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# SYNTHESIS AND SOME PROPERTIES OF TERTIARY PERFLUOROALKYL HALIDES

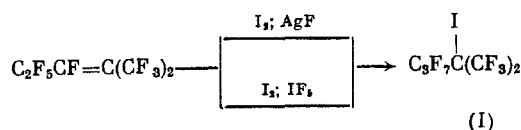S. I. Pletnev, S. M. Igumnov, E. V. Zakharova,   UDC 542.91:547.412
and K. N. Makarov

It is shown for the first time that bromination and iodination of tertiary perfluorocarbanions are reversible. The tendency of teriary perfluoroalkyl halides to undergo dehalofluorination under the influence of weak bases depends on the structure of the perfluoroalkyl halide, and increases in going from lower to higher halides and from linear to cyclic compounds.

The most widely used synthesis of tertiary perfluoroalkyl halides is the halogenation of tertiary perfluorocarbanions, which are generated by the addition of fluoride ion to the appropriate fluoroolefin.

It is known [1, 2] that perfluoro-tert-butyl anion reacts easily with halogens (Cl_2, Br_2, I_2) to form perfluoro-tert-butyl halides:

$$(CF_3)_2C{=}CF_2 \xrightarrow{F^-} [(CF_3)_3C^-] \xrightarrow{X_2} (CF_3)_3CX$$
$$X = Cl, Br, I.$$
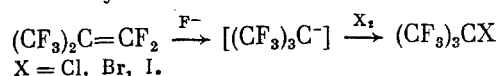
Bromination of perfluoro-tert-hexyl anion [3] and chlorination of perfluoromethylcyclopentyl anion [4] also take place easily and in good yield. However iodination of perfluoro-tert-hexyl anion with N-iodosuccinimide goes with low yield; in the opinion of the authors of [5] this is related to the instability of the 2-iodo-2-trifluoromethylperfluoropentane (I) that is formed under reaction conditions. Indeed it was shown in [6] that perfluoro-tert-hexyl iodide is easily deiodofluorinated by the action of such bases as I^-, OH^-, SCN^-, N_3^-. In this connection those authors proposed a synthesis of (I) that excludes iodide ion from the reaction mixture:

$$C_2F_5CF{=}C(CF_3)_2 \xrightarrow[\;I_2;\; IF_5\;]{\;I_2;\; AgF\;} C_3F_7\overset{\displaystyle I}{\underset{\displaystyle |}{C}}(CF_3)_2$$

(I)

From the data of [5, 6] it can be assumed that the deiodofluorination of perfluoro-tert-hexyl iodide by the action of iodide ion is evidence for the reversibility of the iodination of tertiary perfluorocarbanions, and consequently for the possibility of determining the equilibrium of this process.

It was important to establish the relation of the equilibrium point of the halogenation of tertiary perfluorocarbanions to their structure, in order to elucidate the prospects of applying this reaction to the synthesis of new tertiary perfluoroalkyl halides.

RESULTS AND DISCUSSION

We found that the reaction of perfluoro-2-methylpentene with I_2 and CsF in acetonitrile at 20°C, just as that of iodide (I) with CsI under the same conditions, gives an equilibrium mixture that contains 30% iodide and 70% olefin:

$$C_2F_5CF{=}C(CF_3)_2 + I_2 + CsI \underset{\text{MeCN; 20°}}{\overset{}{\rightleftarrows}} (I) + CsI$$
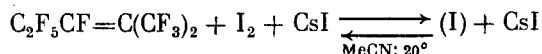
In a similar reaction of perfluoroisobutylene only perfluoro-tert-butyl iodide was found in the reaction mixture; it follows that in this case the equilibrium is shifted entirely to the final products. The reaction could not be reversed.

At the same time, when perfluoromethylcyclopentene reacts with I_2 and CsF the corresponding iodide (II) could not be found. The reverse reaction proceeds extremely easily and stops at the perfluoromethylcyclopentyl anion:
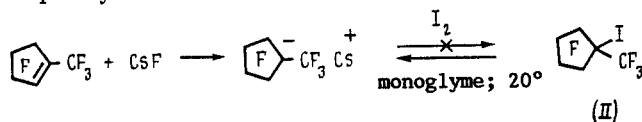

We were able to synthesize iodides (I) and (II) in preparative yield; like the authors of [6] we used a method that excluded iodide ion, and included the reaction of the respective olefin with CsF and iodine chloride or iodine bromide. We were also able to show that chloride and bromide ions do not cause deiodofluorination of these iodides:
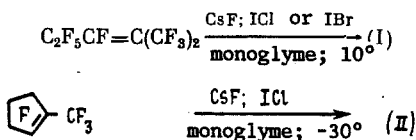

