CONDENSATION OF PERFLUOROISOBUTYLENE WITH COMPOUNDS CONTAINING DIHALOMETHYLENE GROUPS

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Perfluoroisobutylene (PFIB) and compounds with active methylene groups in the presence of CsF form either bis(trifluoromethyl)allenes or their adducts with CsF [1].

We established that this reaction leads to the same result with certain compounds that contain dihalomethylene groups instead of methylene groups. Thus, the reaction of PFIB with 2,2-dibromohexafluoropropane* (Ia) and CsF in diglyme at 20°C gives the adduct of tetrakis(trifluoromethyl)allene with CsF (IIa) and perfluoro-tert-butyl bromide (III). The stoichiometry of this reaction is such that the complete conversion of dibromide (Ia) and the maximum yield of the products are reached using a threefold mole excess of PFIB with respect to the dibromide and CsF; unreacted dibromide (Ia) remains in the reaction mixture if a deficiency of the fluoroolefin is used.

$$3(CF_3)_2C{=}CF_2 + \underset{(I)}{Br_2CRR'} \xrightarrow{CsF} \underset{(II)}{(CF_3)_2C{=}CF\overset{\ominus}{C}RR'\overset{\oplus}{Cs}} + \underset{(III)}{(CF_3)_3C{-}Br}$$

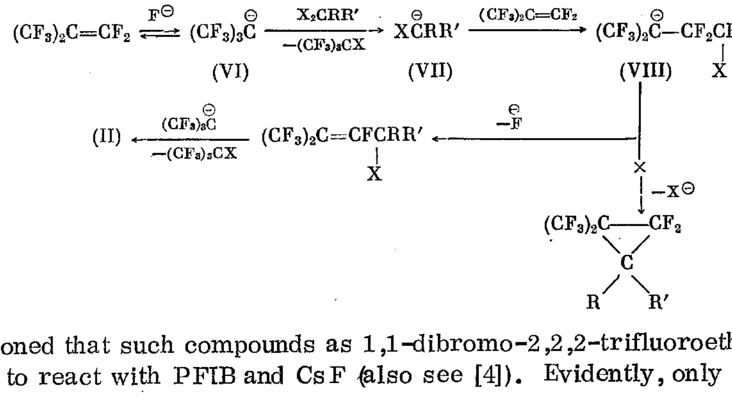
$$R = R' = CF_3\ (a);\ R = CF_3,\ R' = CN\ (b);\ R = COOEt,\ R' = CN\ (c).$$

In a similar manner, the gem-dibromides (Ib, c),† and also dichloromalonic ester, easily react with PFIB and CsF. In the latter case perfluoro-tert-butyl chloride is formed along with the adduct of 1,1-bis(carbethoxy)-3,3-bis(trifluoromethyl)allene and CsF (IId).

The structure of adducts (IIb–d) was proved by the ^{19}F NMR method, and also by conversion to the olefins (IV) by treatment with mineral acids [1]. Allene (V) was isolated from adduct (IIa) by thermolysis [2]:

$$\underset{(IVb-d)}{(CF_3)_2CHCF{=}CRR'} \xleftarrow{H^{\oplus}} (II) \xrightarrow{t^{\circ}} \underset{(V)}{(CF_3)_2C{=}C{=}C(CF_3)_2}$$

Apparently, the key step of the described reaction is the reaction of the perfluoro-tert-butyl anion (VI) with gem-dihalides (I) on the type of halophilic reactions [3], which lead to the halogenation of anion (VI) and the generation of the α-halocarbanion (VII). This carbanion then substitutes the vinylic F atom in the PFIB molecule to give the intermediate product (IX). The latter also halogenates anion (VI), which leads to the end products:



It should be mentioned that such compounds as 1,1-dibromo-2,2,2-trifluoroethylbenzene or benzotribromide could not be made to react with PFIB and CsF (also see [4]). Evidently, only compounds containing a quite

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*A convenient method for the synthesis of dibromide (Ia) is the fluorobromination of 2-bromopentafluoropropylene (see the Experimental part).

