EXCHANGE OF FLUORINE BY CHLORINE IN PERFLUOROISOBUTYLENE

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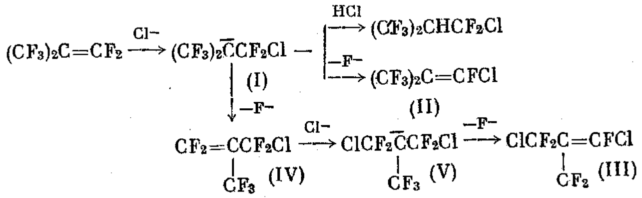
Perfluoroisobutylene (PFIB) easily adds HCl in the presence of Cl^- [1]. This reaction represents a characteristic example of nucleophilic addition to fluoroolefins, and evidently consists in the initial additions of Cl^- to the multiple bond and the subsequent protonation of carbanion (I). Starting with this, it could be expected that the nucleophilic replacement of F by Cl will occur when PFIB is reacted with Cl^- in an aprotic medium.

Howoever, it proved that PFIB practically does not react with triethylbenzylammonium chloride (TEBA) when heated in CH_3CN or diglyme, and only traces of the substitution product, 1-chloro-1,3,3,3-tetrafluoro-2-trifluoromethyl-1-propene (II), are formed here. This raised the assumption that the nucleophilic exchange of F by Cl in PFIB is reversible, in which connection the equilibrium of the exchange is shifted substantially toward the starting compounds. The possibility of effecting the reverse reaction was shown experimentally: when monochloride (II) is reacted with tetraethylammonium fluoride polyhydrofluoride under mild conditions the Cl is replaced by F (however, the product formed here is not PFIB itself, but rather its hydrofluorination product, namely $(CF_3)_3CH$).

In order to shift the equilibrium of the exchange toward the formation of the substitution product it is necessary to use a reagent that irreversibly binds the F^-. The acid chlorides, and in particular $POCl_3$, proved to be such reagents. Thus, monochloride (II) was obtained in satisfactory yield when PFIB is heated with excess $POCl_3$ in the presence of catalytic amounts of TEBA (160-180°C). Together with it, the disubstitution product, 1,3-dichloro-1,3,3-trifluoro-2-trifluoromethyl-1-propene (III), was isolated from the reaction mixture. The formation of dichloride (III) is due to the fact that carbanion (I) is stabilized by the elimination of F^- from either the $CClF_2$ or CF_3 group. The "vinylic" chloride (II) is formed in the first case, while the "allylic" chloride (IV) is formed in the second case. Monochloride (IV), which contains a terminal difluoromethylene group, in its reactivity is comparable to PFIB and under the reaction conditions undergoes further attack by Cl^-, which in the final analysis gives dichloride (III) via carbanion (V). The fluorine anion, which is cleaved from carbanions (I) and (V), is bound irreversibly by reaction with $POCl_3$, in which connection Cl^- is regenerated.



$$POCl_3 + F^- \rightarrow POCl_2F + Cl^-$$

It should be mentioned that usually the vinylic F atom is replaced when nucleophiles act on PFIB [2], but in the reactions with organometallic compounds both the vinylic and allylic F atoms are replaced, so the fact that dichloride (III) is formed is not unexpected [3, 4] (also see [5]).

The proposed mechanism for the formation of chlorides (II) and (III), which includes the addition of Cl^- to PFIB, is confirmed by the fact that PFIB fails to react with $POCl_3$ at 180-200°C in the absence of

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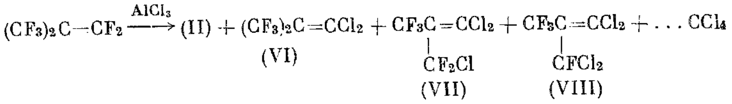
TEBA. PFIB does not react with PCl_3, $SnCl_4$ or BCl_3 under the same conditions. Only when PFIB is heated with $AlCl_3$ (150-170°C) is the F replaced by Cl*, in which connection the reaction is nonselective and, along with monochloride (II), substantial amounts of the geminal dichloride (VI), and also the tri- and tetrachloropolyfluoroisobutylenes (VII) and (VIII), are formed. The complete exchange of F by Cl cannot be achieved here: the reaction is accompanied by the degradation of the molecule with the formation of CCl_4.

