On the Prins reaction of terminal olefins and formaldehyde in trifluoroacetic acid

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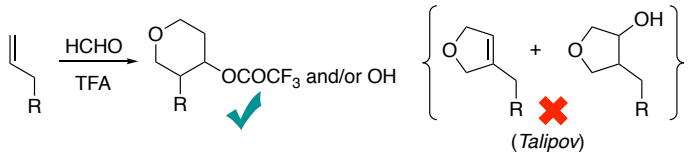
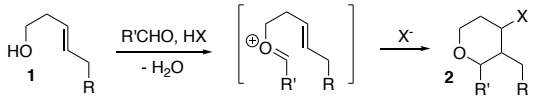


The Prins reaction of 1-heptene, as a representative terminal alkene, with formaldehyde in trifluoroacetic acid produces 3-butyl-4-(trifluoroacetoxy)tetrahydropyran and/or 3-butyl-4-hydroxytetrahydropyran; it does not provide (as previously reported by Talipov and co-workers) a route to 3-alkyl-2,5-dihydrofurans and 4-alkyl-3-hydroxytetrahydrofurans.

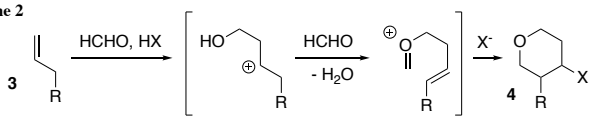
Keywords: Prins reaction, terminal alkenes, formaldehyde, trifluoroacetic acid, tetrahydropyrans.

Acid-induced reaction between homoallylic alcohols **1** and aldehydes (Prins cyclisation) provides a straightforward entry to substituted tetrahydropyrans **2** (Scheme 1).[1] The original Prins reaction, using simpler terminal olefins **3**, can produce a range of products depending on the substrate and experimental conditions.[2] In general, the latter is not viewed as a useful strategy to tetrahydropyrans, although 3-alkyl-4-chlorotetrahydropyrans **4** (X = Cl) are accessible in good yields from terminal olefins using paraformaldehyde and gaseous HCl at low temperature (Scheme 2).[3] Using H_2SO_4 with formaldehyde and acetic acid or under aqueous conditions is known to generate 4-acetoxy- or 4-hydroxy- 3-substituted tetrahydropyrans, together with significant quantities of 4-substituted-1,3-dioxanes.[4]

Scheme 1

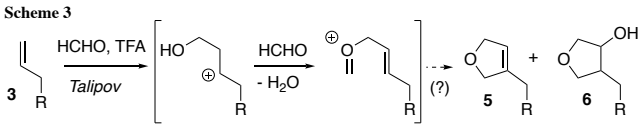


Scheme 2



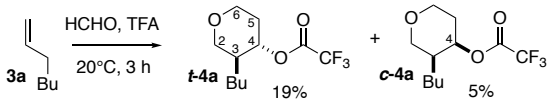
Starting in in 1993, Talipov and co-workers claimed in a series of papers,[5] a patent[6] and a review article,[7] that switching to trifluoroacetic acid (TFA) as solvent with terminal olefins **3** and paraformaldehyde led, remarkably, to a mixture of 3-alkyl-2,5-dihydrofurans **5** and 4-alkyl-3-hydroxytetrahydrofurans **6** (4:1 to 2:1, depending on water content) in good overall yields (Scheme 3). Further studies (including kinetic and computational) on this latter transformation were subsequently reported, even up to 2015.[8] This process was also reported as being successful for higher aldehydes (using R'CHO instead of HCHO) giving 2,3,5-trisubstituted-2,5-dihydrofurans,[5b] and (in this Journal) as giving a mixture of 4-alkyl-3-trifluoroacetoxy- and 4-alkyl-3-chloro-tetrahydrofurans with formaldehyde and Me_3SiCl in TFA.[9] Herein, we disclose our re-examination of the reaction of a terminal alkene with formaldehyde in TFA.

