 1955, 423.

36. Lewis and von Elbe, Combustion, Flames and Explosions, Academic Press, New York, 1961, 558.

37. Ettre, J. Chromatog., 1962, 8, 525.

38. Ongkiehong, Gas Chromatography 1960, Butterworth, London, Ed. Scott, 7.

39. Desty, Geach and Goldup, Gas Chromatography 1960, Butterworth, London, Ed. Scott, 46.

40. Purnell, op. cit.[30], p. 244.

41. Bayer, op. cit.[29], p. 45.

42. Bradford, Harvey and Chalkley, J. Inst. Petroleum, 1955, 41, 80.

43. Janák, J. Chromatog., 1960, 3, 308.

44. Clarke, Unpublished Work.

45. The International Conference of Benzole Producers, J. Chromatog., 1963, 12, 293.

46. van den Dool and Kratz, J. Chromatog., 1963, 11, 463.

47. Ray, J. Appl. Chem., 1954, 4, 21.

48. Bayer, op. cit.[29], p. 13.

49. Knox, Gas Chromatography, Methuen, London, 1962, 24.

50. Purnell, op. cit.[30], p. 117.

51. van Deemter, Zuiderberg and Klinkenberg, Chem. Eng. Sci., 1956, 5, 271.

52. Knox, op. cit.[49], p. 28.

53. Knox, op. cit.[49], p. 25.

54. Purnell, op. cit.[30], p. 336.

55. Bayer, Angew. Chem., 1959, 71, 299.

56. Brown, J. Chromatog., 1963, 10, 284.

57. Kuffner and Kalina, Monatsh., 1959, 90, 463; 1960, 91, 289.

58. Cardnell, D. Phil. Thesis, Oxford, to be submitted.

59. Cruikshank and Everett, J. Chromatog., 1963, 11, 289.

60. Keulemans, Kwantes and Zaal, Analyt. Chim. Acta, 1955, 13, 369.

61. Fredericks and Brooks, Analyt. Chem., 1956, 28, 297.

62. Knight, Analyt. Chem., 1958, 30, 9.

63. Armitage, J. Chromatog., 1959, 2, 655.

64. Bendel and Kern, Angew. Chem. - International Edition, 1962, 1, 599.

65. Trieselt, Gas Chromatography 1962, Butterworth, London, Ed. van Swaay, 117.

66. Boheman, Langer, Perrett and Purnell, J., 1960, 2445.

67. Horning, Private Communication to Professor Sir Ewart Jones

68. Moritani, Nishida and Murakami, J. Amer. Chem. Soc., 1959, 81, 3420.

69. Goering, J. Amer. Chem. Soc., 1956, 78, 4931.

70. Klyne and Prelog, Experientia, 1960, 16, 521.

71. Sachse, Ber., 1890, 23, 1363.

72. Hazebroek and Oosterhoff, Disc. Far. Soc., 1951, 10, 87.

73. Johnson, Bauer, Margrave, Frisch, Dreger and Hubbard, J. Amer. Chem. Soc., 1961, 83, 606.

74. Hendrickson, J. Org. Chem., 1964, 29, 991.

75. Anet, Ahmed and Hall, Proc. Chem. Soc., 1964, 145.

76. Hendrickson, J. Amer. Chem. Soc., 1961, 83, 4537.

77. Allinger and Frieberg, J. Amer. Chem. Soc., 1960, 82, 2393.

78. Armitage, Kenner and Robinson, Tetrahedron, 1964, 20, 747.

79. Hückel and Hanack, Annalen, 1958, 616, 18.