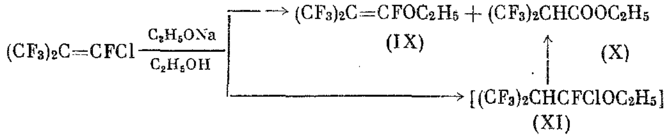


$$(CF_3)_2C{=}CF_2 \xrightarrow{AlCl_3} (II) + \underset{(VI)}{(CF_3)_2C{=}CCl_2} + \underset{(VII)}{CF_3\underset{CF_2Cl}{C}{=}CCl_2} + \underset{(VIII)}{CF_3\underset{CFCl_2}{C}{=}CCl_2} + \ldots CCl_4$$

The exchange of F by Cl in PFIB is also achieved by treating it with benzoyl chloride in the presence of catalytic amounts of pyridine. In this case the Cl^- source is evidently benzoylpyridinium chloride (cf. [7]), while the equilibrium of the exchange is shifted toward the formation of chlorination products via the conversion of the benzoyl chloride to benzoyl fluoride. The analogous reaction of PFIB with benzoyl bromide and pyridine gave the product of replacing the F by Br.†

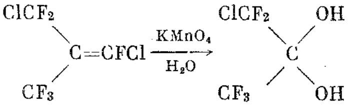
$$(CF_3)_2C{=}CF_2 + C_6H_5COX \xrightarrow{C_5H_5N} (CF_3)_2C{=}CFX + C_6H_5COF$$
$$X = Cl,\ Br$$

Olefins (II), (III), and (VI) proved to be less active than PFIB in the reactions with nucleophilic reagents. Thus, monochloride (II) remains unchanged when refluxed with alcohol, and only when treated with sodium ethylate and alcohol does it give ethyl perfluoroisobutenyl ether (IX) and ethyl hexafluoroisobutyrate (X). The latter is probably formed by the alcoholysis of the alcohol addition product (XI).



$$(CF_3)_2C{=}CFCl \xrightarrow[C_2H_5OH]{C_2H_5ONa} \underset{(IX)}{(CF_3)_2C{=}CFOC_2H_5} + \underset{(X)}{(CF_3)_2CHCOOC_2H_5};\quad \underset{(XI)}{[(CF_3)_2CHCFClOC_2H_5]} \rightarrow (X)$$

The reaction of monochloride (II) with Et_2NH leads to replacement of the chlorine atom and the formation of diethylperfluoroisobutenylamine. The structure of dichloride (III) was confirmed by its oxidation with $KMnO_4$, which resulted in the formation of chloropentafluoroacetone hydrate.



EXPERIMENTAL METHOD

The IR spectra were taken on a UR-20 instrument. The ^{19}F NMR spectra were recorded on a Hitachi H-6013 instrument (56.46 MHz), and the chemical shifts were measured from CF_3COOH (external standard). The GLC analysis was run on an LCM-8M chromatograph, using a column packed with Fluorosilicone deposited on Aeropak.

1-Chloro-1,3,3,3-tetrafluoro-2-trifluoromethyl-1-propene (II). a) A mixture of 80 ml of $POCl_3$, 3.5 g of TEBA, and 68 g of PFIB was heated in a steel autoclave at 160-170°C for 25 h. The fraction with bp up to 80-90°C was distilled from the reaction mass, treated with ice, and the organic layer was separated, mixed with several ml of alcohol under cooling, poured into water, and the organic layer was shaken under cooling with conc. H_2SO_4, separated, and kept over K_2CO_3. Distillation through a fractionating column gave 25 g (34%) of monochloride (II) and 7 g (9%) of dichloride (III). Monochloride (II): bp 40-42°C; n_D^{20} 1.3005. Found: C 21.90; F 61.47%. C_4F_7Cl. Calculated: C 22.12; F 61.43%. Infrared spectrum: 1665 cm^{-1} (C=C). ^{19}F NMR spectrum, ppm: −28.5 q.q. (CF); −17.4 m [$(CF_3)_2C=$]; $J_{cis\text{-}CF_3\text{-}F}$ = 27 Hz, $J_{trans\text{-}CF_3\text{-}F}$ = 12 Hz. Dichloride (III): bp 71-72°C. Found: C 20.17; F 48.48%. $C_4F_6Cl_2$. Calculated: C 20.60; F 48.92%. Infrared spectrum: 1670 cm^{-1} (C=C). ^{19}F NMR spectrum, ppm: −30 m (CF_2); −28 m (CF); −19.2 m (CF_3).

b) A mixture of 35 ml of benzoyl chloride, 1.5 ml of pyridine, and 34 g of PFIB was heated in a steel autoclave at 160-170°C for 25 h. Distillation of the reaction mixture gave 18 g (49%) of monochloride

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*In this reaction, the same as in other reactions with electrophilic reagents, PFIB is much less active than perfluoropropylene [6].

†Bromoperfluoroisobutylene was obtained recently by the reaction of hexafluoroacetone with bromofluoromethylenetriphenylphosphorane [8].

(II) and 8.7 g (21%) of 1, 1-dichloro-3,3-trifluoro-2-trifluoromethyl-1-propene (VI) with bp 71-74°C. The IR and NMR spectra of dichloride (VI) were identical with those described in [9].