Scheme 3



The reaction of formaldehyde and 1-heptene (Scheme 3, R = butyl) in TFA was reported to give 3-pentyl-2,5-dihydrofuran **5a** (R = Bu) in good yields and has been the most extensively investigated;[5a,b] consequently, this synthesis was re-examined. Following an exact experimental procedure of Talipov, which reportedly gave a 43% yield of 3-pentyl-2,5-dihydrofuran,[5b] 1-heptene was reacted with HCHO in TFA for 3 h at 20°C. The major component we isolated was a non-polar colourless oil, possessing ^{1}H NMR data [eg (400 MHz, $CDCl_3$), δ, ppm: 4.87 (1H, td)] similar to the reported data [lit.[5a,b]: (80 MHz, $CDCl_3$), δ, ppm: 4.63-5.09 (1H, m]. However, the data is inconsistent with that for 3-pentyl-2,5-dihydrofuran (**5a**) [eg[10a] (60 MHz, CCl_4), δ, ppm: 5.4 (1H, =CH)]).[10]

Scheme 4



The material isolated under Prins conditions in anhydrous TFA is most straightforwardly assigned as tetrahydropyranyl trifluoroacetates ***t*-4a** and ***c*-4a** (Scheme 4), which would arise from a reaction akin to Scheme 2 (X^- = $F_3CCO_2^-$). Indeed, our spectroscopic data is consistent with trifluoroacetate data reported by Talipov from the reaction mentioned above of terminal alkenes with formaldehyde and Me_3SiCl in TFA,[9] albeit Talipov assigned the products as 4-alkyl-3-trifluoroacetoxytetrahydro*furans*. Our 2D NMR data (^{1}H–^{1}H COSY, DEPT–HSQC, and ^{1}H–^{13}C HMBC, see Supplementary information for spectra) provides strong evidence for the 3,4-disubstituted tetrahydropyran structure

4a. For ***t*-4a**, ^{1}H–^{1}H COSY correlations between H–4 and H–3 and H_a–5/H_b–5 revealed the existence of a C–3/C–4/C–5 sequence, and the alkyl group is located at C–3 based on DEPT–HSQC. ^{1}H–^{1}H COSY and DEPT–HSQC data showed that the protons at δ 3.19 (1H, dd) and one H of δ 3.93–4.01 (2H, m) are the C–2 methylene, whereas the protons at 3.50 (1H, dd) and the second H of δ 3.93–4.01 (2H, m) are the C–6 methylene. Both H–2/C–2 and H–6/C–6 are connected by an ether linkage based on HMBC, and long–range HMBC correlations were observed between H–4 and C–2 and C–6. That the major component ***t*-4a** possessed the *trans* configuration was based on the vicinal *J* values for H–4 being larger for ***t*-4a** (td, J = 9.5, J = 4.5) compared with those observed for the minor *cis*-3,4-disubstituted tetrahydropyran ***c*-4a** (q, J = 3.5).

Following correspondence with Talipov in 2008,[†] he repeated the reaction between formaldehyde and 1-heptene in TFA, followed by neutralisation with ammonia (the latter would expected to cleave trifluoroacetates to alcohols). This gave a mixture of two compounds for which he kindly provided the ^{13}C NMR data, assigning them as *cis*- and *trans*-4-pentyl-3-hydroxytetrahydro*furan*. We obtained essentially identical data following addition of ammonia at the end of the Prins reaction. The same data were obtained if the individual tetrahydropyranyl trifluoroacetates ***t*-4a** and ***c*-4a** underwent methanolysis in the presence of K_2CO_3, to give ***t*-4b** and ***c*-4b**. A comparison of this data with literature ^{13}C NMR data for 4-hydroxytetrahydropyrans[11,12] and 3-hydroxytetrahydrofurans[12,13] is given in Fig. 1.

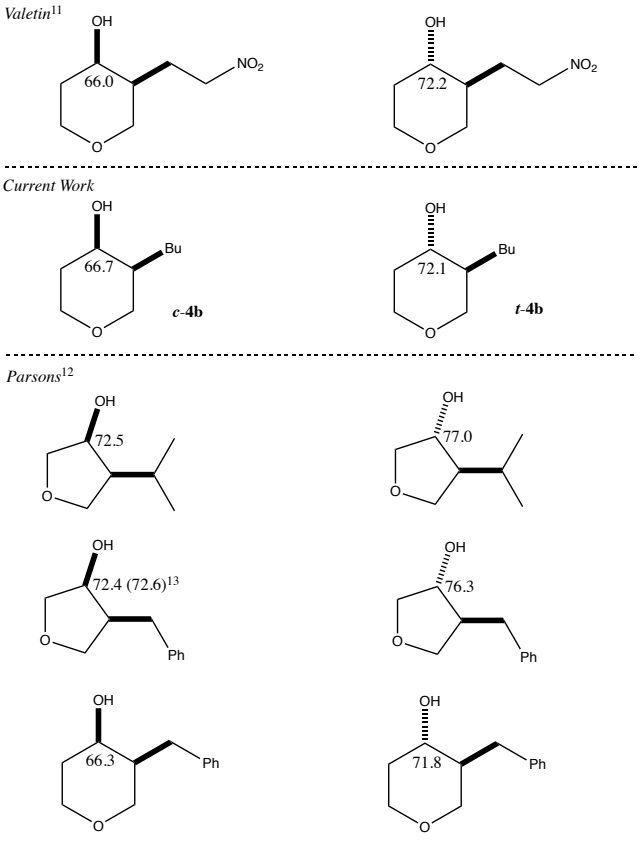


Figure 1. Comparison of selected ^{13}C NMR data for 3-hydroxytetrahydrofurans and 4-hydroxytetrahydropyrans.

