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REACTION OF PERFLUORO-tert-BUTYL ANION WITH VICINAL DIHALOPOLYFLUOROALKANES

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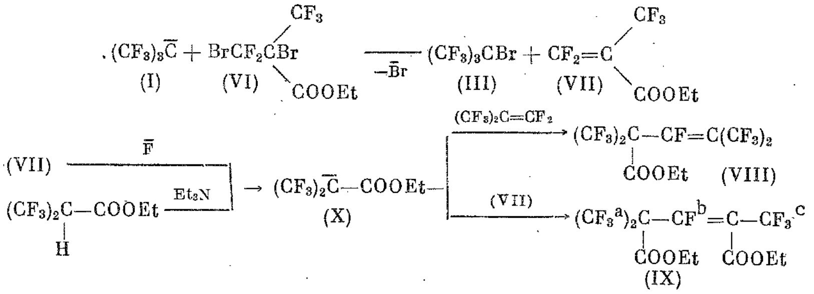
The perfluoro-tert-butyl anion (I) formed by the addition of fluoride anion to perfluoroisobutylene (PFIB) is readily alkylated by alkyl halides [1], including geminal [2] and vicinal [1] dihaloalkanes. In contrast, and in accordance with the inertness under normal conditions of the S_N reactions characteristic of perfluoroalkyl halides, the reaction of anion (I) with certain gem-dibromopolyfluoroalkanes proceeds according to the type of halogenophilic reactions. Thus, bromination of anion (I) takes place in this case [2, 3].

We found that anion (I) reacts in a similar way also with vicinal dibromopolyfluoroalkanes.* Dibromides give the corresponding fluoroolefins or products of their further transformations. In the reaction of anion (I) with 1,2-dibromohexafluoropropane (II) under mild conditions (0-20°C), perfluoro-tert-butyl bromide (III) and a mixed dimer of PFIB and hexafluoropropylene, the olefin (V), are formed.

$$(CF_3)_2C{=}CF_2 \overset{\bar{F}}{\rightleftarrows} \underset{(I)}{(CF_3)_3\bar{C}} \xrightarrow[-\bar{B}r]{BrCF_2CFBrCF_3\ (II)} \underset{(III)}{(CF_3)_3CBr} + CF_2{=}CFCF_3$$

$$CF_3CF{=}CF_2 \xrightarrow{(I)} \underset{(IV)}{CF_3\bar{C}FCF_2C(CF_3)_3} \xrightarrow[-\bar{F}]{} \underset{(V)}{CF_3CF{=}CFC(CF_3)_3}$$

Similarly, the reaction of anion (I) with the ester of 2,3-dibromo-2-trifluoromethyl-3,3-difluoropropionic acid (VI) proceeds readily. In this case, together with the tertiary bromide (III), transformation products of perfluoromethacrylic ester (VII), i.e., α-perfluoroisobutenylhexafluoroisobutyric ester (VIII) and the dimer of perfluoromethacrylic ester (IX) are formed. These compounds can be obtained by reacting perfluoromethacrylic ester with PFIB in the presence of a fluoride anion, or by a triethylamine-catalyzed reaction of the ester of α-hydrohexafluoroisobutyric acid with PFIB



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[*] It has been shown that anion $CF_3\bar{C}FCF_2CF_3$ is brominated by 2,3-dibromoperfluorobutane [4].

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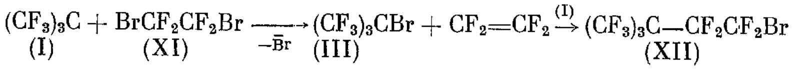
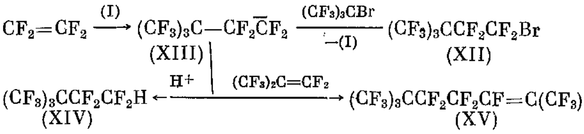
It should be noted that the condensation of ester (VII) with PFIB with $\bar{F}$ catalysis proceeds with the C-anion of the hexafluoroisobutyric ester (X), and not with anion (I), clearly because of the greater readiness of formation in the case of the former anion.

