REACTION OF PERFLUORO-TERT-BUTYL CARBANION WITH OLEFINS, CONTAINING AN ACTIVATED DOUBLE BOND, AND WITH THREE-MEMBERED HETEROCYCLES AND VARIOUS HALO DERIVATIVES

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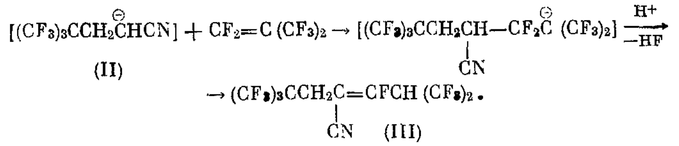
Perfluoro carbanions are easily generated by the reaction of bases with CH acids or by the reaction of fluoride ion with perfluoroolefins [1]. From the results reported in [2] it follows that the perfluoro-tert-butyl carbanion (I), generated from tris(trifluoromethyl)methane and a tertiary amine, is easily alkylated by compounds that bear a positively charged carbon atom. As was shown in the present communication, the alkylation reactions of the same anion (I), generated from perfluoroisobutylene and alkali metal fluorides in aprotic bipolar solvents, exhibit a greater diversity. Thus, anion (I) easily reacts with the nitrile or an ester of acrylic acid to respectively give either the nitrile or the ester of β-(perfluoro-tert-butyl)propionic acid

$$(CF_3)_2C{=}CF_2 \overset{CsF}{\rightleftarrows} \underset{(I)}{(CF_3)_3\overset{\ominus}{C}} + CH_2{=}CH{-}X \rightarrow \underset{(II)}{[(CF_3)_3CCH_2\overset{\ominus}{C}HX]} \xrightarrow{H^+} (CF_3)_3CCH_2CH_2X,$$
$$X = -CN, -COOCH_3.$$

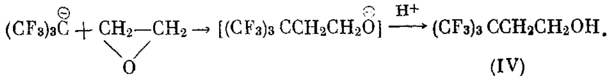
A by-product here is a more complex compound, which is formed as the result of the nucleophilic attack of the perfluoroisobutylene molecule by the intermediately formed anion (II)



$$\underset{(II)}{[(CF_3)_3CCH_2\overset{\ominus}{C}HCN]} + CF_2{=}C(CF_3)_2 \rightarrow [(CF_3)_3CCH_2\underset{\displaystyle CN}{\underset{|}{C}H}{-}CF_2\overset{\ominus}{C}(CF_3)_2] \xrightarrow[-HF]{H^+}$$
$$\rightarrow (CF_3)_3CCH_2\underset{\displaystyle CN}{\underset{|}{C}}{=}CFCH(CF_3)_2. \quad (III)$$

Only β-(perfluoro-tert-butyl)propionitrile is formed at a temperature between −50 and 0°C, while at room temperature there is formed, together with β-(perfluoro-tert-butyl)propionitrile, also nitrile (III) in in a 4:1 ratio. The reaction of carbanion (I) with acrolein goes in a similar manner, but the yield of β-(perfluoro-tert-butyl)propionaldehyde is low due to polymerization. Carbanion (I) also reacts readily with ethylene oxide and the thiooxide.

Ethylene oxide reacts with anion (I) in monoglyme to give β-(perfluoro-tert-butyl)ethanol (IV)



$$(CF_3)_3\overset{\ominus}{C} + \underset{\diagdown O \diagup}{CH_2{-}CH_2} \rightarrow [(CF_3)_3CCH_2CH_2\overset{\ominus}{O}] \xrightarrow{H^+} (CF_3)_3CCH_2CH_2OH.$$

(IV)

This alcohol is identical with that previously obtained by the hydrolysis of β-(perfluoro-tert-butyl)-ethyl iodide.

The reaction of ethylene thiooxide with anion (I) in monoglyme is more vigorous than that of ethylene oxide, but the corresponding mercaptan could not be isolated by us due to the greater nucleophilicity of the formed intermediate anion, which reacts with perfluoroisobutylene to give β-(perfluoro-tert-butyl)ethyl perfluoroisobutenyl sulfide (V) and the bis-[β-(perfluoro-tert-butyl)ethyl] dithioacetal of hexafluorodimethylketene (VI).

