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REACTION OF PERFLUOROISOBUTYLENE WITH SULFUR YLIDES

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The addition of nucleophilic reagents, carrying leaving groups on the nucleophilic center, to perfluoroisobutylene (PFIB) is accompanied by intramolecular cyclization with either the cleavage of leaving groups [1, 2] or the elimination of F anion from the CF₂ group [2, 3], which leads to vinylic substitution products. Here the direction of the process depends both on the nature of the nucleophilic center and on the properties of the leaving group.

$$(CF_3)_2C = CF_2 + \vec{N}u - X \rightarrow (CF_3)_2\vec{C} - CF_2 \xrightarrow{-\vec{F}} (CF_3)_2C - CF_2 \xrightarrow{Nu} V_1$$

Until now the discussed type of reaction, involving PFIB and C-nucleophiles, has been studied only on the example of α -halo carbanions [3]. We reacted this fluoroolefin with another C-anion, carrying a leaving group, and specifically with dimethylsulfonium carbethoxymethylide (I). It is known that (I), like other sulfur ylides, reacts easily with activated olefins, with the cleavage of dimethyl sulfide and the formation of cyclopropane derivatives [4]. The reaction of ylide (I) with PFIB also proceeds under very mild conditions, but instead of the corresponding cyclopropane (V), a new ylide (III) is formed here, probably by the dehydrofluorination of the intermediate fluorosulfuran (II), and also (CF₃)₃CH, the hydrofluorination product of PFIB.



The structure of (III) was confirmed by spectral methods and its conversion to ylide (IV) by treatment with water. Cyclopropane (V) could be obtained by reacting PFIB with diazo-acetic ester (cf. [5, 6]).

As a result, on the example of reacting PFIB with ylide (I), it was established that the reaction of fluoroolefins with S ylides is analogous to their reaction with the P [7] and As

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ylides [8]: Either perfluoroalkenyl-substituted onium fluorides or the products of their further transformations are formed as the result of addition and cleavage.

This also proved to be valid for the reaction of PFIB with N-ethoxycarbonyliminodimethylsulfuran (VI), which is also accompanied by the elimination of the vinylic F atom. Here, azetidine (IX), $(CF_3)_3CH$, and $(CF_3)_3C-CH_2SCH_3$ (X) are formed. Evidently, N-carbethoxy-bis-(trifluoromethyl)ketenimine (VIII) is formed as an intermediate here due to the 1,2-cleavage of dimethyldifluorosulfuran from fluorosulfuran (VII), the vinylic substitution product. Then ketenimine (VIII) reacts with PFIB under the reaction conditions to give cycloadduct (IX) (cf. [9]).

The formation of two other products is explained by the properties of dimethyldifluorosulfuran, which spontaneously undergoes dehydrofluorination and subsequent migration of F from the S atom to the C atom [10]. The hydrofluorination of PFIB, and also its reaction with fluoromethyl sulfide, leads, respectively, to $(CF_3)_3CH$ and sulfide (X). The latter was synthesized independently by the alkylation of the perfluoro-tert-butyl anion with chloromethyl methyl sulfide. The transformations, leading to azetidine (IX) and sulfide (X), require catalysis by F anion, whose source is apparently sulfuran (VII).

 $(CH_{3})_{2}SF_{2} \xrightarrow{-HF} FCH_{2}SCH_{3} \xrightarrow{(CF_{3})_{2}C \Longrightarrow CF_{2}} (CF_{3})_{3}C \longrightarrow (CF_{3})_{3}C \xrightarrow{(CH_{2}SCH_{3})_{3}C} (CF_{3})_{3}C \xrightarrow{(CH_{2}SCH_{3})_{3}C} (X)$

At the present time the reactions of compounds, containing electrophilic multiple bonds, with nucleophiles, carrying leaving groups, are widely used in synthesis, especially for obtaining small carbo- and heterocycles. The specific traits of the fluoroolefins limit the possibility of similar syntheses involving them, since vinylic substitution competes with intramolecular cyclization. In particular, the results of the present paper show that the presence of sulfonium fragments (or other onium fragments, see [11, 12]) that are β to the F atom of the CF₂ group of carbanions, which are formed by the addition of nucleophiles to fluoroolefins, makes vinylic substitution especially preferable.

EXPERIMENTAL

The ¹H and ¹⁹F NMR spectra (δ , ppm) were taken on a Perkin-Elmer R-32 spectrometer (90 and 84.6 MHz) from the external standards TMS and CF₃COOH. The GLC analysis was run on an LKhM-8-MD instrument, using a column packed with Silicone DC-550 deposited on Chromosorb.

