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FREE RADICAL CHEMISTRY. PART 6[1]. HALOGENATION OF POLYFLUORO-ETHERS AND -BORATE ESTERS

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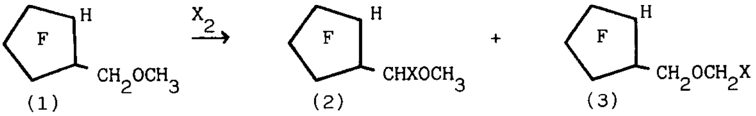
SUMMARY

Chlorination and bromination of $CH_3OCH_2CF_2CFHCF_3$ gave contrasting results for the site of halogenation and a rationalisation based on the lateness of the transition-state is advanced. Direct fluorination supports the theory. Chlorination of fluorinated trialkylborates provides a new route for conversion of fluorinated alkenes to fluorinated acid chlorides.

INTRODUCTION

In earlier parts of this series we described free-radical additions of dimethylether [2] and trimethylborate [3] to various fluorinated alkenes and we are exploring the chemistry of these and other adducts to fluorinated alkenes. We studied [2] chlorinations and bromination of (1) and found that (2) was obtained using bromine but chlorination products were very solvent dependent.



(1) (2) (3)

(X = halogen)

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RESULTS AND DISCUSSION

In the light of the puzzling results obtained in halogenation of (1) w have now explored the corresponding halogenation reactions with (4) i.e. the product obtained from addition of dimethylether to hexafluoropropene. The results of these studies are shown below and a preference for the terminal position is clearly observed. In contrast, reaction of (4) with

$$CF_3CFHCF_2CH_2OCH_3 + Cl_2 \xrightarrow{h\nu} CF_3CFHCF_2CHClOCH_3 + CF_3CFHCF_2CH_2OCH_2Cl$$

(4) (5) (6)

$$+ CF_3CFHCF_2CH_2OCHCl_2 + CF_3CFHCF_2CHClOCH_2Cl$$

(7) (8)

Solvent	% (5)	(6)	[(7) + (8)]
Neat	6	45	47
CCl_4	4	49	45
CS_2	16	76	7

bromine, not only differed through the preference for the position of halogenation but, also, in the fact that substantial amounts of dehydrodimerisation products were obtained. It is clear, however, that although

$$(4) + Br_2 \xrightarrow{\text{Sunlight}} CF_3CFHCF_2CHBrOCH_3 + CF_3CFHCF_2CH_2OH$$

(9) (10)

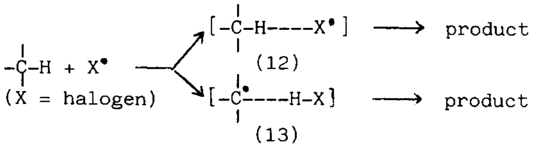
+ Dehydrodimers

(11)

Solvent	% (9)	(10)	(11)
Neat	12	38	49
CS_2	81	9	9

chlorination occurs preferentially at the terminal position, bromination occurs preferentially at the internal CH_2 site.

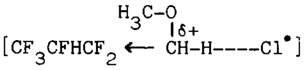
An explanation for these contrasting results lies in the relative reactivity of bromine and chlorine atoms and the consequences of this, that stem from the Hammond postulate [4]. This approach associates greater reactivity with a transition-state that resembles the initial state, whereas lower reactivity would be associated with a transition-state closer to the product. In the present context, of halogenation, these situations could be represented by transition-states (12) and (13) and the consequence of this would be that polar effects would be more important for (12) while the stability of the developing radical would be more important for (13).



