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α-FLUOROALKYLAMIDES, A NEW SOURCE OF NONHYDRATED FLUORIDE ION. 3. ^{19}F NMR SPECTRA OF PERFLUORO CARBANIONS GENERATED BY MEANS OF N,N,N',N'-TETRAMETHYLFORMAMIDINIUM BIFLUORIDE

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It was shown previously [1, 2] that fluoromethyldimethylamine and difluoromethyldimethylamine are sources of the fluoride ion in reactions with electrophilic compounds. Geminal diamines containing fluorine in the α position should have an even greater reactivity with respect to electrophilic agents. In this connection, an attempt has been made to synthesize bis(dimethylamino)fluoromethane $(Me_2N)_2CHF$ (I) by nucleophilic replacement of the mobile F atom in difluoromethyldimethylamine by the dimethylamino group. This reaction is readily carried out at 20°C. However, even with a considerable excess of Me_2NH, we were able to isolate the product (I) only in the form of the hydrofluoride $(Me_2N)_2CHF \cdot nHF$ ($n \sim 1$), which has a number of unusual properties because of the very definitely ionic character of the C—F bond. The compound (I) is readily soluble in polar organic solvents (DMFA, MeCN). In the IR spectrum of (I), bands are observed at 1240, 1450, 1840, and 2050 cm^{-1} that are characteristic for the $HF_2^{\ominus}$ anion [3], a band at 1710 cm^{-1} (C=N), and a band at 3010 cm^{-1} that is typical for a vinyl H atom. In the ^{19}F NMR spectrum of (I), instead of the doublet of the CHF group there is a singlet at 78.0 ppm (relative to CF_3COOH). These data provide evidence in favor of the ionic structure of (I)

(I)

It is known that the addition of $F^{\ominus}$ to fluoroolefins leads to the formation of perfluoroalkyl carbanions [4, 5]. The usual source of F^- is CsF or KF in aprotonic organic solvents. Here, the formation of perfluoroalkyl carbanions is successfully registered by means of ^{19}F NMR only in the case of extremely electrophilic perfluorocycloolefins containing at least three perfluoroalkyl groups at the multiple bond [6]. Some perfluoroolefins under these conditions do not form a concentration of the anion great enough to be registered in the ^{19}F NMR spectrum.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2238-2243, October, 1981. Original article submitted March 13, 1981.

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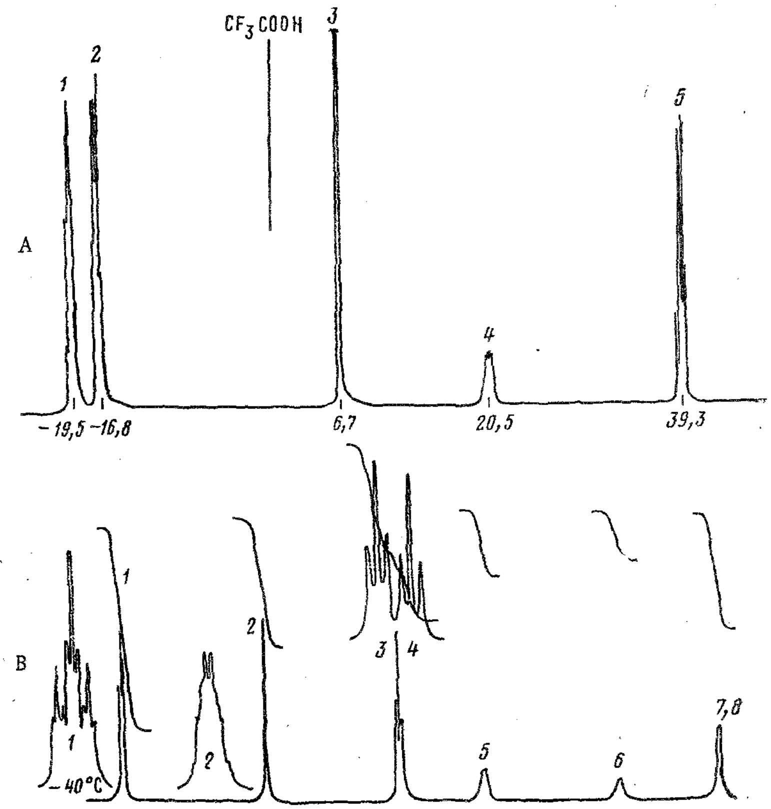
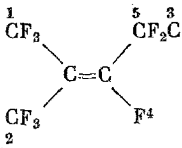


Fig. 1. ^{19}F NMR spectra: A)

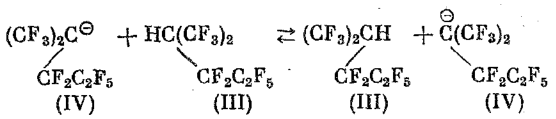


(II) at 36°C; B) $(\overset{2}{C}F_3)_2CH\overset{6}{C}F_2\overset{8}{C}F_2\overset{4}{C}F_3$ (III) and $(\overset{1}{C}F_3)_2\overset{\ominus 5}{C}\overset{7}{C}F_2CF_2\overset{3}{C}F_3$ (IV) at −40°C.

