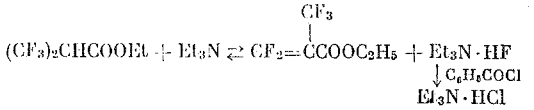
ORGANIC AND BIOLOGICAL CHEMISTRY

REACTIONS OF POLYFLUORONITROALKANES THAT CONTAIN A LABILE HYDROGEN ATOM

A. M. Krzhizhevskii, N. S. Mirzabekyants,
Yu. A. Cheburkov, and I. L. Knunyants

UDC 542.91:547.414.8

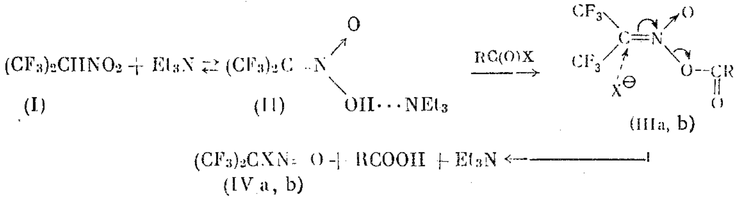
Previously it was shown that an H atom, found in the α-position to CF_3 groups, has proton mobility and is capable of being cleaved in the presence of bases [1]. For example, dehydrofluorination occurs when ethyl monohydroperfluoroisobutyrate is treated with Et_3N.



$$(CF_3)_2CHCOOEt + Et_3N \rightleftarrows CF_2{=}\overset{\displaystyle CF_3}{\overset{|}{C}}COOC_2H_5 + \underset{\displaystyle Et_3N\cdot HCl}{\underset{\downarrow C_6H_5COCl}{Et_3N\cdot HF}}$$

Since the process of HF cleavage is reversible, then in order to shift the equilibrium to the right it is necessary to remove the triethylamine hydrofluoride from the reaction sphere, which is achieved by converting it to the hydrochloride by the addition of C_6H_5COCl. This procedure makes it possible to obtain a number of highly reactive unsaturated compounds that contain the electrophilic fragment $CF_2 = CX$, where X is an electronegative substituent. Since 2-hydrohexafluoro-2-nitropropane (I) and 3,3,3-trifluoro-1-nitroethane (XI) contain analogous H atoms, an attempt was made to obtain the corresponding nitroolefins by the same procedure.

However, in contrast to the hexafluoroisobutyrate, nitropropane (I) does not cleave HF when treated with a mixture of Et_3N and C_6H_5COCl, and instead gives 2-chlorohexafluoro-2-nitrosopropane (IVa) as the end product. This is explained by the ability of nitropropane (I) to change to the aci-form under the influence of organic bases. The adduct of the aci-form with Et_3N (II) is acylated by C_6H_5COCl to give the nitronic anhydride (III). * The C=N bond in anhydride (III) is attacked by the chlorine anion, which leads to nitrosopropane (IVa).



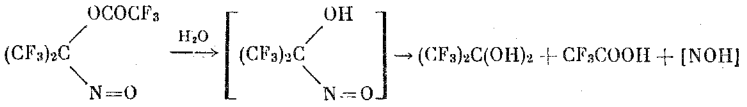
(I) (II) (IIIa, b)

$(CF_3)_2CXN{=}O + RCOOH + Et_3N$

(IVa, b)

$R = C_6H_5$, $X = Cl$ (IVa); $R = CF_3$, $X = OCOCF_3$ (IVb)

This behavior by (I) makes it possible to synthesize new nitroso compounds by this procedure. And, actually, when C_6H_5COCl is replaced by trifluoroacetic anhydride we obtain 2-nitrosohexafluoropropyl fluoroacetate (IVb), which is a member of a new type of perfluoronitroso compounds. An attempt to convert the latter to 2-nitrosohexafluoroisopropanol (V) proved unsuccessful, and the hydrolysis of ester (IVb) leads to hexafluoroacetone hydrate (VI) and CF_3COOH. It should be mentioned that, as the



(IV b) (V) (VI)

$$(CF_3)_2C(OCOCF_3)(N{=}O) \xrightarrow{H_2O} \left[(CF_3)_2C(OH)(N{=}O)\right] \rightarrow (CF_3)_2C(OH)_2 + CF_3COOH + [NOH]$$

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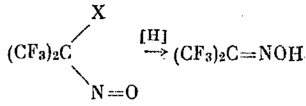
*The formation of mixed anhydrides during acylation is inherent to the salts of perfluorinated nitro compounds [2].

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2513-2517, November, 1974. Original article submitted March 6, 1974.