In comparing chlorination and bromination, it is likely that the transition-state for chlorination is more like (12) and, for bromination, the character of the transition-state will move towards (13). On this basis, the preferential attack of a chlorine atom at the terminal position in (4) is consistent with a transition-state like (14) because this involves attack at

$[CF_3CFHCF_2CH_2O\text{-}CH_2\text{-}H\text{----}Cl^{\bullet}]$

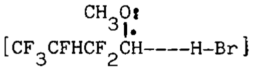
(14)



$[CF_3CFHCF_2 \leftarrow \overset{H_3C\text{-}O\ |\delta+}{CH}\text{-}H\text{----}Cl^{\bullet}]$

(15)

the least electrophilic site. Electron withdrawal by the polyfluoroalkyl group would inhibit formation of (15), while attack at the CF_3CFH-site would be even less likely, by the electrophilic chlorine atom. Assuming a transition-state like (13) for attack by bromine, then we can appreciate that (16) is preferred to (17). Although both of these transition-states would be stabilised by adjacent oxygen (18), nevertheless, (16) is preferred



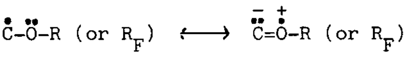
$[CF_3CFHCF_2\overset{CH_3\ddot{O}|}{\dot{C}H}\text{----}H\text{-}Br]$

(16)

$[CF_3CFHCF_2CH_2\ddot{O}\text{-}\dot{C}H_2\text{---}H\text{-}Br]$

(17)

as a developing secondary radical, rather than the developing primary radical (17). Although attack by a bromine atom at the CF_3CFH site would



$\dot{C}\text{-}\ddot{O}\text{-}R$ (or R_F) $\longleftrightarrow$ $\overset{-}{\ddot{C}}\text{=}\overset{+}{\dot{O}}\text{-}R$ (or R_F)

(18a) (18b)

[R = alkyl
R_F = Polyfluoroalkyl]

lead to a developing tertiary radical in the transition-state, this is obviously less favourable than the known stabilising influence of adjacent oxygen [5,6].

A consequence of this model for reactivity, is that attack by a fluorine atom on (4) should be even more governed by polar effects than chlorine. We have tested this by bubbling fluorine, diluted with nitrogen, through a solution of (4) in $CF_2ClCFCl_2$, at room temperature and the products (19) - (21) arise wholly from attack at the terminal position, together with a small amount of alcohol (10) probably arising from acid-induced cleavage of (4). The formation of (21) probably partly arises from the presence of oxygen impurity in the fluorine, since the functionalisation of hydrocarbon groups, using fluorine containing oxygen, has been reported by other workers [7,8].

$$(4)\ \xrightarrow[CF_2ClCFCl_2,\ R.T.]{F_2,\ N_2}\ CF_3CFHCF_2CH_2OCH_2F\ (44\%)$$

(19)

$$+\ CF_3CFHCF_2CH_2OCHF_2\ (18\%)$$

(20)

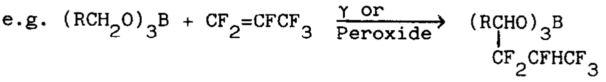
$$+\ CF_3CFHCF_2CH_2OCOH\ (20\%)$$

(21)

$$+\ CF_3CFHCF_2CH_2OH\ (7\%)$$

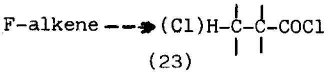
(10)

We have recently shown [3] that free-radical additions of trialkylborates to fluorinated alkenes, occurs readily, to give high yields of corresponding fluorinated trialkylborates (22). These derivatives are readily chlorinated and, overall, this provides a route for conversion of fluorinated alkenes to corresponding acid chlorides (23) (see Table).



$$\text{e.g. } (RCH_2O)_3B + CF_2{=}CFCF_3 \xrightarrow[\text{Peroxide}]{\gamma\text{ or}} (R\underset{\substack{|\\ CF_2CFHCF_3}}{C}HO)_3B$$

(22)



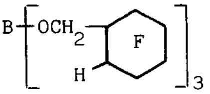
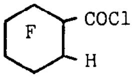
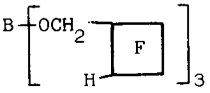
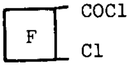
$$\text{F-alkene} \longrightarrow (Cl)H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-COCl$$

(23)

Earlier workers have described chlorination of corresponding methanol adducts but these reactions usually gave complex mixtures of products, containing little or none of the acid chloride [9,10].