80. Hückel, Acta Chim. Acad. Sci. Hung., 1959, 18, 27.

81. Streitwieser and Walsh, Tetrahedron Letters, 1963, 1, 27.

82. Gleave, Hughs and Ingold, J., 1935, 236.

83. Ingold, Structure and Mechanism in Organic Chemistry, Bell, London, 1935, 306.

84. Doering and Zeiss, J. Amer. Chem. Soc., 1953, 75, 4733.

85. Hyne and Robertson, Canad. J. Chem., 1956, 34, 863.

86. Swain and Eddy, J. Amer. Chem. Soc., 1948, 70, 2989.

87. Winstein, Grunwald and Jones, J. Amer. Chem. Soc., 1951, 73, 2700.

88. Streitwieser, Solvolytic Displacement Reactions, McGraw-Hill, New York, 1962, 171.

89. Bird, Hughs and Ingold, J., 1954, 634.

90. Gold, J., 1956, 4633.

91. Brown and Moritani, J. Amer. Chem. Soc., 1955, 77, 3623.

92. Brown, The Transition State, Special Publication no. 16, Chemical Society, London, 1962, 140.

93. Foote and Woodward, Tetrahedron, 1964, 20, 687.

94. Brown, Science, 1946, 103, 385.

95. Doering, Levitz, Sayigh, Sprecher and Whelan, J. Amer. Chem. Soc., 1953, 75, 1008.

96. Doering and Finkelstein, unpublished work quoted by Streitwieser, op. cit.[88], p. 70.

97. Grunwald and Winstein, J. Amer. Chem. Soc., 1948, 70, 846.

98. Kosower, J. Amer. Chem. Soc., 1958, 80, 3253.

99. Stranathen, J. Chem. Phys., 1938, 6, 395.

100. Appendix (compiled by Sidgwick), Trans. Far. Soc., 1934, 30, i (Following p. 94).

101. Groves and Sugden, J., 1935, 971.

102. Hückel, Theoretical Principals of Organic Chemistry, Elsevier, Amsterdam, 1958, vol. II, 147.

103. Winstein, Clippinger, Fainberg, Heck and Robinson, J. Amer. Chem. Soc., 1956, 78, 328.

104. Winstein and Robinson, J. Amer. Chem. Soc., 1958, 80, 169.

105. Mossel, Romers and Havinga, Tetrahedron Letters, 1963, 19, 1247; Groth and Hassel, Proc. Chem. Soc., 1963, 218; Stolow and Bonaventura, Tetrahedron Letters, 1964, 2, 95.

106. Djerassi, Chemical Society Centenary Lecture, Oxford, 1964.

107. Nace, J. Amer. Chem. Soc., 1952, 74, 5937.

108. Pappas, Keschino, Fournier and Nace, J. Amer. Chem. Soc., 1956, 78, 1967.

109. Southam and Whiting, unpublished work.

110. Hückel et al., op. cit.[5b], p. 156.

111. Hückel et al., op. cit.[13], p. 122.

112. Hückel et al., op. cit.[5b], p. 150.

113. Turner, Meador and Winkler, J. Amer. Chem. Soc., 1957, 79, 4122.

114. Lillien and Khaleeluddin, Chem. and Ind., 1964, 1028.

115. Eliel, Gianni, Williams, and Stother, Tetrahedron Letters, 1962, 741.

116. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, Pergamon, Oxford, 1959, 117.