An interesting example is the reaction of anion (I) with 1,2-dibromotetrafluoroethane (XI). It was shown* that a product of replacement of bromine by the $(CF_3)_3C$ group, i.e., perfluoroisohexyl bromide (XII), is thus formed in a good yield. However, apparently, also in this reaction bromination of anion (I) initially takes place, resulting in the formation of tertiary bromide (III) and tetrafluoroethylene (TFE), and then bromide (III) adds to the multiple bond of TFE in the presence of anion (I)



$$\underset{(I)}{(CF_3)_3\bar{C}} + \underset{(XI)}{BrCF_2CF_2Br} \xrightarrow[-\bar{Br}]{} \underset{(III)}{(CF_3)_3CBr} + CF_2{=}CF_2 \xrightarrow{(I)} \underset{(XII)}{(CF_3)_3C{-}CF_2CF_2Br}$$

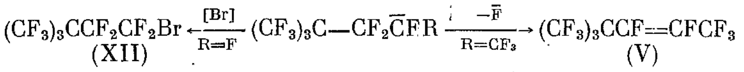
This sequence of transformations in the reaction of anion (I) with dibromide (XI) is confirmed by the fact that tertiary bromide (III) in fact reacts with TFE during catalysis by anion (I) by a scheme of conjugated nucleophilic addition to give isohexyl bromide (XII) via the intermediate fluorocarbanion (XIII) [6]



$$\begin{tikzcd}[column sep=large] CF_2{=}CF_2 \arrow[r, "(I)"] & \underset{(XIII)}{(CF_3)_3C{-}CF_2\bar{C}F_2} \arrow[r, "(CF_3)_3CBr", "-(I)"'] \arrow[d, dash] & \underset{(XII)}{(CF_3)_3CCF_2CF_2Br} \\ \underset{(XIV)}{(CF_3)_3CCF_2CF_2H} & \arrow[l, "H^+"'] \arrow[r, "(CF_3)_2C{=}CF_2"] & \underset{(XV)}{(CF_3)_3CCF_2CF_2CF{=}C(CF_3)_2} \end{tikzcd}$$

In accordance with this mechanism, hydride (XIV) and olefin (XV) are formed as side products. The compounds are the main products of the transformations of the fluorocarbanion (XIII) in the absence of brominating agents [7]. It was recently shown that the reaction of anion (I) with CF_2Br_2 also leads to products of the substitution of bromine by the $(CF_3)_3C$ group. The process proceeds in stages, including the debromination of CF_2Br_2 with the formation of difluorocarbene, followed by addition of anion (I) and bromine to it [3].

The unique reactions of anion (I) with 1,2-dibromotetrafluoroethane compared with other vic-dibromopolyfluoroalkanes, for example, with 1,2-dibromohexafluoropropane, is determined by differences in the behavior of the corresponding intermediate fluorocarbanions; the less reactive secondary fluorocarbanion (IV) is preferentially stabilized by β-elimination of fluoride anion, and not by capture of bromide as in the case of primary fluorocarbanion (XIII)

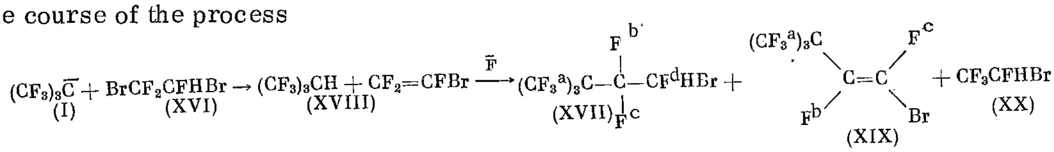


$$\underset{(XII)}{(CF_3)_3CCF_2CF_2Br} \xleftarrow[R=F]{[Br]} (CF_3)_3C{-}CF_2\bar{C}FR \xrightarrow[R=CF_3]{-\bar{F}} \underset{(V)}{(CF_3)_3CCF{=}CFCF_3}$$

$R = CF_3$ (IV), F (XIII)

In the sequence of transformations leading to isohexyl bromide (XII), the slowest is apparently the first stage, the debromination of dibromide (XI) by anion (I), since neither TFE nor the tertiary bromide (III) are accumulated in noticeable amounts in the reaction mixture. In contrast, in the reaction of anion (I) with 1,2-diiodotetrafluoroethane, the fastest reaction is the stage of dehalogenation, whereby TFE and perfluoro-tert-butyl iodide are formed in a high yield.