On analysing the ^{13}C NMR data in Fig. 1, it can been seen, in particular, that the carbinol carbons are always greater than 70 ppm for 4-alkyl-3-hydroxytetrahydrofurans, with the *trans* greater than 76 ppm. In contrast, the carbinol carbons of 3-alkyl-4-hydroxytetrahydropyrans are ~66 ppm and ~72 ppm for *cis*- and *trans*-isomers, respectively. This data comparison provides strong evidence that *cis*- and *trans*-4-butyl-3-hydroxytetrahydropyran were prepared and not the 3-hydroxytetrahydrofurans, and further implies that the process proceeds as in Scheme 2 not Scheme 3 and by analogy this pathway is likely for higher aldehydes in TFA as well.

Finally, the data for 3-alkyl-4-chloro-tetrahydro'furans', obtained by Talipov as the additional product from terminal olefins with formaldehyde and Me_3SiCl in TFA,[9] was compared with data for a representative literature 3-alkyl-4-chlorotetrahydropyran[15] (Fig. 2). The data is consistant with the products from Talpov as also being the six- not five-ring ethers.

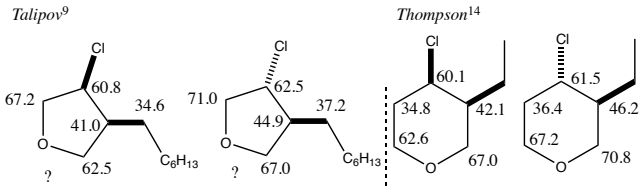


Figure 2. Comparison of selected ^{13}C NMR data for 3-alkyl-4-chloro-tetrahydro'furans' and -tetrahydropyrans.

In summary, Prins reactions of terminal alkenes with formaldehyde in trifluoroacetic acid produce substituted tetrahydropyrans, and not the erroneously reported 2,5-dihydrofurans or substituted tetrahydrofurans.

Experimental

Paraformaldehyde was dried overnight under high vacuum prior to use. 1-Heptene was freshly distilled from CaH_2. Trifluoroacetic acid (99%, extra pure) was used as received (Acros). Petrol (petroleum ether) of bp 40–60°C was used in flash column chromatography. Flash column chromatography was carried out using silica gel (VWR chemicals, BDH), monitored by thin layer chromatography (TLC) (Merck 60 F_{254}) plates. TLC plates were viewed by immersion in $KMnO_4$, followed by heating. Infrared spectra were obtained using a PerkinElmer FT–IR spectrometer (Universal ATR Sampling Accessory), with absorption maxima quoted in wavenumbers (cm^{-1}). Peak intensities are described as broad (br), weak (w), medium (m) or strong (s). Nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR, ^{1}H–^{1}H COSY, DEPT–HSQC, and ^{1}H–^{13}C HMBC) spectra were recorded on a Bruker Avance AVIIIHD 400 spectrometer in $CDCl_3$, referenced to residual $CHCl_3$ singlet at δ 7.26, and to the central line of $CDCl_3$ triplet at 77.16 for ^{13}C NMR spectra. Proton coupling constants (*J*) are measured to the nearest 0.5 Hz. The splittings are quoted as singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of doublet of doublets (ddd), triplet of doublets (td), doublet of triplets (dt) or multiplet (m). ^{13}C NMR peaks were assigned by standard methods using HSQC. High resolution mass spectra were obtained by electrospray ionisation, using tetraoctylammonium bromide or sodium dodecyl sulfate as the lock mass.