†Adduct (IIb) was also obtained by the reaction of PFIB and CsF with 3,3,3-trifluoropropionitrile.

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"positive" halogen atom are capable of halogenating anion (VI).

Our earlier study of the reactions of PFIB with N-anions that carry leaving groups disclosed that the addition of these nucleophiles to a fluoroolefin is accompanied by intramolecular cyclization to aziridines [5]. In the discussed case such transformation involving C-anion (VIII) could lead to cyclopropanation of the PFIB, as is observed in the series of ordinary activated olefins [6]. However, fluoro-containing cyclopropanes could not be detected in the reaction products of PFIB with dihalides (I). This serves as evidence that the intermediate carbanion (VIII), which is responsible for the cyclization, is stabilized in the usual manner for fluoroolefins, by the elimination of F^- anion from the difluoromethylene group. In contrast to the gem-dihalides (I), methylene iodide when reacted with PFIB and CsF gives only the product of replacing iodine by the $(CF_3)_3C$ group, namely iodide (X):

$$(CF_3)_3\overset{\ominus}{C} + CH_2I_2 \xrightarrow[-I^{\ominus}]{} \underset{(X)}{(CF_3)_3C{-}CH_2I}$$

Similar to CH_2I_2, dibromodifluoromethane when reacted with PFIB and CsF gives perfluoroneopentyl bromide [7]. At the present time we are studying the reasons for the different behavior of CF_2Br_2 and dibromides (I) toward the perfluoro-tert-butyl anion.

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra (δ, ppm) were taken on a Perkin–Elmer R-32 spectrometer (90 and 84.6 MHz) from the external standards TMS and CF_3COOH. The IR spectra were recorded on a UR-20 instrument.

2,2-Dibromohexafluoropropane (Ia). An equimolar mixture of 2-hydropentafluoropropylene and bromine in Freon-113 was kept in a sealed ampul in the light until it became colorless (8-10 days). Distillation gave 1,2-dibromo-2-hydropentafluoropropane (XI), bp 89-91°, n_D^{20} 1.3801 (cf. [8]). PMR spectrum: 4.27 t.q (CH). ^{19}F NMR spectrum: −28.8 m (CF_2), −11.8 d.t (CF_3); $J_{CF_3-CF_2} = J_{CF_2-H} = 9.4$, $J_{CF_3-H} = 5.6$ Hz.

To 30 g of granulated KOH was added in drops, at 50-55°, 30 g of dibromide (XI), and the distilled liquid was redistilled to give 15.6 (72%) of 2-bromopentafluoropropylene (XII), bp 26-28° (cf. [8]). ^{19}F NMR spectrum: −14.7 m (CF_3), −5.8 m (CF_2).

To a suspension of 7.0 g of freshly ignited CsF in 15 ml of abs. MeCN was added 5.9 g of bromine and then, with stirring and cooling with ice, was added 7.8 g of olefin (XII) in 5 ml of MeCN. The mixture was stirred for 1 h at 20°, poured into chilled HCl solution (1:5), and the organic layer was vacuum-distilled (10 mm) over conc. H_2SO_4 into a cooled trap (−78°) to give 8.2 g (70%) of dibromide (Ia), which was identical with that described in [9].

Reaction of 2,2-Dibromohexafluoropropane with Perfluoroisobutylene in Presence of CsF. With stirring and cooling with ice, into a mixture of 4.9 g of CsF and 8.2 g of dibromide (Ia) in 30 ml of abs. diglyme was passed 17 g of PFIB, after which the reaction mass was kept for 1.5 h at 20°, and then the low-boiling products were distilled at 10 mm into a trap (−78°), the redistillation of which gave 14 g (86%) of bromide (III), identical with that described in [10]. The residue from distilling off the volatile products was heated in vacuo as described in [2] to give 6.2 g (76%) of allene (V) with bp 46-48°, which was identical with the authentic sample (GLC, ^{19}F NMR).