We also studied the reaction between anion (I) and 1,2-dibromotrifluoroethane (XVI). In this case, as in the reaction with dibromide (XI), a product of substitution of bromine by the $(CF_3)_3C$ group, the bromide (XVII), is formed. However, in contrast to the above cases, in this reaction first dehydrobromination of dibromide (XVI) by anion (I) takes place, which leads to trifluorobromoethylene and monohydroperfluorobutane (XVIII), and the addition of this hydride to fluoroethylene, catalyzed by fluoride anion, accompanied by the formation of bromoolefin (XIX) and bromoalkane (XX). The preliminary formation of hydride (XVIII) and $CF_2{=}CFBr$ and their subsequent transformation into reaction products were confirmed by ^{19}F NMR and GLC analysis of the reaction mixture in the course of the process



$$\underset{(I)}{(CF_3)_3\bar{C}} + \underset{(XVI)}{BrCF_2CFHBr} \rightarrow \underset{(XVIII)}{(CF_3)_3CH} + CF_2{=}CFBr \xrightarrow{\bar{F}} \underset{(XVII)}{(CF_3^a)_3C{-}CF^bF^c{-}CF^dHBr} + \underset{(XIX)}{(CF_3^a)_3C(F^b)C{=}C(F^c)Br} + \underset{(XX)}{CF_3CFHBr}$$

In conclusion, it should be noted that the mechanism of cleavage–addition reaction, proceeding during the replacement of bromine by perfluoro-tert-butyl group in the reaction of 1,2-dibromotetrafluoroethane with anion (I) is general in character for the reactions of this dibromide with nucleophilic reagents. This is indicated

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* Preliminary communication, see [5].

by the results of its reactions with EtONa [8] and MeSeNa [9].

EXPERIMENTAL

The IR spectra were run on a UR-20 apparatus, and the NMR spectra on a Perkin–Elmer R-32 apparatus (PMR 90 MHz, ^{19}F NMR 86.46 MHz) with reference to HMDS and CF_3COOH as external standards. The GLC analysis was carried out on an LKhM-8MD apparatus using a Krytox column on Chromosorb.

The reaction of perfluoroisobutylene with 1,2-dibromohexafluoropropane (II) was carried out in the presence of CsF.

A 16.5 g portion of PFIB was added with stirring and cooling by ice-water to a mixture of 6.3 g of CsF and 40 ml of abs. diglyme. Then 10 g of dibromide (II) in 10 ml of diglyme were added dropwise. The reaction mixture was stirred for 2.5 h, and then distilled in a 2 mm Hg vacuum into a trap (−78°C) to yield 18.6 g of a mixture containing (GLC) 31% of tertiary bromide (III), 50% of olefin (V) [10], and 6.5% of dibromide (II).

Ethyl Ester of 2,3-Dibromo-2-trifluoromethyl-3,3-difluoropropionic Acid (VI). A solution of 10.6 g of bromine in 5 ml of MeCN was added to a solution of 13.5 g of ethyl perfluoromethacrylate (VII) in 15 ml of abs. MeCN. The mixture was left to stand for 1 day, and was then poured into water, and the organic layer was extracted by ether, dried and distilled. Yield, 19.9 g (82%) of dibromide (VI), bp 64-66°C (10 mm), n_D^{20} 1.4205. Found: C 19.98; H 1.35%. $C_6H_5Br_2F_5O_2$. Calculated: C 19.78; H 1.37%. IR spectrum: 1760 cm^{-1}. ^{19}F NMR spectrum: −12.9 d.d (CF_3), −26.9 (F_A), −31.6 (F_B) (CF_2, AB system, each component of which is resolved into a quadruplet); $J_{CF_3-F_A} = 15$; $J_{CF_3-F_B} = 9.4$; $J_{F_A-F_B} = 174$ Hz.

Ethyl Ester of 2,2,4-Tris(trifluoromethyl)perfluoropenten-3-oic Acid (VIII). 1) A 10.6 g portion of dibromide (VI) in 10 ml of diglyme was added in the course of 30 min, with stirring and cooling, to a mixture of 5.6 g of CsF, 13.6 of PFIB, and 30 ml of abs. diglyme. After 1 h, 7.8 g (90%) of bromide (III) was distilled off. From the residue, after treatment with HCl (1 :5), extraction by ether, evaporation, and distillation over conc. H_2SO_4 in 2 mm Hg vacuum, 10.3 g of a mixture was obtained, containing (GLC) 13% of bromide (III), 84% of ester (VIII), and 3% of dimer (IX). Subsequent distillation gave 8.4 g (70%) of ester (VIII), bp 140-142°C, 38-39°C (10 mm), n_D^{20} 1.3240. Found: C 29.07; H 1.19; F 60.54%. $C_{10}H_5F_{13}O_2$. Calculated: C 29.70; H 1.24; F 61.14%. IR spectrum: 1685, 1790 cm^{-1}. ^{19}F NMR spectrum: −18.2 and −17.5 ($CF_3C=$, multiplets, 6F), −12.7 m (CF_3C-, 6F), +2.5 m (CF, 1F).