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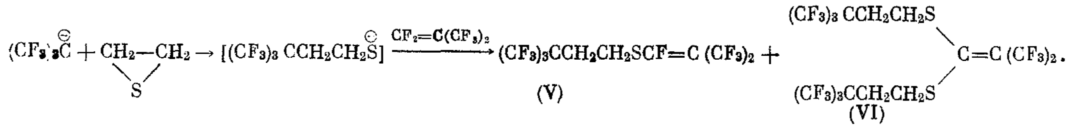

Great synthetic possibilities for preparing various organic compounds, containing the perfluoro-tert-butyl group, are opened up by the alkylation reactions of the perfluoro-tert-butyl carbanion with various halo derivatives. Attempts to alkylate monohydroperfluoroisobutane by reaction with ethyl iodide in the presence of triethylamine ended in failure; in the opinion of the authors, the formed quaternary ammonium salt is incapable of alkylating $(CF_3)_3CH$ [4]. As our studies disclosed, the perfluoro-tert-butyl carbanion, generated from perfluoroisobutylene and cesium fluoride, is alkylated under very mild conditions by halo derivatives to give saturated and unsaturated hydrocarbons, containing the perfluoro-tert-butyl grouping, in nearly quantitative yields

$$(CF_3)_3C^- + R-X \rightarrow (CF_3)_3C-R,$$
$$R = -CH_3,\ -C_4H_9,\ -CH_2CH=CH_2,\ -CH_2C_6H_5.$$

EXPERIMENTAL

β-(Perfluoro-tert-butyl)propionitrile. Into a solution of 0.05 M of acrylonitrile and 0.05 M of either potassium or cesium fluoride in 20 ml of monoglyme was passed at room temperature, with stirring, 0.05 M of perfluoroisobutylene. The mixture was stirred for 2 h at room temperature, after which the reaction mass was poured over ice, and the lower layer was separated and dissolved in ether. The aqueous layer was extracted with ether. The combined ether solutions were dried over $MgSO_4$. Vacuum-distillation gave β-(perfluoro-tert-butyl)propionitrile in 42% of the theoretical yield; mp 25°C; bp 70-72°C (31 mm); n_D^{20} 1.3355. From [2]: bp 80-81°C (55 mm). Found: C 30.21; H 1.46; F 63.28; N 5.28%. $C_7H_4F_9N$. Calculated: C 30.76; H 1.46; F 62.63; N 5.20%. ^{19}F NMR spectrum: −10.0 [$(CF_3)_3$, singlet]. NMR spectrum: δ 2.6 ppm (CH_2, broad singlet).

Together with β-perfluoro-tert-butyl)propionitrile, we obtained 2,2,6-tris(trifluoromethyl)−4-cyano−3,3,6-trihydroperfluoro−4-heptene in 10% of the theoretical yield; bp 83-85°C (15 mm); mp 65-67°C. Found: C 29.18; H 0.89; F 67.88; N 3.61%. $C_{11}F_{16}H_3N$. Calculated: C 29.13; H 0.64; F67.10; N 3.09%. ^{19}F NMR spectrum: +9 (CF, multiplet), −11.5 [$(CF_3)_3$, doublet], $J_{(CF_3)_3-CF}$ 4.05 Hz, −13.5 [$(CF_3)_2$, triplet], $J_{(CF_3)_2-CH}$ and $J_{(CF_3)_2-CF}$ 8.10 Hz. NMR spectrum: δ 5.55 ppm (CH, doublet of heptets), $J_{CH-(CF_3)_2}$ 8, J_{CH-CF} 26.6 Hz; δ 3.5 ppm (CH_2, broad singlet). Infrared spectrum (ν, cm^{-1}): 1680 ($>C=C<$), 2230 ($C\equiv N$).

In a similar manner, from 0.1 M of acrylonitrile, 0.1 M of CsF and 0.05 M of perfluoroisobutylene, at −70°C, we obtained δ-(perfluoro-tert-butyl)propionitrile in 33% of the theoretical yield.

In a similar manner, from 0.1 M of acrylonitrile, 0.5 M of KF and 0.05 M of perfluoroisobutylene in 100 ml of monoglyme, at 35°C, we obtained β-(perfluoro-tert-butyl) propionitrile in 22% of the theoretical yield.