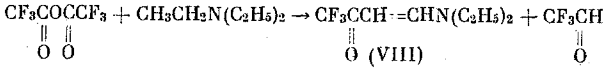
result of the reduction of nitroso compounds (IVa, b) with excess Et_3N, hexafluoroacetone oxime (VII) is formed as a secondary product with both C_6H_5COCl and $(CF_3CO)_2O$ (cf. [3]).



$$(CF_3)_2C\begin{matrix}\diagup X\\ \diagdown N{=}O\end{matrix} \xrightarrow{[H]} (CF_3)_2C{=}NOH$$

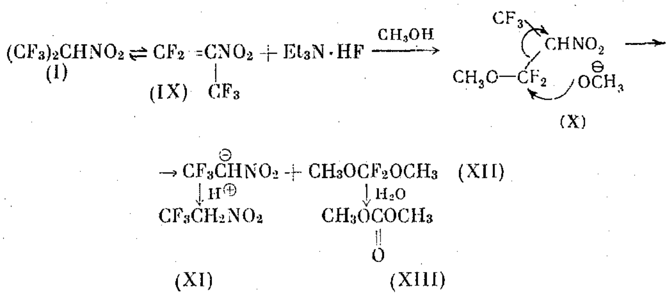
(IV a,b) (VII)

The known diethylaminotrifluorobutenone (VIII) [4] is also formed as a secondary product in the case of $(CF_3CO)_2O$, and is the reaction product of $(CF_3CO)_2O$ with Et_3N.

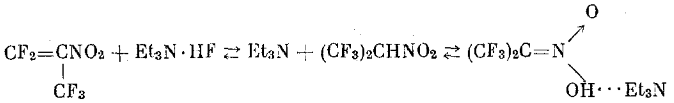


$$CF_3\underset{O}{\underset{\|}{C}}O\underset{O}{\underset{\|}{C}}CF_3 + CH_3CH_2N(C_2H_5)_2 \rightarrow CF_3\underset{O\ (VIII)}{\underset{\|}{C}}CH{=}CHN(C_2H_5)_2 + CF_3\underset{O}{\underset{\|}{C}}H$$

Different results were obtained when nitropropane (I) was reacted with Et_3N in the presence of methanol. Trifluoronitroethane (XI) and dimethyl carbonate (XIII) were isolated as the end products in this case. Evidently, the cleavage of HF from (I) is still possible, while the intermediately formed strongly electrophilic 2-nitropentafluoropropene (IX) adds methanol to give 1-methoxy-2-hydro-2-nitropentafluoropropane (X). Here the latter apparently decomposes to trifluoronitroethane (XI) and bisester (XII). The mechanism of this decomposition is not entirely clear, but it may be assumed that the formed trifluoronitroethyl anion is a good leaving group.

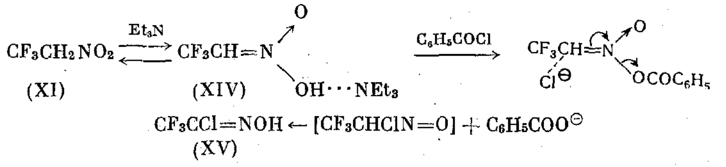


On the basis of the obtained results it may be concluded that the equilibrium of the reversible reactions, namely the cleavage of HF and the formation of the aci-form in 2-nitrohexafluoropropane (I), is shifted in either direction depending on the character of the reagent found in the mixture. Thus, nucleophilic reagents (methanol), by adding to the unsaturated product (IX), facilitate the cleavage of HF from nitro compound (I), and in this way shift the equilibrium to the left; in contrast, electrophilic reagents (benzoyl chloride) react with the aci-form of the nitro compound (II), which leads to a shift of the equilibrium in the opposite direction.



$$CF_2{=}\underset{CF_3}{\underset{|}{C}}NO_2 + Et_3N\cdot HF \rightleftarrows Et_3N + (CF_3)_2CHNO_2 \rightleftarrows (CF_3)_2C{=}N\begin{matrix}\nearrow O\\ \diagdown OH\cdots Et_3N\end{matrix}$$

Trifluoronitroethane (XI), as it proved, shows no tendency whatsoever to cleave HF under the influence of a base, and in this case the corresponding reactions proceed exclusively via the intermediate formation of the adduct of the nitronic acid with Et_3N (XIV). When (XI) is treated with benzoyl chloride in the presence of Et_3N the transformations that take place are analogous to the transformations of trifluoronitropropane (I), and the acid chloride of trifluoroacethydroxamic acid (XV)* is formed as the end product.