The bifluoride (I) proved to be a far more effective source of F$^-$ in these reactions, so that we have been able for the first time to synthesize, and register in the ^{19}F NMR spectrum, a number of perfluoroalkyl carbanions. Examples are the observed ^{19}F NMR spectra of perfluoro-(2-methyl-2-pentene) (II) when a solution of (I) in DMFA is added (Fig. 1). At −40°C, signals are observed from two compounds: a product of addition of HF to (II) [(signals 2, 4, 6, and 8 correspond to 2-hydroperfluoro-(2-methylpentane) (III)] and perfluorobis-(methyl)propylmethyl carbanion (IV) (on the basis of the chemical shifts and the structure of signals 1, 3, 5, 7). The formation of (III) and (IV) probably proceeds in accordance with the scheme

$$\underset{(I)}{[(Me_2N)_2CH]^{\oplus}HF_2^{\ominus}} + \underset{(II)}{(CF_3)_2C{=}CFC_2F_5} \rightarrow \underset{(III)}{(CF_3)_2CHF_2CF_2CF_3} + [(Me_2N)_2CH]^{\oplus}F^{\ominus} \xrightarrow{(II)} [(Me_2N)_2CH]^{\oplus} + \underset{(IV)}{(CF_3)_2\bar{C}CF_2CF_2CF_3}$$

The signal at +43.5 ppm corresponds to the CF$_2$ groups (7, 8) of compounds (III) and (IV). At 0°C, the signals (1, 2, 5, 6) are broadened and lose their structure; at 36°C, the signals of the CF$_3$ group (1, 2) and the CF$_2$ group (5, 6) in the α position relative to the reaction center are merged and become broad and diffuse (−32.8 and +18.5 ppm). These changes in the spectra can apparently be explained by fast exchange of a proton between the anion (IV) and its CH acid (III) at the higher temperatures,



$$\underset{(IV)}{\underset{CF_2C_2F_5}{(CF_3)_2C^{\ominus}}} + \underset{(III)}{\underset{CF_2C_2F_5}{HC(CF_3)_2}} \rightleftarrows \underset{(III)}{\underset{CF_2C_2F_5}{(CF_3)_2CH}} + \underset{(IV)}{\underset{CF_2C_2F_5}{\overset{\ominus}{C}(CF_3)_2}}$$

At 36°C, the signals of the CF$_2$ (5, 6) are less intense, apparently because of a decrease in the concentration of (III) and (IV) and the appearance of the original olefin (II). Thus, at 36°C, the olefin (II) also takes part in the exchange. When the mixture is poured into water, the compounds (II) and (III) are recoved in a 3:1 ratio (as determined by GLC and ^{19}F NMR).

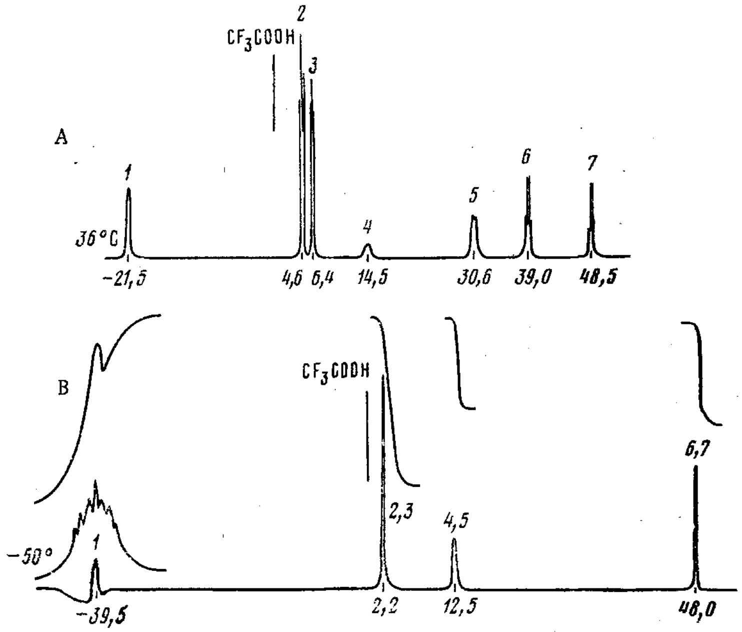
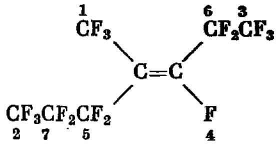
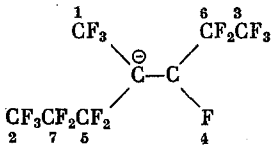