2) A 9.0 g portion of PFIB was added, with stirring and ice-cooling, to 1.9 g of CsF in 15 ml of diglyme, and then 6.1 g of ester (VII) in 5 ml of diglyme was added dropwise in the course of 20 min. The mixture was heated for 15 min to 20°C, unreacted PFIB was distilled in vacuo, and the residue was poured into HCl (1 :5). The organic layer was extracted by ether, the extract was washed by water, 5% $NaHCO_3$ solution, again by water, and dried over $MgSO_4$. The ether was distilled, and the residue was distilled in vacuo over conc. H_2SO_4 to yield 6.3 g of a fraction bp 45-80°C (12 mm), which contained 90% of ester (VIII) and 10% of ester (IX).

3) A mixture of 7.8 g of ethyl ester of α-hydrohexafluoroisobutyric acid, 20 ml of abs. MeCN, a few drops of triethylamine, and 14 ml of PFIB was held in a sealed ampul for 12 days at ~ 20°C. The unreacted PFIB and $(CF_3)_3CH$ were distilled, and the residue was poured into water. The organic layer was distilled in a 10 mm Hg vacuum over conc. H_2SO_4 to yield 8 g of a mixture containing 40% of ester (VIII) and 42% of dimer (IX). Subsequent fractionation gave pure diethyl ester of perfluoro(α,α,γ-trimethyl)glutaconic acid (IX), bp 90-92°C (16 mm), n_D^{20} 1.3605. IR spectrum: 1680, 1760, 1780 cm^{-1}. Found: C 35.34; H 2.71; F 46.98%. $C_{12}H_{10}F_{10}O_4$. Calculated: C 35.31; H 2.50; F 46.59%. ^{19}F NMR spectrum: −16.8 d (F^c), −12.3 d (F^a), +6.6 m (F^b); $J_{F^a-F^b} = 12.8$; $J_{F^b-F^c} = 21$ Hz.

In the same way as for ethyl ester (VIII), from PFIB and methyl perfluoromethacrylate, the methyl ester of 2,2,4-tris(trifluoromethyl)perfluoropenten-3-oic acid, bp 50-52°C (35 mm), n_D^{20} 1.3195, was obtained. Found: C 27.52; H 0.58%. $C_9H_3F_{13}O_2$. Calculated: C 27.69; H 0.77%. IR spectrum: 1680, 1790 cm^{-1}. ^{19}F NMR spectrum: −17.8 m ($CF_3C=$, 6F), −12.5 m (CF_3C-, 6F), +2.9 m (CF, 1F).

1-Bromo-perfluoro-3,3-dimethylbutane (XII). A mixture of 14.9 g of CsF, 22 g of 1,2-dibromotetrafluoroethane, 50 ml of abs. diglyme, and 17.6 g of PFIB was heated in a sealed ampul for 7.5 h at 80°C. The mixture was then poured into water, and the lower layer was distilled in a 10 mm Hg vacuum over conc. H_2SO_4 into a trap (−78°C). Distillation gave 7 g of a fraction, bp 40-98°C [contains (GLC) 18% of dibromide (XI), 32% of hydride (XIV), and 50% of bromide (XII)], and 16.8 g (49.5%) of bromide (XII), bp 99-102°C, n_D^{20} 1.3161. Found: C 18.14; F 61.76%, C_6BrF_{13}. Calculated: C 17.96; F 61.75%. ^{19}F NMR spectrum: −18.4 dec. t. (CF_2Br), −15.1 t.t (CF_3), +21.1 dec. t (CF_2); $J_{CF_3-CF_2Br} = 14.1$; $J_{CF_3-CF_2} = 10.4$; $J_{CF_2-CF_2} = 0.9$ Hz. From the distillation residue, 3 g of bromide (XII) containing 40% of olefin (XV) were obtained.