However, we were unable to iodinate perfluorobicyclodecene by this method. The assumption that the lack of success was due to the absence of the corresponding carbanion was not confirmed, because we were able to chlorinate and brominate the compound:

X = Cl(III), Br(IV).
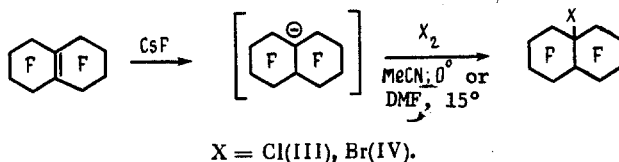
When perfluorobicyclodecene was brominated in the presence of CsF the reaction is an equilibrium process that contains 25% of bromide (IV) at equilibrium; the reverse reaction (debromofluorination) is initiated by the reaction of bromide (IV) with bromide ion:
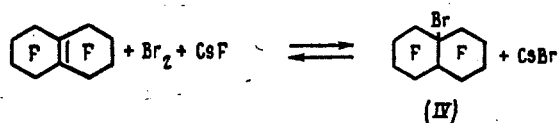
The tendency of bicyclic tertiary perfluoroalkyl bromides to undergo debromofluorination by the action of bromide ion was also confirmed by the formation of the unsaturated alcohol (V) when perfluoro-9,10-epoxybicyclodecane reacts with LiBr:
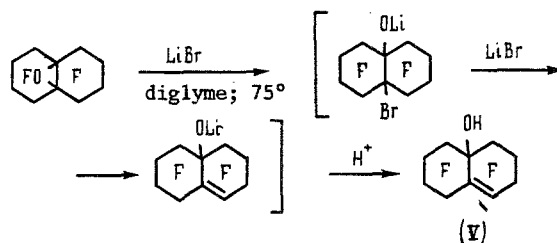
Further study of these tertiary perfluoroalkyl halides showed that bicyclic bromide (IV) undergoes debromofluorination under homogeneous conditions extremely easily by the action of such weak bases as acetonitrile and dimethylformamide. The monocyclic iodide (II) behaves similarly toward acetonitrile, whereas acyclic iodide (I) is indifferent to acetonitrile.

The availability of tertiary perfluoroalkyl halides is thus inversely proportional to their tendency to undergo dehalofluorination in synthesis by halogenation of tertiary perfluorocarbanions. To a first approximation this availability is a function of carbanion structure, and decreases in going from lower halides to higher, and from linear halides to cyclic. If we consider dehalofluorination as a reductive process, we assume that the observed tendency is related to the increase in positive charge on the halogen atom; this facilitates halide reduction in the presence of weak bases.

EXPERIMENTAL

^{19}F and ^{1}H NMR spectra were obtained with a Perkin-Elmer R-32 spectrometer (85.6 and 90 MHz) relative to CF_3COOH and TMS external standards. IR spectra were obtained with a UR-20 spectrometer; mass spectra with a Varian MAT CH-8 mass spectrometer.

Perfluoro-tert-butyl iodide, and the hexafluoropropylene (HFP) dimer, perfluoromethylcyclopentyl anion, and perfluorobicyclo[4.4.0]dec-(10)-ene were identified by ^{19}F NMR and GLC.

2-Iodo-2-trifluoromethylperfluoropentane (I). To 60 g (0.2 mole) of HFP dimer and 35 g (0.23 mole) of CsF in 100 ml of absolute monoglyme were added 35 g (0.22 mole) of ICl with stirring and cooling to 10°C. The mixture was stirred for 1 h until it became colorless. It was then poured into water and the lower layer was separated, washed with water, filtered, and dried with $MgSO_4$. Vacuum distillation yielded 64.5 g (69.8%) of product with bp 45-46°C (70 mm). Found, %: C 16.7. C_6F_{13}. Calculated, %: C 16.15. Mass spectrum: 427 ($M^+ - F$). $(\overset{1}{C}F_3)_2C I - \overset{3}{C}F_2 - \overset{4}{C}F_2\overset{2}{C}F_3$. ^{19}F NMR spectrum: ($\delta$, ppm): −16.0 t.t ($CF_3{}^1$), 3.6 t ($CF_3{}^2$), 24.5 m ($CF_2{}^3$), 43.7 m ($CF_2{}^4$), $J_{1-3} = 11.3$, $J_{1-4} = 11.3$, $J_{2-3} = 13.1$ Hz.

1-Iodo-1-trifluoromethylperfluorocycloheptane (II). To 70 g (0.27 mole) of perfluoromethylcyclopent-1-ene and 31 g (0.2 mole) of CsF on 100 ml of abs. monoglyme was added dropwise 30 g (0.19 mole) ICl with stirring and cooling to −30°C. The cold reaction mixture was poured into water, and the lower layer was separated, washed with water, and dried with $MgSO_4$. Vacuum distillation yielded 46 g (92%, 57% conversion) of product with bp 46-47°C (65 mm).