Fig. 2. ^{19}F NMR spectra: A)



(VII) at 36°C; B)



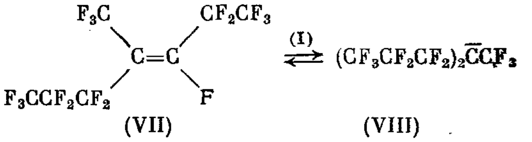
(VIII) at −50°C.

A similar temperature dependence of the ^{19}F NMR spectrum was observed for perfluoroisobutylene (Va) in the presence of (I). At −100°C, two signals are observed in the spectrum (−39.0 and −13.9 ppm), corresponding to the perfluoro-tert-butyl anion (V) and monohydroperfluoroisobutane (VI)

$$\underset{(Va)}{(CF_3)_2C{=}CF_2} \xrightarrow{(I)} \underset{(V)}{(CF_3)_3C^{\ominus}} + \underset{(VI)}{(CF_3)_3CH}$$

The changes in the spectrum at temperatures above −90°C can be explained by the same exchange processes as for the compound (II). In the present case, proton exchange takes place between the anion (V) and its CH acid (VI). After adding allyl bromide at approximately 20°C to a solution of (Va) and (I) in DMFA, (VI) was recovered, along with the compound we described in [7], 5,5,5-trifluoro-4,4-bis(trifluoromethyl)-1-pentene (GLC, ^{19}F NMR). It should be noted that in contrast to the olefin (II), perfluoroisobutylene (Va) will also readily form the anion (V) in the presence of CsF [8].

Perfluoro-(4-methyl-3-heptene) (VII) in the presence of (I) forms the anion (VIII)



The ^{19}F NMR spectrum of the anion (VIII) at −50°C is shown in Fig. 2. At higher temperatures, there is a broadening of the signals from the CF_3 (1) and CF_2 (4, 5) groups bonded to the anionic center. The ^{19}F NMR spectrum did not show up any product of the addition of HF to the olefin (VII); and from the reaction mixture after it was poured into water, only the olefin (VII) was recovered.

In Fig. 3 we show the ^{19}F NMR spectrum of the perfluoroethylcyclohexyl anion (XI)

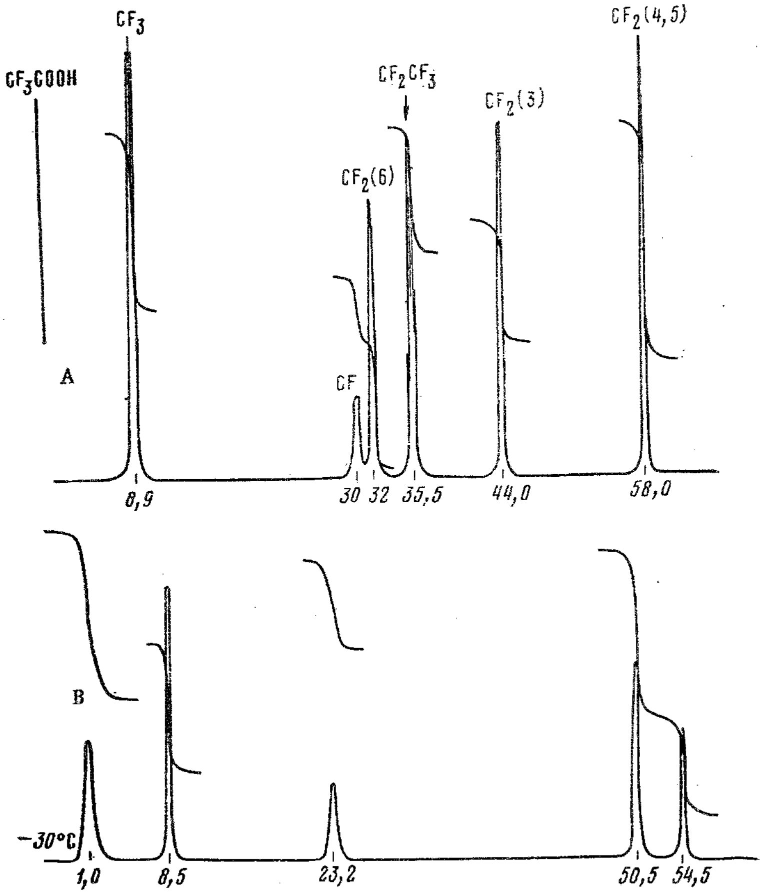
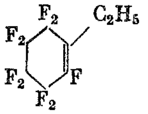
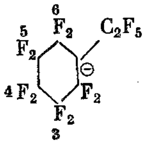
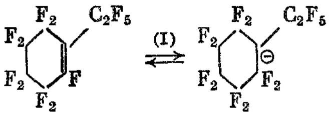


Fig. 3. ^{19}F NMR spectra: A) 

(X) at 36°C; B) 

(XI) at −30°C.