Reaction of Perfluoroisobutylene with 1,2-Diiodotetrafluoroethane in the Presence of CsF. A 9 g portion of PFIB was added with stirring and ice-cooling to a suspension of 7.5 g of CsF in 30 ml of diglyme. Then, 16 g of 1,2-diiodotetrafluoroethane in 10 ml of diglyme were added in the course of 1 h, and the tetrafluoroethylene evolving (0.7 liter) was collected in a gasometer. The reaction mixture was poured into HCl (1 :5), the organic layer was washed with sodium thiosulfate solution, and distilled in vacuo over conc. H_2SO_4 to yield 7.2 g of a mixture containing (GLC) 60% of perfluoro-tert-butyl iodide and 40% of the initial diiodide.

A mixture of 10 g of CsF, 18.6 g of diiodotetrafluoroethane, 15.3 g of PFIB, and 40 ml of MeCN was shaken for 70 h in a 100-ml steel autoclave. Tetrafluoroethylene was removed, and from the residue, by the usual treatment, 9.3 g (50%) of $(CF_3)_3CI$ were isolated, containing ~1% of $(CF_3)_3C-CF_2CF_2I$. ^{19}F NMR spectrum: −24.0 dec. t (CF_2I), −15.0 t.t (CF_3), +16.0 dec. t (CF_2); $J_{CF_3-CF_2I} = 14.1$; $J_{CF_3-CF_2} = 11.1$; $J_{CF_2-CF_2} = 5.6$ Hz.

Reaction of Perfluoroisobutylene with 1,2-Dibromotrifluoroethane in the Presence of CsF. A 13.5 g portion of PFIB was added with stirring and ice-cooling to a suspension of 12 g of CsF in 25 ml of abs. monoglyme. Then, 16.1 g of dibromide (XVI) in 10 ml of monoglyme were added dropwise, and the mixture was heated to 20°C, and held 6 h to complete conversion of $CF_2=CFBr$ (control by GLC). The volatile compounds containing $(CF_3)_3CH$ and CF_3CFHBr * were distilled, and the residue was poured into water. The organic layer was distilled in vacuo over conc. H_2SO_4 to yield 11.7 g of a fraction, bp 100-108°C, containing (GLC) 80% of bromoalkane (XVII) and 20% of bromoalkene (XIX). By preparative GLC (QF on Chromosorb W), pure 1-hydro-1-bromo-perfluoro-3,3-dimethylbutane (XVII), bp 108°C, n_D^{20} 1.3258, was isolated. Found: C 18.76; H 0.29; F 59.63%. C_6HBrF_{12}. Calculated: C 18.90; H 0.26; F 59.84%. PMR spectrum: 6.7 d.d (CH). ^{19}F NMR spectrum: −14.4 d.t (F^a), +17.1 d.d.dec (F^b), +36.1 d.d.dec (F^c), +74.0 m (F^d); $J_{F^b-F^c} = 296$; $J_{F^c-F^d} = 15$; $J_{F^a-F^b} = J_{F^a-F^d} = 12.2$; $J_{F^a-F^c} = 9.4$; $J_{F^d-H} = 48$; $J_{F^b-H} = 22$ Hz.

1-Bromo-perfluoro-3,3-dimethyl-1-butene (XIX). A mixture of 12 g of bromoalkane (XVII) containing 20% of olefin (XIX), 12 g of KOH powder, and 15 ml of abs. ether was boiled for 3 h. The precipitate was filtered, and the filtrate was mixed with an equal volume of conc. H_2SO_4, and distilled in 10 mm Hg vacuum into a trap (−78°C) to yield 5.5 g of olefin (XIX), which after repeated distillation had bp 95-97°C, n_D^{20} 1.3315. Found: C 20.06; F 57.73%. C_6BrF_{11}. Calculated: C 19.94; F 57.89%. IR spectrum: 1690 cm^{-1}. ^{19}F NMR spectrum: −13.8 d.d (F^a), +21.6 d. dec (F^b), +64.4 d. dec (F^c); $J_{F^a-F^b} = 17$; $J_{F^a-F^c} = 12.2$; $J_{F^b-F^c} = 147$ Hz.

CONCLUSIONS

Vicinal dibromopolyfluoroalkanes are dehalogenated by perfluoro-tert-butyl anion. In the reaction of 1,2 dibromotetrafluoroethane with this anion, bromine is replaced by the perfluoro-tert-butyl group by a cleavage–addition mechanism.

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*PMR spectrum: 6.12 d.q (CH). ^{19}F NMR spectrum: +4.65 d.d (CF_3); +84.5 d.q (CF); $J_{CF_3-F} = 13.1$; $J_{CF_3-H} = 4.7$; $J_{F-H} = 47$ Hz.