(II)
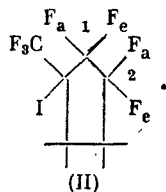
^{19}F NMR spectrum (δ, ppm): −17.1 t.t (CF_3), 20.9 d.q (1a), 40.2 d (1b), 41.1 d.q (2a), 53.1 d (2e). $J_{CF_3-1a} = 19.4$ Hz, $J_{CF_3-2a} = 5.6$, $J_{1AB} = 241$, $J_{2AB} = 246$ Hz.

trans-1-Chloroperfluorobicyclo[2.4.0]decane (III). Into a mixture of 8.5 g (20 mmoles) of perfluorobicyclo[4.4.0]dec-1(6)-ene and 3.8 g (25 mmoles) of CsF in 30 ml of abs. MeCN was bubbled Cl_2 with intense stirring and cooling to 0°C until absorption stopped. The lower layer was separated, washed with $NaHCO_3$ solution and water, dried with $MgSO_4$ and distilled. There was obtained 8.9 g (92.5%) of product with bp 164°C. Found, %: C 25.03; F 67.39. $C_{10}ClF_{17}$. Calculated, %: C 25.80; F 67.50. Mass spectrum: 461, 459 ($M^+ - F$).

(III)
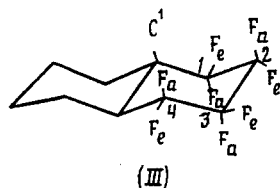
^{19}F NMR spectrum (δ, ppm): 32.9 d.d (1a), 44.4 d (1e), 38.0 d (2a), 59.2 d (2e), 48.9 d.d (3a), 61.3 d (3e), 35.3 d (4a), 49.9 d (4e), 99.0 t.t (F), J_{1AB} = 276.0, J_{2AB} = 282.0, J_{3AB} = 291.0, J_{4AB} = 288, J_{1a-F} = 47, J_{3a-F} = 32 Hz.

trans-1-Bromoperfluorobicyclo[4.4.0]decane. To a mixture of 4.8 g (30 mmoles) of Br_2 and 4.6 g (30 mmoles) of CsF in 30 ml of abs. DMF was added dropwise 8.5 g (20 mmoles) of perfluorobicyclo[4.4.0]dec-1(6)-ene with intense stirring and cooling to 0°C. The mixture was stirred for 1 h at 10-15°C; the lower layer was separated, washed with $NaHCO_3$ solution and water; then it was vacuum distilled twice from an equal volume of conc. H_6SO_4, then it was distilled at atmospheric pressure. There was obtained 7.4 g (71%) of product with bp 177°C. Found, %: C 22.85; F 62.18. $C_{10}F_{17}Br$. Calculated, %: C 22.94; F 61.76. Mass spectrum: 505, 503 ($M^+ - F$).
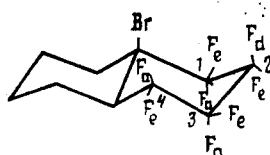
^{19}F NMR spectrum (δ, ppm): 30.2 d.d (1a), 38.6 d (1e), 33.7 d (2a), 58.4 d (2e), 42.0 d.d (3a), 60.0 d (3e), 32.0 d (4a), 49.2 d (4e); 95.1 t.t (F), J_{1AB} = 272, J_{2AB} = 282, J_{3AB} = 289.5, J_{4AB} = 287, J_{1a-F} = 44.5, J_{3a-F} = 28 Hz.

Perfluorobicyclo[4.4.0]dec-1(2)-en-6-ol (V). A mixture of 8.8 g (20 mmoles) of 9,10-epoxyperfluorodecalin and 3.5 g (40 mmoles) of LiBr in 40 ml of abs. diglyme was heated at 80-86°C with intense stirring until the lower layer disappeared. The mixture was cooled, and the solution was decanted from the precipitate and diluted with 10 ml of 10% HCl. The oil that separated was extracted with·Freon-113, washed with water, and dried with $MgSO_4$. The solvent was distilled off and the residue was vacuum distilled from conc. H_2SO_4, then distilled at atmospheric pressure. There was obtained 5.5 g (64%) of product with bp 173-174°C. Found, %: C 28.40; H 0.26; F 67.64. $C_{10}HF_{15}O$. Calculated, %: C 28.44; H 0.24; F 67.64. Mass spectrum: 432 (M^+). IR spectrum (ν, cm^{-1}): 3500 (OH), 1665 (C=C). PMR spectrum (δ, ppm): 4.0 br. s (OH). ^{19}F NMR spectrum (δ, ppm): 21.2-68.7 (7 AB quartets, 14F), 34.8 m (CF).

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