(X)* (XI)

At 40°C, there are no signals in the spectrum from the F atoms in positions 2 and 6 of the perfluoroethylcyclohexene, but there is a broad signal in the region of +2 ppm. At −30°C, we find a very clear signal from CF groups in positions 2 and 6 of the compound (XI). With further cooling, the spectrum does not change; this indicates the formation of the stable anion (XI). The same as in the case of (VII), there is no addition of HF to (XI).

EXPERIMENTAL

The ^{19}F and ^{1}H NMR spectra were recorded in a Perkin–Elmer R-32 instrument (84.6 and 90 MHz); the chemical shifts are given in parts per million relative to CF_3COOH and HMDS, respectively (^{1}H NMR in the δ scale). The IR spectra were recorded in a UR-20 spectrometer.

N,N,N',N'-Tetramethylformamidinium Bifluoride (I). To 27 g of difluoromethyldimethylamine [2] in 100 ml of absolute DMFA, while cooling and stirring, 45 g of Me_2NH was added gradually. Then the mixture was held under vacuum until there was no more evolution of

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*The olefin (X) was obtained by splitting perfluoro-(2-ethylcyclohexanesulfofluoride) in the presence of CsF.

Me_2NH, after which 100 ml of absolute ether was added, the oil that separated out was removed, and the solution was washed with ether (10 × 50 ml). After removing the ether under vacuum 38g (90.5%) of (I) was obtained in the form of a light-yellow viscous oil. Found: C 40.41; H 9.31; F 29.71; N 19.80%. $C_5H_{13}N_2 \cdot 1.17HF$. Calculated: C 40.43; H 9.87; F 28.75; N 19.04%. ^{19}F NMR spectrum: +78.0 s (F). ^1H NMR spectrum: 3.3 s (Me), 8.5 s (CH), 15.2 s ($HF_2^{\ominus}$). IR spectrum (ν, cm^{-1}): 1240, 1450, 1840, 2050 ($HF_2^{\ominus}$), 1710 (C=N), 2940 (Me), 3010 (vinyl proton).

Perfluoroethylcyclohexene (X). A mixture of 4.5 g of CsF, 12 g of perfluoro-(4-ethylcyclohexanesulfofluoride), and 20 ml of absolute diglyme was heated to 130°C with vigorous stirring, with simultaneous distillation. The distillate was redistilled. Obtained 6.6 g (81.5%) of (X), bp 90-91°C. Found: C 26.61; F 73.81%. C_8F_{14}. Calculated: C 26.52; F 73.48%. ^{19}F NMR spectrum: +8.9 m (CF_3), +30.0 m (2-CF), +32.0 m (6-CF_2), +35.5 m ($\underline{CF_2}CF_3$), +44.0 m (3-CF_2), +58.0 m (4,5-CF_2). IR spectrum (ν, cm^{-1}): 1710 (C=C).

Preparation of Perfluoroalkyl Carbanions (IV), (V), (VIII) and (XI). a) To a solution of 3 mmoles of (I) in 1 ml of absolute DMFA, 6 mmoles of the perfluoroolefin (II) or (Va) was added, and the reaction mixture was stirred thoroughly. The ^{19}F NMR spectrum was taken on the homogeneous solution.

b) To a solution of 3 mmoles of (I) in 1 ml of absolute DMFA, 6 mmoles of the perfluoroolefin (VII) or (X) was added, and the reaction mixture was stirred thoroughly. The ^{19}F NMR spectrum was taken on the upper layer.

SUMMARY

A new source of fluoride ion has been obtained: N,N,N',N'-tetramethylformamidinium bifluoride. In the presence of this bifluoride, from perfluoro-(2-methyl-2-pentene), perfluoro-(4-methyl-3-heptene), and perfluoroethylcyclohexene, perfluoroalkyl carbanions have been obtained and have been registered by means of ^{19}F NMR; such carbanions have not been found in the presence of such sources of fluoride ion as CsF and KF. The perfluoroalkyl carbanions that have been obtained are stable at low temperatures.

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