Methyl Ester of β-(perfluoro-tert-butyl)propionic Acid. Into a stirred solution of 0.1 M of methyl acrylate and 0.1 M of either cesium or potassium fluoride in 50 ml of monoglyme at room temperature was passed 0.1 M of perfluoroisobutylene. After 1 h the reaction mass was poured on ice, and the lower layer was separated and dissolved in ether. The aqueous layer was extracted with ether. The combined ether extracts were washed with 2% $NaHCO_3$ solution, then with water, and dried over $MgSO_4$. Distillation gave the methyl ester of β-(perfluoro-tert-butyl)propionic acid in 20% of the theoretical yield; bp 70-71°C (50 mm); n_D^{20} 1.3360. Found: C 30.95; H 1.95; F 55.66%. $C_8H_7F_9O_2$. Calculated: C 31.37; H 2.28; F 55.88%. From [2]: bp 63-64°C (33 mm).

Reaction of Perfluoroisobutylene with Acrolein in the Presence of Metal Fluorides. Into a solution of 0.1 M of acrolein and 0.05 M of either cesium or potassium fluoride in 80 ml of monoglyme at room temperature was passed 0.05 M of perfluoroisobutylene. Subsequent treatment was the same as described in the experiments with acrolein. We obtained β-(perfluoro-tert-butyl)propionaldehyde with bp 40-45°C (35 mm); yield 3%. Found: F 36.62; N 12.65%. $C_{13}H_9N_4F_9O_4$. Calculated: F 37.50; N 12.28%. From [2]: bp 50-53°C (40 mm). 2,4-Dinitrophenylhydrazone; mp 168-170°C (absolute ethanol). In addition, we obtained 13 g of a low-molecular polymer of β-(perfluoro-tert-butyl)propionaldehyde with bp 122-124°C (5 mm); n_D^{20} 1.708; mol. wt. 932 (cryoscopically). Found: C 30.69; H 1.27; F 63.11%. $(C_7H_5F_9)_x$. Calculated: C 30.43; H 0.8; F 61.95%.

Analogous results were obtained when the reaction was run at temperatures ranging from 0°C to −60°C.

β-(Perfluoro-tert-butyl)ethanol. Into a stirred suspension of 0.2 M of CsF in 40 ml of monoglyme at room temperature was passed 0.2 M of perfluoroisobutylene. Then the reaction mass was stirred for 1 h, cooled to −20°C, and 0.2 M of ethylene oxide was passed in. The reaction mass was allowed to stand overnight at −10°C, poured over ice, acidified with conc. H_2SO_4, and the lower layer was separated, dissolved in ether, washed twice with cold water, and dried over anhydrone. Distillation gave β-(perfluoro-tert-butyl)ethanol in 33% of the theoretical yield; bp 133-135°C; mp 35-37°C. Found: C 27.47; H 1.32; F 64.25%. $C_6H_5F_9O$. Calculated: C 27.29; H 1.89; F 64.75%. From [3]: bp 134-135°C; mp 36-37°C.

Reaction of Perfluoroisobutylene with Ethylene Thiooxide in the Presence of Cesium Fluoride. To the perfluoro-tert-butyl carbanion, obtained from 0.1 M of CsF and 0.1 M of perfluoroisobutylene in 20 ml of monoglyme, was added 0.1 M of ethylene thioxide at such a rate that the temperature did not rise above 50°C. The stirring was continued for another 2 h, after which the reaction mass was poured over ice. The lower layer was separated, dissolved in ether, and dried over anhydrone. Distillation gave (V) in 50% of the theoretical yield; bp 69-70°C (5 mm); n_D^{20} 1.3540. Found: C 26.07; H 1.30; F 66.58; S 6.97%. $C_{10}H_4F_{16}S$. Calculated: C 26.00; H 0.87; F 67.00; S 6.96%. ^{19}F NMR spectrum: −10.0 [$(CF_3)_3$, singlet]; ~3.5 (CF, multiplet); −19.0 [$(CF_3)_2$, multiplet]. The NMR spectrum is typical for the A_2B_2 system (δ_1 ~2.4; δ_2 ~ 3.2). Infrared spectrum: ν 1630 cm^{-1} (CF = C$\langle$).