TABLE

Chlorination of fluorinated trialkylborates[a]

Borate	Acid Chloride	% Yield
B(OCH$_2$CF$_2$CFHCF$_3$)$_3$ (24)	CF$_3$CFHCF$_2$COCl (27)	75
 (25)	 (28)	83
 (26)	 (29)	63

(a) Sealed pyrex tube, excess chlorine, UV irradiation, 18 - 50°C.

EXPERIMENTAL

The radical induced addition products of ethers and borates to fluoroalkenes used as starting materials were prepared as outlined in a previous paper [3]. Chlorine was used as supplied and transferred from the cylinder by normal vacuum line techniques. Quantitative analyses by glc were carried out on a Varian Aerograph Model 920 equipped with a gas density balance detector (di-isodecylphthalate 20%, on chromosorb P). A similar instrument equipped with a cold trap for sample collection was used to purify the products. Proton and fluorine nmr spectra were recorded on a Varian EM360L spectrometer operating at 60 and 56.46 MHz respectively and chemical shifts are quoted relative to tetramethylsilane and trichlorofluoromethane. Mass spectra were recorded on an A.E.I. MS9 spectrometer and glc/ms were recorded on a V.G. Micromass 12B spectrometer fitted with a Pye 104 glc.

Chlorination of 2,2,3,4,4,4-hexafluorobutylmethyl ether (4)

(a) Neat

Adduct (4) (1.95 g, 10 mmol), contained in a pyrex tube with 'rotaflo' tap, was degassed and chlorine (0.7 g, 10 mmol) introduced by vacuum transfer. The mixture was left in sunlight until the chlorine colour disappeared (∿ 30 mins.). The tap was opened and the gaseous products vented to give a liquid product (2.49 g). Separation by preparative glc gave 1-chloro-2,2,3,4,4,4-hexafluorobutyl methyl ether (5) (0.14 g, 6%) (nc); δ_H 3.78 (3H, s, CH_3), 5.77 (1H, t (broad), CHF), δ_F 74.2, 74.6 (3F, m, CF_3), 122.4, 124.0, 124.7 (2F, m, CF_2), and 214.9, 216.0 (1F, dm, J 44 Hz, CFH); m/z 195 (M^+-Cl, 12), 81(14), 79(36), 2,2,3,4,4,4-hexafluorobutyl chloromethyl ether (6) (1.10 g, 45%) (nc), b.p. 133°C (Found: C, 26.4; H, 2.3; F, 48.5; Cl, 15.7. $C_5H_5ClF_6O$ requires: C, 26.0; H, 2.2; F, 49.5; Cl, 15.4%); δ_H 4.13 (2H, m, CH_2CF_2), 5.10 (1H, dm, J 44 Hz, CFH), 5.63 (2H, s, OCH_2Cl), δ_F 75.0 (3F, m, CF_3), 117.3, 122.0 (2F, AB, J 221 Hz, CF_2), and 214.3 (1F, dm, J 44 Hz, CFH); m/z 195 (M^+-Cl, 45), 81(32), 79(97), 51(66), 49(100), and a mixture of di-chlorinated species (7) and (8) (1.14 g, 47%) (Found: C, 23.0; H, 1.8; F, 41.1; Cl, 26.9. $C_5H_4Cl_2F_6O$ requires: C, 22.6; H, 1.5; F, 43.0; Cl, 26.8%); δ_H 4.37 (m, CF_2CH_2O) and 5.10 (dm, CFH) (3.8 H), 5.70 (0.6 H, s, OCH_2Cl), 7.48 (1H, s, $O\underline{C}HCl_2$).

(b) Carbon tetrachloride solvent

A mixture containing adduct (4) (0.99 g, 5 mmol), chlorine (0.51 g, 7 mmol) and carbon tetrachloride (3.11 g, 20 mmol), contained in a pyrex tube equipped with a rotaflo tap was irradiated with sunlight for 1 hour. The gaseous by-products were allowed to evaporate leaving a liquid product and comparison of glc retention times with port (a) gave the chlorinated adducts (5) (4%), (6) (49%) and (7) and (8) (45%).