Trans*- and *cis*-3-butyltetrahydro-2*H*-pyran-4-yl 2,2,2-trifluoroacetate (*t*-4a and *c*-4a)**. The procedure and reaction scale of Talipov was followed.[5b] TFA (15 ml) was added to paraformaldehyde (5.00 g, 170 mmol), and the mixture heated until a clear solution formed (3–5 min). The mixture was cooled to rt, then 1-heptene (**3a**) (9.3 ml, 80 mmol) was added dropwise. After 3 h at rt,[15] unreacted 1-heptene and TFA were removed by distillation (< 40°C, ~100 mbar). The residue, a yellow oil (~11 g), was distilled at ~15 mbar and the fraction of bp 60–70°C (5.3 g, an impure 75:25 mixture of ***t*-4a** and ***c*-4a**) further purified by flash column chromatography (0–20% Et_2O in petrol). First eluted a colourless liquid, *trans*-3-butyltetrahydro-2*H*-pyran-4-yl 2,2,2-trifluoroacetate (t*-4a**). Yield 3.2 g (19%). R_f = 0.26 (20% Et_2O in petrol). IR spectrum (film), ν, cm^{-1}: 1249 s, 1139 w, 1164 s, 1222 m, 1781 s, 2861 w, 2934 m, 2962 m. ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.88 (3H, t, *J* = 7, CH_3); 1.14–1.34 (5H, m, 8,9–CH_2 and 7–CH_a); 1.40–1.47 (1H, m, 7–CH_b); 1.71–1.79 (1H, m, 5–CH_a); 1.81–1.88 (1H, m, 3–CH); 2.02–2.08 (1H, m, 5–CH_b); 3.19 (1H, dd, *J* = 12, *J* = 9, 2–CH_a); 3.50 (1H, ddd, *J* = 12, *J* = 10.5, *J* = 3, 6–CH_a); 3.93–4.01 (2H, m, 2–CH_b and 6–CH_b); 4.87 (1H, td, *J* = 9.5, *J* = 4.5, 4–CH). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 13.9 (CH_3); 22.9 (C–9); 28.1 (C–7); 28.8 (C–8); 30.7 (C–5); 40.7 (C–3); 65.6 (C–6); 69.9 (C–2); 78.9 (C–4); 114.7 (Q, $J_{C\text{-}F}$ = 286, CF_3), 157.3 (q, $J_{C\text{-}F}$ = 42, C=O). ^{19}F NMR spectrum (376 MHz, $CDCl_3$), δ, ppm: -75.2. Found, *m/z*: 277.1023 $[M+Na]^+$. $C_{11}H_{17}O_3F_3Na$. Calculated, *m/z*: 277.1022. Second eluted a colourless liquid, *cis*-3-butyltetrahydro-2*H*-pyran-4-yl 2,2,2-trifluoroacetate (***c*-4a**). Yield 0.89 g (5%). R_f = 0.2 (20% Et_2O in petrol). IR spectrum (film), ν, cm^{-1}: 775 m, 1031 w, 1121 m, 1158 m, 1219 m, 1781 s, 2862 w, 2933 w, 2961 w. ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.88 (3H, t, *J* = 7, CH_3); 1.18–1.33 (6H, m, 3xCH_2); 1.84–1.98 (3H, m, 3–CH and 5–CH_2); 3.51 (1H, t, *J* = 11, 2–CH_a); 3.63–3.79 (3H, m, 2–CH_b and 6–CH_2); 5.32 (1H, q, *J* = 3.5, 4–CH). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 13.9 (CH_3); 22.8 (C–9); 26.5 (C–7); 28.7 (C–8); 30.1 (C–5); 39.2 (C–3); 63.0 (C–6); 67.8 (C–2); 74.9 (C–4); 114.7 (Q, $J_{C\text{-}F}$ = 286, CF_3); 157.1 (q, $J_{C\text{-}F}$ = 42, C=O). ^{19}F NMR spectrum (376 MHz, $CDCl_3$), δ, ppm: -75.1. Found, *m/z*: 141.1274 $[M–OCOCF_3]^+$. $C_9H_{17}O$. Calculated, *m/z*: 141.1273.