Together with (V), we obtained 5 g (20%) of (VI) with bp 138-140°C (18 mm); mp 28°C. Found: C 26.62; H 1.11; F 63.04; S 8.9%. $C_{16}H_8F_{24}S_2$. Calculated: C 26.50; H 0.98; F 63.24; S 9.24%. ^{19}F NMR spectrum: −11 [$(CF_3)_3$, singlet]; −22 [$(CF_3)_2$, singlet]. The NMR spectrum is typical for the A_2B_2 system (δ_1 ~ 2.3; δ_2 ~ 3.3). Infrared spectrum: ν 1550 cm^{-1} ($\rangle$C=C$\langle$).

Only (VI) was obtained in 75% yield when the same reaction was run at −30°C.

Typical Experiment for Alkylation of Perfluoro-tert-butyl Carbanion with Halo Derivatives. In a four-necked flask was placed 0.1 M of CsF in 40 ml of the solvent and 0.1 M of perfluoroisobutylene was passed through the vigorously sitrred mass. The reaction mass was heated for 2 h at 40°C. To the obtained solution of the perfluoro-tert-butyl carbanion was gradually added 0.1 M of the halo derivative; the reaction with iodides was run at room temperature, while the reaction with the bromides and chlorides was run at 50-60°C. The $(CF_3)C-R$ was obtained by distillation. The yield, physical constants, solvent, and analysis results of the obtained compounds are given in Table 1.

The IR spectra were taken on a UR-10 instrument. The NMR spectra were recorded on a Perkin–Elmer R-12 instrument at an

TABLE 1. $(CF_3)_3C + RX \rightarrow (CF_3)_3C-R$

RX	Solvent	Yield, %	Mp, °C	n_D^{20}	Found, %			Calc., %			^{19}F NMR spectrum chemical shift of $(CF_3)_3$ (singlet)	NMR spectrum δ, ppm (External standard TMS)
					C	H	F	C	H	F		
CH_3I	Diglyme	86	Mp 20	—	24,82	1,22	69,50	25,60	1,28	73,07	−8,0	1,2 (CH_3, broad singlet)
C_4H_9Br	"	90	107—109	1,3190	34,71	3,35	61,89	34,80	3,26	61,95	−9,0	3,15 (CH_2, singlet)
$C_6H_5CH_2Cl$	Monoglyme	74,5	159—161	1,3901	42,55	2,41	55,31	42,6	2,26	55,02	−12,0	7,15 (C_6H_5, singlet) (internal standard HMDS)
$CH_2=CHCH_2I$	Diglyme	80	75—76		32,48	2,04	65,66	32,30	1,92	65,50	−10,0	2,47 (CH_2, doublet) 5,06 - 5,26 ($CH_2=CH$, multiplet)
$NCCH_2CH_2Br$	THF	30	70—72 (31 мм)									

operating frequency of 60 MHz. Hexamethyldisiloxane (HMDS) was used as the internal standard and the values of the shifts are given on the δ scale. The ^{19}F NMR spectra were recorded on a Hitachi H-60 instrument at an operating frequency of 56.46 MHz, and the chemical shifts are given in ppm from CF_3COOH (external standard).

CONCLUSIONS

1. The alkylation of the perfluoro-tert-butyl carbanion with acrylonitrile and the esters of acrylic acid is a convenient method for the preparation of β-(perfluoro-tert-butyl)propionic acid derivatives.

2. The alkylation of the perfluoro-tert-butyl carbanion with ethylene oxide gave β-(perfluoro-tert-butyl)ethanol.

3. The alkylation of the perfluoro-tert-butyl carbanion with ethylene thiooxide gave β-(perfluoro-tert-butyl)ethyl perfluoroisobutenyl sulfide and the bis-[β-(perfluoro-tert-butyl)ethyl] dithioacetal of hexafluorodimethylketone.

4. The reaction of perfluoroisobutylene with halo derivatives in the presence of metal fluorides gave (perfluoro-tert-butyl)methane, 1-(perfluoro-tert-butyl)butane, 1-(perfluoro-tert-butyl)-2-propene, and ω-(perfluoro-tert-butyl)toluene in 70-90% yield.

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