The formation of acid chloride (XV) can also be explained by another scheme, which includes the dehydration of nitronic acid (XVI) with benzoyl chloride to trifluoroacetonitrile oxide (XVII). The latter adds the elements of HCl to give acid chloride (XV). The reaction of nitroethane (XI) with $(CF_3CO)_2O$ in the presence

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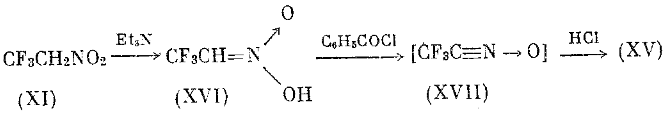
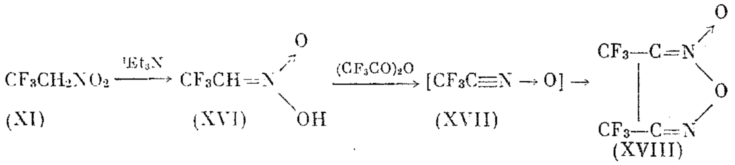
*An analogous reaction scheme was proposed for the reaction of certain fluoronitro compounds with strong acids [5, 6].


$$CF_3CH_2NO_2 \xrightarrow{Et_3N} CF_3CH{=}\overset{O}{\underset{OH}{N}} \xrightarrow{C_6H_5COCl} [CF_3C{\equiv}N \rightarrow O] \xrightarrow{HCl} (XV)$$

of Et_3N serve as some confirmation of this scheme. In this case the formed nitrile oxide (XVII) is dimerized to 1,2-bis(trifluoromethyl)furoxan (XVIII).



EXPERIMENTAL

The ^{19}F NMR spectra were taken on a Hitachi H-6013 spectrometer (56.46 MHz), using CF_3COOH as the external standard. The chemical shifts are given in ppm. The ^1H NMR spectra were taken on a Perkin—Elmer R-12 instrument (60 MHz). The IR spectra were taken on a UR-20 instrument, while the visible and UV spectra were taken on a Perkin—Elmer ERS-3T spectrophotometer. The GLC analysis was run on a Perkin—Elmer 452 chromatograph, using a column packed with SE-30 and helium as the carrier gas.

Reaction of 2-Hydrohexafluoro-2-nitropropane (I) with Benzoyl Chloride in the Presence of Et_3N. To a solution of 15 g (0.076 mole) of (I) in 30 ml of C_6H_5COCl, cooled to —15°C, was carefully added 15.7 g (0.157 mole) of Et_3N in drops, making sure that the temperature of the mixture did not exceed —10°C. Then the reaction mixture was warmed up to ~20°C, and all of the volatile products were vacuum-distilled into a trap that was cooled with liquid nitrogen. Distillation of the trap contents gave 4.4 g (29%) of 2-chlorohexafluoro-2-nitrosopropane (IVa) with bp 25°C, which was chromatographically identical with an authentic specimen [7]. The residual reaction mixture was treated with ether, and the obtained precipitate of $Et_3N \cdot HCl$ was filtered, washed with ether, and the ether was distilled off. Vacuum-distillation of the mixture gave 23.8 g of a mixture of benzoyl chloride and hexafluoroacetone benzoyloxime with bp 48-70°C (3-4 mm) (GLC), and 13.7 g of a dark viscous liquid of unknown composition with bp 75-180°C (3-4 mm). The mixture of benzoyl chloride and hexafluoroacetone benzoyloxime was refluxed for several hours with 15 ml of methanol. The methanol was distilled off, and the residue was dried over $CaCl_2$ and distilled. We obtained 2.6 g (17.5%) of a complex of composition $(CF_3)_2C{=}NOH \cdot HOCH_3$ (bp 89-91°C), which was identified via GLC [8], and 12 g of methyl benzoate.

Reaction of 2-Hydrohexafluoro-2-nitropropane (I) with Trifluoroacetic Anhydride in the Presence of Et_3N. To a mixture of 60 ml of $(CF_3CO)_2O$ and 17.5 g (0.089 mole) of (I), cooled to —50°C, was added in drops 19 g (0.182 mole) of Et_3N in 1 h. The temperature of the mixture was —10°C at the end of addition. The reaction mixture was heated on the water bath and the vapors were passed through ice-cold water, which was contained in a separatory funnel that was cooled on the outside with ice. The lower layer, a dark blue liquid, was separated. Distillation gave 9 g (34%) of 2-nitrosohexafluoroisopropyl trifluoroacetate (IVb), bp 55°C, λ_{max}, nm: 640 (ε 1030), 217, ν_{max} 1840 cm^{-1} (C=O). ^{19}F NMR spectrum: —46.5 s $[(CF_3)_2C]$; 6.0 S (CF_3). Found: C 20.5; F 58.4%. $C_5F_9O_3$. Calculated: C 20.5; F 58.4%. The residual mixture was diluted with water, and the lower layer was separated, washed in succession with water, $NaHCO_3$ solution, and water, and dried over $CaCl_2$ in ether solution. Then the ether was distilled off, and the residual mixture was distilled to give 3.4 g (15%) of hexafluoroacetone oxime etherate, bp 94°C (GLC), and 5 g of 4-diethylamino-1,1,1-trifluoro-3-buten-2-one (VIII), bp 105°C (4 mm), which was identified via ^1H NMR and ^{19}F NMR spectroscopy.