Trans* and *cis*-3-butyltetrahydro-2*H*-pyran-4-ol (*t*-4b and *c*-4b)**. Following the above procedure and reaction scale for ***t*-4a** and ***c*-4a**, but after 3 h at rt, the mixture was neutralised by aq. NH_3 (15 ml). The aq. layer was extracted with Et_2O (2 x 30 ml), dried (Na_2SO_4) and evaporated under reduced pressure. The residue, a yellow oil (~8 g), was distilled at ~15 mbar and the fraction of bp 100–110°C (4.7 g, an impure 75:25 mixture of ***t*-4b** and ***c*-4b**) further purified by flash column chromatography (20–40% Et_2OAc in petrol). First eluted a colourless liquid, *trans*-3-butyltetrahydro-2*H*-pyran-4-ol (t*-4b**). Yield 1.72 g (17%). R_f = 0.3 (30% EtOAc in petrol). IR spectrum (film), ν, cm^{-1}: 626 s, 1050 s, 1080 s, 1150 s, 1222 m, 1466 m, 2856 s, 2925 s, 2955 s, 3386 br. ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.88 (3 H, t, *J* = 7, CH_3); 1.03–1.13 (1 H, m, 7–CH_a); 1.17–1.37 (4 H, m, 8,9–CH_2); 1.43–1.62 (2 H, m, 3–CH and 5–CH_a); 1.63–1.72 (1 H, m, 7–CH_b); 1.73–1.92 (2 H, m, 5–CH_b and OH); 3.02 (1 H, t, *J* = 11, 2–CH_a); 3.35–3.44 (2H, m, 4–CH and 6–CH_a); 3.90–3.98 (2H, m, 2–CH_b and 6–CH_b). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 14.1 (CH_3); 23.2 (C–9); 28.3 (C–7); 29.3 (C–8); 35.3 (C–5); 44.6 (C–3); 66.5 (C–6); 70.6 (C–2); 72.1 (C–4). Found, *m/z*: 141.1272 $[M–OH]^+$. $C_9H_{17}O$. Calculated, *m/z*: 141.1273. Second eluted a colourless liquid, *cis*-3-butyltetrahydro-2*H*-pyran-4-ol (***c*-4b**). Yield 0.36 g (3%). R_f = 0.2 (30% EtOAc in petrol). IR spectrum (film), ν, cm^{-1}: 626 s, 1080 s, 1150 s, 1222 m, 1466 m, 2856 s, 2927 s, 2955 s, 3389 br. ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.89 (3 H, t, *J* = 7, CH_3); 1.19–1.36 (6 H, m, 3xCH_2); 1.58 (1H, br, OH); 1.63–1.73 (2 H, m, 3–CH and 5–CH_a); 1.77–1.86 (1 H, m, 5–CH_b); 3.51–3.56 (2 H, m, 2–CH_2); 3.64 (1 H, ddd, *J* = 11.5, *J* = 4.5, *J* = 3.5, 6–CH_a); 3.78 (1H, td, *J* = 11, *J* = 3, 6–CH_b); 4.00 (1H, dt, *J* = 5.5, *J* = 3.0, 4–CH). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 14.1 (CH_3); 23.1 (C–9); 26.6 (C–7); 29.1 (C–8); 33.5 (C–5); 40.9 (C–3); 63.2 (C–6); 66.7 (C–4); 67.6 (C–2). Found, *m/z*: 141.1272 $[M–OH]^+$. $C_9H_{17}O$. Calculated, *m/z*: 141.1273.

Trans*-3-butyltetrahydro-2*H*-pyran-4-ol (*t*-4b)**. *Trans*-3-butyltetrahydro-2*H*-pyran-4-yl 2,2,2-trifluoroacetate (t*-4a**) (250 mg, 0.98 mmol) was stirred with K_2CO_3 (270 mg, 1.96 mmol) in MeOH (1 ml) at rt. After 3 h, the mixture was quenched with 10% HCl (1 ml) and extracted with EtOAc (2×5 ml). The combined organic layers were washed with brine (2 ml) and dried (Na_2SO_4). Evaporation under reduced pressured followed by chromatography (30% EtOAc in petrol) gave a colourless liquid, *trans*-3-butyltetrahydro-2*H*-pyran-4-ol (***t*-4b**). Yield 138 mg (89%). Data as above.

Cis*-3-butyltetrahydro-2*H*-pyran-4-ol (*c*-4b)**. *Cis*-3-butyltetrahydro-2*H*-pyran-4-yl 2,2,2-trifluoroacetate (c*-4a**) (150 mg, 0.59 mmol) was stirred with K_2CO_3 (163 mg, 1.18 mmol) in MeOH (1 ml) at rt. After 3 h, the mixture was quenched with 10% HCl (1 ml) and extracted with EtOAc (2×5 ml). The combined organic layers were washed with brine (2 ml) and dried (Na_2SO_4). Evaporation under reduced pressured followed by chromatography (30% EtOAc in petrol) gave a colourless liquid, *cis*-3-butyltetrahydro-2*H*-pyran-4-ol (***c*-4b**). Yield 87 mg (93%). Data as above.

The Supplementary information file containing tabular comparisons of ^{13}C NMR data of ***t*-4a**, ***c*-4a, *t*-4b** and ***c*-4b** with that from Talipov's work and NMR spectra of ***t*-4a**, ***c*-4a, *t*-4b** and ***c*-4b** is available from the journal website at http://hgs.osi.lv.

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[†]Email from Prof. R. F. Talipov, 13th February 2008.

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