(c) Carbon disulphide solvent

A mixture containing adduct (4) (1.04 g, 5 mmol), chlorine (0.45 g, 6 mmol) and carbon disulphide (2.81 g, 37 mmol) was irradiated with sunlight for one hour. The gaseous by-products were allowed to evaporate leaving a liquid product containing the chlorinated adducts (5) (16%), (6) (76%) and (7) plus (8) (7%).

Bromination of 2,2,3,4,4,4-hexafluorobutyl methyl ether (4)

(a) Neat

A mixture containing adduct (4) (1.94 g, 10 mmol) and bromine (2.04 g, 13 mmol) contained in a pyrex tube with a rotaflo tap was irradiated with sunlight for 3 days. The tube was opened and the gaseous by-products were allowed to evaporate to leave a yellow liquid (2.7 g). Separation of the components by preparative glc gave 1-bromo-2,2,3,4,4,4-hexafluorobutyl methyl ether (9), (0.32 g, 12%) (nc), b.p. 134°C (Found: C, 22.1; H, 1.8; F, 41.7; Br, 29.7. $C_5H_5BrF_6O$ requires: C, 21.8; H, 1.8; F, 41.5; Br, 29.1%); δ_H 3.63 (3H, s, CH_3), 5.27 (1H, dm, J 44 Hz, CHF), 6.00 and 6.07 (1H, t, J 9 Hz, CHBr); δ_F 76.1 and 76.7 (3F, m, CF_3), 120.1 and 122.1 (2F, m, CF_2), 215.3 and 217.3 (1F, dm, J 44 Hz, CFH); m/z 195 (M^+-Br, 100%), 2,2,3,4,4,4-hexafluorobutan-1-ol (10) [11] (1.02 g, 38%), and unassigned dehydrodimers (11) (1.32 g, 49%), (Found: F, 58.8. $C_{10}H_{10}F_{12}O_2$ requires: F, 58.5%), m/z 195 (100%).

(b) Carbon disulphide solvent

A mixture containing adduct (4) (0.3 g, 1.5 mmol), bromine (0.12 g, 0.75 mmol) and carbon disulphide (2.78 g, 37 mmol) was irradiated with sunlight for 72 hours. The tube was opened and the gaseous by-products allowed to evaporate to leave a liquid containing (9) (81%), (10) (9%) and (11) (9%), assigned by comparison of glc retention times with authentic samples from part (a).

Fluorination of 2,2,3,4,4,4-hexafluorobutyl methyl ether (4)

A mixture containing adduct (4) (2.46 g, 12.5 mmol) and 1,1,2-trichloro-1,2,2-trifluoroethane (55 g) was placed in a pyrex flask assembled with a reflux condenser and an inlet tube attached via a three way valve to a nitrogen cylinder and an electrolytic fluorine generator. Nitrogen (50 ml/min.) was passed for 10 mins. then fluorine (0.48 g over a 22 min. period) and finally flushed out with a flow of nitrogen (50 ml/min.) for 10 mins. The product contained 2,2,3,4,4,4-hexafluorobutyl fluoromethyl ether (19) (44%), δ_H 3.17 (2H, m, CH_2CF_2), 4.36 (2H, d, J 55 Hz, CH_2F), 4.80 (1H, m, CHF); δ_F 76.2 (3F, m, CF_3), 118.9, 123.0 (2F, AB, J 277 Hz, CF_2), 155.7 (1F, t, J 54 Hz, CH_2F), 215.7 (1F, dm, J 44 Hz, CFH); m/z 213 (M^+-H, 1%), 63(100), 2,2,3,4,4,4-hexafluorobutyl difluoromethyl ether (20) (18%) (Found: C, 26.1; H, 1.9. $C_5H_4F_8O$ requires: C, 25.9; H, 1.7%); δ_H 4.52 (2H, m, CH_2), 5.23 (1H, d, J 45 Hz, CHF), 6.55 (1H, t, J 73 Hz, CHF_2); δ_F 76.3 (3F, m, CF_3), 88.4 (2F, d, J 71 Hz, CF_2H), 120.9 (2F, m, CF_2CH_2), 215.7 (1F, d, J 43 Hz, CFH), 2,2,3,4,4,4-hexafluorobutyl formate (21) [3] (20%), and 2,2,3,4,4,4-hexafluorobutan-1-ol (10) [11] (7%).