Hydrolysis of 2-Nitrosohexafluoroisopropyl Trifluoroacetate (IVb). A mixture of 3.16 g (0.0108 mole) of nitroso acetate (IVb) and 0.4 g (0.02 mole) of water was sealed in a glass ampul. The next day, after decolorization of the mixture, the trifluoroacetic acid was neutralized with solid $KHCO_3$ and the mixture was vacuum-distilled. We obtained 2 g of hexafluoroacetone hydrate (VI), which was identified by GLC, and also by the mixed melting point of the dianiline salt with an authentic specimen (mp 62-64°C) [9].

Reaction of 2-Hydrohexafluoro-2-nitropropane (I) with Methanol in the Presence of Et_3N. To a solution of 30 g (0.152 mole) of (I) in 50 ml of methanol at 0°C was added 15.7 g (0.157 mole) of Et_3N in drops. The next day the mixture was poured into water, and the oil that separated was refluxed for 6 h with 10% HCl solution, separated, washed in succession with water, $NaHCO_3$ solution, and water, and dried over $CaCl_2$. Distillation gave 21 g of a mixture of dimethyl carbonate (XIII) (37.5%) and trifluoronitroethane (XI)

(62.5%). The products were identified by comparison with authentic specimens employing GLC and the IR, ^{1}H NMR, and ^{19}F NMR spectra.

Reaction of 3,3,3-Trifluoro-1-nitroethane (XI) with Benzoyl Chloride in the Presence of Et_3N. To a solution of 13.4 g (0.104 mole) of trifluoronitroethane (XI) in 48 g (0.340 mole) of C_6H_5COCl at 0°C was added 13.7 g (0.136 mole) of Et_3N in 2 h. The mixture was stirred for another 3 h. Then 60 ml of methanol was added and the mixture was refluxed for 6 h, after which it was diluted with water, and the organic layer was separated and dried over $MgSO_4$. Then it was vacuum-distilled into a trap (−78°C) until the methyl benzoate began to distill [80-85°C (10 mm)]. The distillate was distilled at ordinary pressure. The fraction with bp 42-120°C was subjected to preparative GLC to give 3 g (30%) of the acid chloride of trifluoroacethydroxamic acid (XV), which was identified via GLC with an authentic specimen [10].

Reaction of 3,3,3-Trifluoro-1-nitroethane (XI) with Trifluoroacetic Anhydride in the Presence of Et_3N. To a solution of 15.9 g (0.123 mole) of trifluoronitroethane (XI) in 51.8 g (0.247 mole) of $(CF_3CO)_2O$, cooled to 0°C, was added 25.0 g (0.247 mole) of Et_3N in drops. The next day the $(CF_3CO)_2O$ was distilled off on the water bath. The residual mixture was vacuum-distilled at 20 mm (trap, −78°C) on the steam bath. Distillation of the trap contents gave 5.3 g (39%) of 1,2-bis(trifluoromethyl)furoxan with bp 88-89°C; ν_{max}, cm^{-1}: 1650, 1510, 1530, 1368. ^{19}F NMR spectrum: −11.8 q (CF_3); −14.4 q (CF_3); $J_{CF_3/CF_3} = 6.4$ Hz. Found: C 21.7; N 11.6; F 50.3%. $C_4F_6N_2O_2$. Calculated: C 21.6; N 12.6; F 51.4%.

CONCLUSIONS

1. A study was made of the reaction of 2-hydrohexafluoro-2-nitropropane and 3,3,3-trifluoro-1-nitroethane with some electrophilic reagents.

2. In the case of 2-hydrohexafluoro-2-nitropropane the equilibrium of the reversible reactions of HF cleavage or the formation of the nitronic acid depends on the character of the reagents present in the mixture.

3. A member of the previously unknown type of perfluoronitroso compounds was obtained, and specifically 2-nitrosohexafluoroisopropyl trifluoroacetate.

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