NUCLEOPHILIC ADDITION OF SULFENYL CHLORIDES TO HIGHLY ELECTROPHILIC FLUOROOLEFINS

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As a rule, such highly electrophilic unsaturated compounds as perfluoroisobutylene (PFIB) [1] or perfluoromethacrylic acid derivatives [2], are fairly insensitive toward electrophilic attack and in most cases react with electrophilic reagents only in the presence of nucleophilic catalysts. Here conjugated nucleophilic addition to the multiple bond of the fluoroolefin occurs.

$$>C{=}CF_2 \xrightarrow{X^-} >\overline{C}{-}CF_2{-}X \xrightarrow[-X^-]{AX} >\underset{\displaystyle A}{\underset{|}{C}}{-}CF_2{-}X$$

(I)

Reactions of this type, involving the fluorine anion, have been studied extensively in recent years [3]. It was also shown that PFIB, when catalyzed by chlorine anion, adds HCl by an analogous scheme to give the corresponding hydrochloride via the intermediate formation of carbanion (I) [4]. The addition of HCl to methyl perfluoromethacrylate (II) proceeds by a similar scheme [5]. In the absence of electrophilic reagents, capable of reacting with carbanion (I), the reaction of PFIB with chlorine anion leads to the exchange of fluorine by chlorine in the fluoroolefin [6].

We found that the nucleophilic addition scheme also holds when PFIB reacts with certain aliphatic and aromatic sulfenyl chlorides. In contrast to vinyl fluoride [7] and vinylidene fluoride [8], PFIB does not react with sulfenyl chlorides in the absence of catalysts.* However, in aprotic dipolar solvents, in the presence of triethylbenzylammonium chloride (TEBA), it smoothly adds sulfenyl chlorides under mild conditions to give the adducts (III). In a similar manner, the reaction of ester (II) with phenylsulfenyl chloride gave adduct (IV). Pyridine is also an efficient catalyst for this reaction, whose role evidently consists in the generation of chlorine anion when it reacts with RSCl (cf. [10]).

$$(CF_3)_2C{=}CF_2 \xrightarrow{Cl^-} (CF_3)_2\overline{C}{-}CF_2Cl \xrightarrow{RSCl} \underset{\displaystyle SR}{\underset{|}{(CF_3)_2C}}{-}CF_2Cl$$

(I) (III)

R = C_6H_5 (a), C_2H_5 (b), $C_6H_5CH_2$ (c)

$$\underset{\displaystyle CF_3}{\underset{|}{CF_2{=}C}}{-}COOCH_3 + C_6H_5SCl \xrightarrow{C_5H_5N} ClCF_2{-}\underset{\displaystyle SC_6H_5}{\overset{\displaystyle CF_3}{\overset{/}{\underset{\backslash}{C}}}}{-}COOCH_3$$

(II) (IV)

The structure of the (III) adducts was confirmed by the ^{19}F NMR spectra, in which the signals from the $ClCF_2$ group are observed in the −26 to −27 ppm region. With an opposite orientation of the addition of sulfenyl chlorides to PFIB, which would lead to the compounds $(CF_3)_2CClCF_2SR$, it could be expected that the signal from the $RSCF_2$ group would be further upfield. For example, in monohydroperfluoroisobutyl phenyl sulfide (V) the chemical shift of the CF_2 group is −5.5 ppm. Compound (V) is formed along with unsaturated sulfide (VI) when PFIB is reacted with thiophenol.

* Polyfluoroethylenes and perfluoropropylene add CF_3SCl by the radical mechanism using either UV or peroxide initiation [9].