117. Bothner-By and Naar-Colin, Ann. New York Acad. Sci., 1958, 70, 833.

118. Lemieux, Kulling, Bernstein and Schneider, J.Amer.Chem.Soc. 1958, 80, 6098.

119. Shoolery and Rogers, J. Amer. Chem. Soc., 1958, 80, 5121.

120. Pople, Schneider and Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill, New York, 1959, 399.

121. Brown and Garg, J. Amer. Chem. Soc., 1961, 83, 2952.

122. Hückel and Brinkmann, Annalen, 1925, 441, 21.

123. Price and Whiting, Chem. and Ind., 1963, 775.

124. Baumgarten and Hauser, J. Amer. Chem. Soc., 1944, 66, 1039

125. Hatch and Adkins, J. Amer. Chem. Soc., 1937, 59, 1695.

126. Eisenlohr, Fortschr. Ch. Phys., 1924/26, 18, 545, Anm. 5.

127. Meerwein, Dittmar, Göllner, Hafner, Mensch and Steinfort, Ber., 1957, 90, 841.

128. Elseviers' Encyclopaedia of Organic Chemistry, Ed. Radt, 12B, 1375.

129. Rao, J., 1929, 1961.

130. Clarke, Chem. and Ind., 1962, 42, 1830.

131. Bruson and Riener, J. Amer. Chem. Soc., 1943, 65, 23.

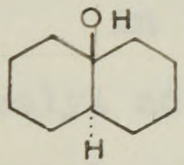
132. Pecsok, Principals and Practices of Gas Chromatography, John Wiley, New York, 1959, 147.

133. Witt, Ber., 1915, 48, 743.

ABSTRACT.

Previouswork has covered some displacement reactions, eliminations and olefine-rearrangements in the systems n-octane[1], t-butylcyclohexane[2], and decalin[3]. In order to facilitate product-analyses in the last-named system, by the author and by future workers, two analytical problems were examined.

The first problem was to devise a gas-liquid chromatographic method of separating the six alcohols (1 - 6) shown below. These alcohols are related to the possible substitution-products to be obtained from the solvolyses of trans-decalyl sulphonate esters.



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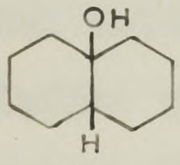

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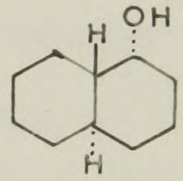

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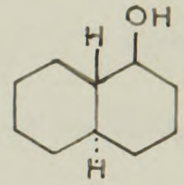

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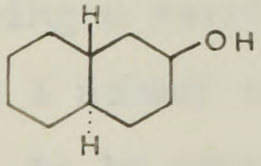

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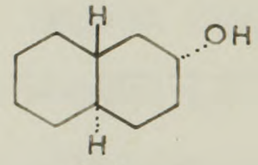
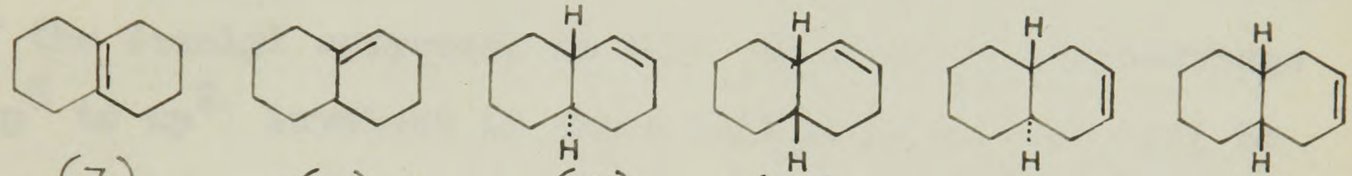


(6)

Out of a survey of three possible stationary phases, 1,1-oxydiglycerol was selected as the successful one.

The second problem was the separation of the following olefines (7 - 12). Although only four of these olefines (7, 8, 9 and 11) are likely products from solvolyses of trans-decalyl compounds, the complete analysis of the octalins would be useful in the study of their equilibration. Previous work has involved the use of more than one partial analysis[3b,3c].



(7) (8) (9) (10) (11) (12)

In this instance a successful phase proved to be 1,2-bis(2'-cyanoethoxy)ethane. It was chosen from a survey of ten phases.

An analytical method was devised whereby mixtures of decalyl acetates (after conversion to the corresponding alcohols *via* treatment with lithium aluminium hydride) or of octalins could be reliably analysed as percentages of products formed during a reaction in solution in acetic acid. It was found that a number of precautions were needed if the former method was to be reliable. Otherwise equilibration (presumably *via* an Oppenauer-Ponndorf mechanism) leads to the more stable (equatorial) epimer.