Nitrile of 2,4-Bis(trifluoromethyl)-3,5,5,5-tetrafluoro-2-pentenoic Acid (IVb). With cooling, to 3.9 g of CsF in 20 ml of monoglyme were added 13 g of PFIB and then 5.7 g of CF_3CBr_2CN [11] in 6 ml of monoglyme. After 3 h the volatile products and solvent were vacuum-distilled and the residue was decomposed with HCl solution (1:5). Distillation of the organic layer gave 3.8 g of a fraction with bp 88-97°, which contained (GLC) 80% of (IVb). The pure compound was isolated by preparative GLC (QF-1 deposited on Chromosorb), bp 94-95°, n_D^{20} 1.3120. Found: C 29.21; H 0.42; F 65.64; N 5.17%. $C_7HF_{10}N$. Calculated: C 29.06; H 0.35; F 65.74; N 4.84%. Infrared spectrum (ν, cm^{-1}): 1685 (C = C). PMR spectrum: 4.26 d. h (CH). ^{19}F NMR spectrum: −16.0 d ($CF_3C=$), −12.2 t (CF_3); + 1.8 m (CF); $J_{CF_3-F} = 18.8$, $J_{(CF_3)_2C-F} = J_{(CF_3)_2C-H} = 7.5$, $J_{CH-CF} =$ 30 Hz. In a similar manner, (IVb) was obtained from PFIB, CsF, and CF_3CH_2CN in 72% yield.

Reaction of Dibromocyanoacetic Ester with Perfluoroisobutylene in Presence of CsF. With cooling and stirring, to 4 g of CsF in 25 ml of monoglyme were added 18 g of PFIB and then 7.2 g of dibromide (Ic) in 5 ml of of monoglyme, after which the mixture was kept for 4 h at 20° and then the volatiles and a part of the monoglyme were vacuum-distilled. We obtained a solution of the (IIc) salt (^{19}F NMR [1]), from which (IVc) was isolated in known manner [1] in 73% yield.

Diethyl Ester of 1,3,3,3-Tetrafluoro-2-trifluoromethylpropylidenemalonic Acid (IVd). The same as the preceding, the reaction of 22 g of PFIB, 7.5 g of dichloromalonic ester, and 5.9 g of CsF in 30 ml of monoglyme gave ester (IVd) in 80% yield, bp 65-67° (4 mm), n_D^{20} 1.3745. Found: C 38.13; H 3.38; F 39.05%. $C_{11}H_{11}F_7O_4$. Calculated: C 38.80; H 3.23; F 39.10%. Infrared spectrum (ν, cm^{-1}): 1695 (C = C), 1730-1760 (C = O). PMR spectrum: 1.0 and 1.02 t (Me), 4.10 and 4.08 q (CH_2), 5.65 d.h. (CH); J = 7.5 Hz. ^{19}F NMR spectrum: −13.1 t (CF_3), +16.0 d.h. (CF); $J_{CF_3-CH} = J_{CF_3-H} = 7.5$, $J_{CF-H} = 29.2$ Hz.

2,2-Bis(trifluoromethyl)-3,3,3-trifluoropropyl Iodide (X). With stirring and cooling with ice, to 17.7 g of CsF, 22 g of PFIB, and 40 ml of diglyme was added 26.7 g of CH_2I_2, and the mixture was stirred for 3 h at 20°. Distillation gave 25 g (70%) of iodide (X), bp 107-109°, 49-50° (90 mm), n_D^{20} 1.3630. Found: C 16.73; H 0.56; F 47.21%. $C_5H_2IF_9$. Calculated: C 16.67; H 0.55; F 47.49%. PMR spectrum: 3.68 s (CH_2). ^{19}F NMR spectrum: −11.1 s (CF_3).

CONCLUSIONS

The reaction of perfluoroisobutylene with some compounds, containing dihalomethylene groups, in the presence of CsF leads to the adducts of the 1,1-disubstituted 3,3-bis(trifluoromethyl)allenes with CsF.

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