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$$(CF_3)_2C{=}CF_2 + C_6H_5SH \rightarrow \underset{(V)}{(CF_3)_2CHCF_2SC_6H_5} + \underset{(VI)}{(CF_3)_2C{=}CFSC_6H_5}$$

As it proved, PFIB reacts in a completely different manner with trichloromethylsulfenyl chloride in the presence of chlorine anion. Here dichloroperfluoroisobutane (VII) and thiophosgene are formed, and not an adduct of the (III) type.

$$(CF_3)_2C{=}CF_2 + CCl_3SCl \xrightarrow{Cl^-} \underset{\underset{(VII)}{Cl\ \ Cl}}{(CF_3)_2C{-}CF_2} + CCl_3\overline{S} \xrightarrow{-\overline{Cl}} CCl_2{=}S$$

Dichloride (VII) was also obtained by the reaction of PFIB with chlorocarbonylsulfenyl chloride. As a result, it is evident that when PFIB and ester (II) react with the phenyl-, ethyl-, and benzylsulfenyl chlorides the intermediate carbanion attacks the sulfur atom of the sulfenyl chloride and chlorine anion is eliminated; at the same time, when reaction is with sulfenyl chlorides that bear electron-acceptor substituents the attack is directed toward the positivized chlorine atom of the sulfenyl chloride, which in sum total leads to chlorination of the fluoroolefin and formation of the decomposition products of the RS anion. A similar dual reactivity was observed previously, and in particular in the reactions of CF_3SCl with Grignard reagent [11].

EXPERIMENTAL

The NMR spectra were taken on Perkin-Elmer R-12 (^1H, 60 MHz), Hitachi, and Perkin-Elmer R-20 (^{19}F, 56.46 MHz) spectrometers in CCl_4 solution. The chemical shifts are given in parts per million from the external standards TMS (^1H, δ scale) and CF_3COOH (^{19}F). The GLC analysis was run on an LKhM-8MD instrument, equipped with a column packed with Silicone DS-550 deposited on Chromosorb.

Chlorooctafluoro-tert-butyl Phenyl Sulfide (IIIa). A mixture of 3.3 g of phenylsulfenyl chloride, 0.5 g of TEBA, and 6 g of PFIB in 15 ml of abs. monoglyme was kept for 2 days at 20°C. The unreacted PFIB was distilled off, the residue was poured into water, and the organic layer was extracted with ether, dried over $MgSO_4$, and distilled to give 4.7 g (60%) of sulfide (IIIa) with bp 56-58° (2 mm); n_D^{20} 1.4470. Found: C 34.65; H 1.53%. $C_{10}H_5ClF_8S$. Calculated: C 34.83; H 1.45%. PMR spectrum: 7.6 m (C_6H_5). ^{19}F NMR spectrum: −14.9 t (CF_3), −26.7 h (CF_2); J = 10 Hz. PFIB does not react with C_6H_5SCl in Freon-113 (8 h, 150°).

Chlorooctafluoro-tert-butyl Ethyl Sulfide (IIIb). To a solution of 30 g of PFIB and 0.2 g of C_5H_5N in 30 ml of monoglyme was added in drops, with stirring and cooling in ice, 13.5 g of ethylsulfenyl chloride in 15 ml of monoglyme. The mixture was kept for 4 h at 20°, the unreacted PFIB was distilled off, the residue was poured into water, and the organic layer was separated and vacuum-distilled over conc. H_2SO_4 to give 28.7 g (70%) of sulfide (IIIb) with bp 56-59° (60 mm); n_D^{20} 1.3719. Found: C 24.02; H 1.60; F 50.83%. $C_6H_5ClF_8S$. Calculated: C 24.28; H 1.69; F 51.26%; PMR spectrum: 1.2 t (CH_3), 2.98 q (CH_2); J = 8 Hz. ^{19}F NMR spectrum: −14.2 t (CF_3), −26.6 h (CF_2); J = 10.4 Hz.

Reaction of Perfluoroisobutylene with Benzylsulfenyl Chloride. With stirring and cooling, to a solution of 28 g of PFIB and 0.2 g of C_5H_5N in 25 ml of monoglyme was added 21 g of benzylsulfenyl chloride [12] in 10 ml of monoglyme. The mixture was kept for 6 h at 20°, poured into dilute HCl solution, and the obtained oil was extracted with ether, dried over $MgSO_4$, and distilled. We obtained 12.2 g of a fraction with bp 60-110° (2 mm), which contained (GLC) 80% of sulfide (IIIc) and 20% of chlorooctafluoro-tert-butyl benzyl disulfide (VIII). Subsequent fractional distillation gave: sulfide (IIIc), bp 63-64° (2 mm): n_D^{20} 1.4510. Found: C 36.74; H 1.95; F 42.17%. $C_{11}H_7ClF_8S$. Calculated: C 36.82; H 1.95; F 42.39%. PMR spectrum: 3.7 s (CH_2), 6.65 s (C_6H_5). ^{19}F NMR spectrum: 14.2 t (CF_3), −26.3 (CF_2); J = 10 Hz. Disulfide (VIII): bp 98-102° (2 mm); n_D^{20} 1.4822. Found: C 33.77; H 1.89; F 39.31; S 16.33%. $C_{11}H_7ClF_8S_2$. Calculated: C 33.80; H 1.79; F 38.92; S 16.39%. PMR spectrum: 3.8 s (CH_2), 7.0 s (C_6H_5). ^{19}F NMR spectrum: −15.3 t (CF_3), −27.2 h (CF_2); J = 10 Hz.