The first application of the above methods was the analysis of products from the acetolysis of toluene-*p*-sulphonates of axial (5) and equatorial (6) trans-β-decalols.

These compounds react more slowly than the corresponding compounds in the 4-t-butylcyclohexyl system[3g]. The products from these latter reactions have recently been analysed[2b]. Comparison with these results indicated that the higher rate in the 4-t-butylcyclohexyl system is parallelled by a higher olefine-yield in the equatorial case (but not in the axial one). A possible explanation of the slower rate of reaction of the decalyl compounds is that the hybridisation-change (sp^3 to sp^2) involved in these reactions is less easy to accomplish in the fused ring system of trans-decalin. Another factor contributing to the rate- and product- differences may be that non-chair forms are significant reacting conformations; possible non-chair forms are different for the two systems. A more detailed comparison of the products shows a much higher ratio of retention/inversion from the decalyl compounds. This is probably due to material rearranged to the other β-position. This ambiguity could be solved by repeating the work with resolved material.

The effect of different cations (included as acetates to neutralise toluene-p-sulphonic acid formed during the reaction) on the reaction was found to be very small. The effects of the nature of leaving group and the temperature were small and in the same sense as was observed in other systems[1c,2b].

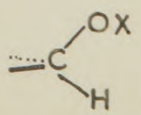
Streitwieser obtained kinetic evidence for sulphonate-

exchange during the acetolysis of 2-octyl sulphonates[4]. Evidence was obtained that decalyl naphthalene-β-sulphonates are formed during the acetolyses of trans-β-decalyl toluene-p-sulphonates in the presence of potassium naphthalene-β-sulphonates. The extent was such that any effect on products would be negligibly small.

Products were analysed from the acetolyses of the toluene-p-sulphonates of the trans-α-decalols (3 and 4). Kinetics[3g] and product-analyses from the axial epimer (3) suggest hydrogen-participation leading to the tertiary carbonium ion. The equatorial epimer is slow to react and the products contain material derived from a rearranged β-carbonium ion-pair, apparently similar to the one formed during the acetolysis of the toluene-p-sulphonate of the β-axial alcohol (5).

A preliminary study of the reaction of trans-β-octalin (11) with solutions of toluene-p-sulphonic acid in acetic acid showed the reaction to be reduced in rate by tetrahydrofuran. An analysis of such acetylated material as was formed from this reduced reaction showed it to be largely axial.

Nuclear magnetic resonance spectra of some decalyl compounds were recorded. Differences in chemical shifts for the proton marked (13) in pairs of epimers were in moderately good agreement with the value based on calculations of long-range shielding[5].



(13)

References.

1. (a) Clarke, D. Phil. Thesis, Oxford, 1963;

(b) Carr, Clarke, and Whiting, Proc. Chem. Soc., 1963, 333.

(c) Southam, Part II Thesis, Oxford, 1963, also unpublished work.

2. (a) Winstein and Holness, J. Amer. Chem. Soc., 1955, 77, 5562;

(b) Campbell, Part II Thesis, Oxford, 1964.

3. (a) Powell and Whiting, Tetrahedron, 1961, 12, 172;

(b) Powell and Whiting, Proc. Chem. Soc., 1960, 412;

(c) Oberhänsli, D. Phil. Thesis, Oxford, 1962;

(d) Hückel, Tappe and Legutke, Annalen, 1940, 543, 206;

(e) Hückel, Gross, Fechtig, Feltkamp, Geiger, Hanack, Heinzel, Hubele, Kurz, Maier, Maucher, Naher, Neidlein and Rashingkar, Annalen, 1959, 624, 142;

(f) Hückel, Maucher, Fechtig, Kurz, Heinzel and Hubele, Annalen, 1961, 645, 115;

(g) Moritani, Nishida and Murakami, J. Amer. Chem. Soc., 1959, 81, 5420.

4. Streitwieser and Walsh, Tetrahedron Letters, 1963, 1, 27.

5. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, Pergamon, Oxford, 117.