Reaction of Perfluoroisobutylene with Dimethylsulfonium Carbethoxymethylide (I). With stirring and cooling to 0°, 20 g of PFIB was passed into a solution of 6.5 g of ylide (I) in 40 ml of absolute MeCN. The next day the unreacted PFIB, $(CF_3)_3CH$, and solvent were evaporated. We obtained 10.5 g (71%) of ylide (III), mp 115-117° (from benzene). Found, %: F 40.31. $C_{10}H_{11}F_7O_2S$. Calculated, %: F 40.55. ¹⁹F NMR spectrum (in CHCl₃): -24.5 d.q (cis-CF₃), -19.8 d.q (trans-CF₃), -15.3 m (CF), $J_{CIS}-CF_3-F = 20.6$, $J_{trans}-CF_3-F = 13.2$, $J_{CF_3}-CF_3 = 7.5$ Hz.

A solution of 4.3 g of ylide (III) in 15 ml of acetone and 2 ml of water was refluxed for 6 h, diluted with water, and the obtained crystals were dried to give 3.6 g (80%) of ylide (IV), mp 86-88° (from CC1₄). Found, %: C 36.64; H 3.58; F 34.78. C₁₀H₁₂F₆O₃S. Calculated, %: C 36.81; H 3.68; F 34.96. ¹H NMR spectrum (in CHCl₃): 1.4 t (CH₃), 3.1 s [(CH₃)₂S], 4.3 q (CH₂), 6.3 h (CH), $J_{CH_3-CH_2} = 7.3$, $J_{H-F} = 8.5$ Hz. ¹⁹F NMR spectrum: -15.1 d (CF₃). Reaction of Perfluoroisobutylene with N-Ethoxycarbonyliminodimethylsulfuran (VI). With stirring and cooling, 25 g of PFIB was passed into a solution of 4.8 g of iminosulfuran (VI) [13] in 25 ml of absolute MeCN, the mixture was kept for 3 h at about 20°, the unreacted PFIB and $(CF_3)_3CH$ were distilled off, the residue was poured into 1:5 HCl solution, and the organic layer was distilled over conc. H_2SO_4 to give 12 g of a fraction with bp 25-58° (12 mm), which contained (GLC) 30% of sulfide (X) and 47% of azetidine (IX). Based on the GLC and ¹⁹F NMR data, the reaction mixture is devoid of 1-ethoxycarbonyl-2,2-difluoro-3,3-bis-(trifluoromethyl)aziridine [2].

Methyl 2,2-Bis(trifluoromethyl)-3,3,3-trifluoropropyl Sulfide (X). With stirring and cooling with ice, to 6.5 g of freshly ignited CsF and 9 g of PFIB in 35 ml of absolute monoglyme was added 3.7 g of CH₃SCH₂Cl, and after 5 h the mixture was poured into water, and the lower layer was separated and distilled over conc. H_2SO_4 into a trap (-78°) at 10 mm Hg. Redistillation gave 6.2 g (58%) of sulfide (X), bp 115-116°, $n_D^{2\circ}$ 1.3429. Found, %: C 25.59; H 1.85; F 61.14. $C_6H_5F_9S$. Calculated, %: C 25.71; H 1.79; F 61.07. ¹H NMR spectrum: 2.0 s (CH₃), 3.1 s (CH₂). ¹⁹F NMR spectrum: -10.5 s (CF₃).

Ethyl Ester of 2,2-Difluoro-3,3-bis(trifluoromethyl)cyclopropanecarboxylic Acid (V). A mixture of 5.7 g of diazoacetic ester and 10 g of PFIB in 25 ml of ether was heated in a steel autoclave for 20 h at 100-120°, the volatiles and a part of the ether were distilled off, and the residue was distilled over conc. H₂SO₄ to give 3.7 g (26%) of ester (V), bp 55-58° (25 mm), np^{2°} 1.3330. Found, %: C 33.52 H 2.11. C₈H₆F₈O₂. Calculated, %: C 33.56 H 2.06. ¹H NMR spectrum: 1.05 t (CH₃), 3.4 d.d (CH), 4.1 q (CH₂), J_{CH₃-CH₂ = 6.5 Hz. ¹⁹F NMR spectrum: -16.9 d.d.q (F^a), -12.9 d.d.q (F^b), +53.7 d.d.q.q (F^c), +75.1 d.d.q.q. (F^d), J_{F^a-F^b} = 9, J_{F^a-F^c} = 18.8, J_{F^a-F^d} = 3, J_{F^b-F^d} = 15.1, J_{F^b-F^c} = 3.5, J_{F^d-H} = 14.1, J_{F^c-H} = 4.0, J_{F^c-F^d} = 177 Hz.}

CONCLUSIONS

The reaction of perfluoroisobutylene with sulfur ylides leads to the substitution products of the vinylic F atom in the fluoroolefin.

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