Chlorination of borate adducts

(a) Tri(2,2,3,4,4,4-hexafluorobutyl)borate (24)

A mixture of borate (24) (0.97 g, 1 mmol) and chlorine (6.61 g, 93 mmol), contained in a thick pyrex tube fitted with a rotaflo valve, was sealed under vacuum and irradiated with a high pressure UV lamp for 1 hour (with a temperature rise to 50°C). The gaseous by-products were allowed to evaporate leaving a liquid residue which was transferred under vacuum at 18°C to give 2,2,3,4,4,4-hexafluorobutanoyl chloride (27) (0.85 g, 75%) (nc) (Found: C, 22.4; H, 0.7; Cl, 16.1; F, 49.8. C_4HClF_6O requires: C, 22.4; H, 0.5; Cl, 16.5; F, 53.1%); δ_H 5.08 (dm, J 44 Hz, CFH); δ_F 76.0 (3F, m, CF_3), 112.3, 117.1 (2F, AB, J 278 Hz, CF_2), 214.2 (1F, dm, J 42 Hz, CFH); m/z 213 (M^+-H, 1%), 151(58), 69(95), 65(32), 63(100).

(b) Tri[(1,2,3,3,4,4,5,5,6,6-decafluorocyclohexyl)methyl]borate (25)

A mixture of borate (25) (0.68 g, 0.8 mmol) and chlorine (6.06 g, 85 mmol), contained in a thick pyrex tube fitted with a rotaflo tap, was sealed under vacuum and irradiated with a high pressure UV lamp for 2 hours (with a temperature rise to 50°C). The gaseous by-products were allowed to evaporate and the remaining liquid was transferred under vacuum at 18°C to give 1,2,3,3,4,4,5,5,6,6-decafluorocyclohexylmethanoyl chloride (28) (0.62 g, 83%) (mixture of isomers) (Found: C, 25.9; H, 0.0%; Cl, 13.4; F, 59.4. $C_7HClF_{10}O$ requires: C, 25.7; H, 0.3; Cl, 10.9; F, 58.2%), δ_H 5.32 (m, CHF); δ_F 118.1 to 149.8 (8F, overlapping AB, $4CF_2$), 167.5 and 179.3 (1F, m, CF), 210.0 and 229.3 (1F, dm, J 42 Hz, CFH); m/z 291 (M^+-Cl, 15%), 65(56), 63(100).

(c) Tri (1,2,3,3,4,4-hexafluorocyclobutyl)methyl borate (26)

A mixture of borate (26) (0.75 g, 1.3 mmol) and chlorine (10.34 g, 146 mmol), contained in a thick pyrex tube fitted with a rotaflo tap, was sealed under vacuum and irradiated with a high pressure UV lamp for 1 hour (with a temperature rise to 50°C). The gaseous by-products were allowed to evaporate and the remaining liquid was transferred under vacuum at 18°C to give 3-chlorohexafluorocyclobutyl methanoyl chloride (29) (nc) (0.73 g, 63%) (Found: C, 22.3; F, 44.4. $C_5Cl_2F_6O$ requires: C, 23.0; F, 43.7%); δ_F 126.8 (2F, m, CF_2), 122.6, 131.4 (2F, AB, J 214 Hz, CF_2), 136.2 and 141.4 (1F, m, CF), 159.0 and 168.1 (1F, m, CFH); m/z 227 (M^+-Cl, 14%), 225(48), 149(21), 147(68), 118(31), 116(100), 65(26), 63(82).

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