Methyl Ester of α-Chlorodifluoromethyl-α-phenylthiotrifluoropropionic Acid (IV). To 2.8 g of phenylsulfenyl chloride and 0.1 g of C_5H_5N in 5 ml of monoglyme was added in drops 3.9 g of ester (II) in 7 ml of monoglyme. At the end of exothermic reaction the mixture was poured into water, and the obtained oil was extracted with ether, dried, and distilled. We obtained 4.5 g (70%) of ester (IV), bp 90-93° (1 mm); n_D^{20} 1.4795. Found: C 39.49; H 2.35; F 28.29%. $C_{11}H_5ClF_5O_2S$. Calculated: C 39.40, H 2.41; F 28.39%. Infrared spectrum: 1760 cm^{-1} (C=O). PMR spectrum: 3.6 s (CH_3), 7.5 m (C_6H_5). ^{19}F NMR spectrum: −14.7 d. d (CF_3), −25.9 (F_A), and −28.5 (F_B) (CF_2, AB system, each component of which is split into a quadruplet); $J_{CF_3-F(A)} = 15$, $J_{CF_3-F(B)} = 11$, $J_{F(A)-F(B)} = 184$ Hz.

Reaction of Perfluoroisobutylene with Trichloromethyl- and Chlorocarbonylsulfenyl Chlorides. A mixture of 7.8 g of CCl_3SCl, 0.75 g of TEBA, and 9.5 g of PFIB in 20 ml of monoglyme was heated in a sealed ampul for 8 h at 100°. A fraction with bp up to 82° was distilled from the reaction mixture, the distillation of which over conc. H_2SO_4 gave 5.2 g of a mixture with bp 50-62°, which, based on the GLC data, contained 63% of dichloride (VII), 24% of thiophosgene, and 14% of PFIB. ^{19}F NMR spectrum of dichloride (VII): −9.0 t (CF_3), −21.3 h (CF_2); J = 12 Hz. In a similar manner, from 4.2 g of ClCOSCl, 0.3 g of TEBA, and 7.5 g of PFIB in 25 ml of monoglyme we obtained, after 5 h at 20°, 3.6 g of a fraction with bp 55-63°, which contained 80% of dichloride (VII) and 20% of PFIB.

Reaction of Perfluoroisobutylene with Thiophenol. A mixture of 2 g of thiophenol, 5 ml of abs. MeCN, and 5 g of PFIB was heated in an autoclave for 7 h at 150°. Distillation of the reaction mixture gave 5 g of a fraction with bp 82-86° (15 mm), which contained (GLC) 88% of sulfide (V) and 12% of sulfide (VI) [13]. PMR spectrum of (V): 3.16 m (CH), 7.1 m (C_6H_5). ^{19}F NMR spectrum: −5.5 d. h. (CF_2), −15.0 d. t. (CF_3); $J_{CF_3-CF_2} = J_{CF_2-CH} = 10$, $J_{CF_3-CH} = 7.5$ Hz.

CONCLUSIONS

1. When catalyzed by chlorine anion or pyridine, alkyl- or arylsulfenyl chlorides add to perfluoroisobutylene or to methyl perfluoromethacrylate by the nucleophilic mechanism.

2. Perfluoroisobutylene when reacted with either trichloromethyl- or chlorocarbonylsulfenyl chloride in the presence of chlorine anion adds chlorine at the multiple bond.

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