Reaction of PFIB with $AlCl_3$. A mixture of 48 g of anhydrous $AlCl_3$ and 55 g of PFIB was heated in a steel autoclave at 150-160°C for 28 h, the unreacted PFIB (18 g) was distilled off, and the mixture of chlorides was collected in a trap (−78°C) by heating the residue on the steam bath in vacuo (10 mm). Redistillation of this mixture gave 4.7 g of a fraction with bp 35-71°C, which contained 77% of monochloride (II) and 8% of dichloride (VI), and 15 g of a fraction with bp 71-74°C, which contained 94% of dichloride (VI) and 6% of CCl_4; the 7 g of residue was a mixture that contained 13% of dichloride (VI), 51% of trichloride (VII), and 36% of tetrachloride (VIII). The composition of the fractions was determined by GLC. ^{19}F NMR spectrum of trichloride (VII): −30.5 g (CF_2); −20 t (CF_3); J = 14.5 Hz; tetrachloride (VIII): −26.6 g (CF); −21.4 d (CF_3); J = 17 Hz. The main product was CCl_4 when the reaction was run under more drastic conditions.

Reactions of 1-chloro-1,3,3,3-tetrafluoro-2-trifluoromethyl-1-propene (II). a) To a solution of 4 g of $Et_4NF \cdot 3HF$ (see [10] for preparation) in 10 ml of absolute CH_3CN was added 2.4 g of monochloride (II) in 5 ml of CH_3CN. After 0.5 h, distillation into a trap (−78°C) gave 1.8 g (75%) of $(CF_3)_3CH$, which was identical with an authentic sample (GLC, NMR).

b) With cooling, to a solution of 5.6 g of monochloride (II) in 6 ml of absolute alcohol was added in drops a solution of sodium alcoholate (from 1.38 g of Na and 15 ml of alcohol), after which the mixture was stirred for 0.5 h and then diluted with water; the organic layer was separated, washed with water, and dried over $CaCl_2$. We obtained 3.8 g of a mixture that contained 54% of ether (IX) and 29% of ester (X) (identified by GLC and the NMR spectra).

c) With strong cooling and stirring, to a solution of 4.33 g of monochloride (II) in 10 ml of absolute ether was gradually added a solution of 2.92 g of Et_2NH in 5 ml of absolute ether, after which the mixture was stirred for 0.5 h and then let stand at 0°C for 12 h. The $Et_2NH \cdot HCl$ (1.5 g) was filtered off, and the filtrate was distilled to give 1.9 g (38%) of diethylperfluoroisobutenylamine, bp 64.5-65°C (10 mm), which was identical with an authentic specimen [11] (GLC, NMR).

Oxidation of 1,3-dichloro-1,3,3-trifluoro-2-trifluoromethyl-1-propene (III). A mixture of 4.6 g of dichloride (III), 4.7 g of $KMnO_4$, and 10 ml of water was stirred at 100°C for 20 h. The reaction mass was decolorized by the passage of SO_2, extracted with ether, and the ether extract was dried over $MgSO_4$. Distillation gave 1.45 g (37%) of chloropentafluoroacetone hydrate, bp 45-52°C (85 mm). The ^{19}F NMR spectrum was identical with the spectrum of an authentic specimen [12].

1-Bromo-1, 3, 3, 3-tetrafluoro-2-trifluoromethyl-1-propene. A mixture of 33 ml of benzoyl bromide, 2 ml of pyridine, and 34 g of PFIB was heated in a steel autoclave at 170-180°C for 18 h. Distillation of the reaction mixture gave 22.5 g (54.5%) of the monobromide with bp 56-58°C; n_D^{20} 1.3260. Found: C 18.39; F 50.87%. C_4F_7Br. Calculated: C 18.41; F 50.95%. Infrared spectrum: 1640 cm^{-1} (C = C). ^{19}F NMR spectrum, ppm: −37 g.g. (CF); −17 m $[(CF_3)_2C=]$; $J_{cis\text{-}CF_3-F}$ = 26 Hz, $J_{trans\text{-}CF_3-F}$ = 12.5 Hz. Distillation of the residue gave 5.4 g (10%) of 1,1-dibromo-3,3,3-trifluoro-2-trifluoromethyl-1-propene (XII) with bp 108-110°C. Found: C 15.63; F 36.61%. $C_4F_6Br_2$. Calculated: C 14.99; F 35.40%. Infrared spectrum: 1670 cm^{-1} (C = C). ^{19}F NMR spectrum, ppm: −19.1 s. When the reaction time is reduced to 6-8 h the fraction with bp 108-110°C represents a mixture of dibromide (XII) and $CF_3C(CF_2Br) = CFBr$. Infrared spectrum: 1640 cm^{-1} (C = C). ^{19}F NMR spectrum, ppm: −40 m (CF); −34.8 m (CF_2); −20 m (CF_3).

CONCLUSIONS

1. Treatment of perfluoroisobutylene with various halides resulted in the exchange of fluoride for chlorine.

2. A method was developed for the synthesis of the monochloro- and monobromoperfluoroisobutylenes.

3. Substitution of chlorine for fluorine at the multiple bond of perfluoroisobutylene lowers the reactivity of the fluoroolefin toward nucleophilic reagents.

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