SYNTHESIS AND SOME REACTIONS OF PENTAFLUOROACETONE

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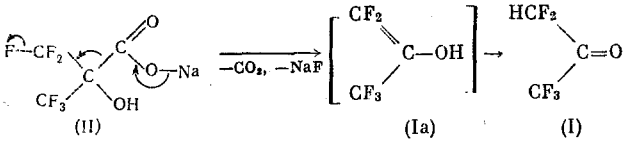
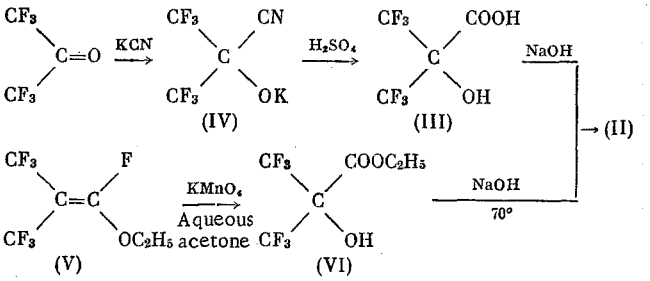
Several methods are known for the preparation of pentafluoroacetone (I) [1-4], including by the Perkov reaction from chloropentafluoroacetone and subsequent hydrolysis [4]. Despite the fact that the latter method made (I) relatively available, still its chemical properties have as yet received little study.

A new method was proposed in the present paper for the preparation of (I)* and some of its reactions were studied. One of the methods for the preparation of fluoroolefins consists in the cleavage of CO_2 and metal fluoride from the salts of perfluorocarboxylic acids [6, 7]. It proved that (I) is obtained by the analogous transformation of the salts of α-hydroxyhexafluoroisobutyric acid (II), evidently due to the rearrangement of the enol (Ia)



The starting salt (II) can be obtained by the neutralizaion of acid (III), which is formed by heating the hexafluoroacetone cyanohydrin salt (IV) with conc. H_2SO_4 [8] (cf. [9]). The method, based on the oxidation of the alkylperfluoroisobutenyl ester (V) (cf. [10]) and subsequent alkaline saponification of the α-hydroxyhexafluoroisobutyric acid ester (VI), proved to be equally convenient



The carbonyl group of fluoroketones is especially active in the reactions with nucleophilic agents [11, 12]. Similar to other fluoroketones, (I) reacts easily with NaCN [13, 14], triphenylphosphine N-phenylimine [15, 16], and sulfene [17]. In all of the reactions of (I) studied up to now, in contrast to trifluoroacetone [17, 18], the protic lability of the hydrogen atom was not detected. It is possible that the conjugated base, the mesomeric carbanion (VII), is destabilized due to the presence of two fluorine atoms in the α-position [19, 20].

Instead of the expected diketone (VIII), the attempted acylation of (I) by treatment with benzoyl chloride (BzCl) in the presence of pyridine under mild conditions gave the ester (IXa)

*See [5] for preliminary communication.

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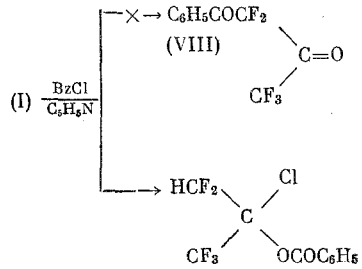
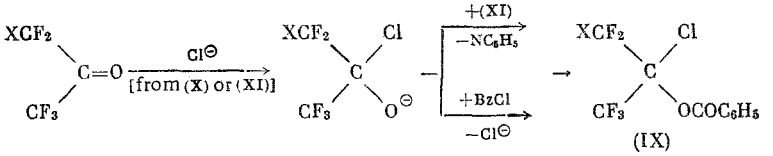


(IXa)

Other fluoroketones, like hexafluoroacetone and chloropentafluoroacetone, also enter into the same reaction. The reaction does not go in the absence of a catalyst, while in the presence of triethylbenzylammonium chloride $C_6H_5CH_2\overset{\oplus}{N}(C_2H_5)_3Cl^{\ominus}$ (X) the fluoroketone reacts with BzCl much more slowly than in the presence of pyridine. Under the same conditions, benzoyl fluoride and benzyl chloride do not enter into the reaction.

It is probable that the BzCl reacts with pyridine to form the salt $C_6H_5C\overset{\oplus}{O}NC_5H_5Cl^{\ominus}$ (XI); then the $Cl^{\ominus}$ attacks the CO group of the ketone, while the acylation of the thus formed alcoholate anion (XII) with either benzoyl chloride or salt (XI) leads to the end product (IX)



(IX)

X=H (a), F (b), Cl (c)

The fact that the reaction is sharply retarded when salt (X) is used instead of pyridine is evidently explained by the lower acylating activity of BzCl when compared with salt (XI) (cf. [21]).*

Reaction of fluoroketones, accomplished by a similar scheme (addition of halide anion and subsequent acylation), are known [22-31], but with the involvement of $F^{\ominus}$, and not $Cl^{\ominus}$ (cf. [11, 12]).† The addition of carboxylic acid chlorides is known for aliphatic aldehydes, devoid of F atoms, but it is accomplished either by heating without a catalyst, or in the presence of a Lewis acid ($ZnCl_2$) [32], so that here the reaction evidently begins with electrophilic addition to the oxygen atom of the CO group of the aldehyde. Fluorinated ketones add boron halides, probably also by an electrophilic mechanism [33, 34]. In contrast, nucleophilic attack on the oxygen atom of the CO group of the fluoroketone is postulated during the addition of trivalent phosphorus halides [35].

The adducts of fluoroketones with BzCl (IXa-c) are quite stable. They can be distilled at atmospheric pressure (bp ~190°C) and, in addition, they hardly undergo decomposition when treated with $NaHCO_3$ solution.‡

As a result, (I) is not acylated in the α-position when reacted with BzCl in the presence of pyridine, and instead it adds the acid chloride at the CO group. This is evidently due to three reasons: the comparatively low protic activity of the H atom, the activity of the CO group toward nucleophilic attack, and the irreversibility of the acylation of the alcoholate anion (XII) under the reaction conditions. It could be expected that the use of other electrophilic reagents instead of BzCl will lead to success in replacing the labile H atom in (I). The fluoroketones and, in particular, pentafluoroacetone itself, proved to be such electrophiles.

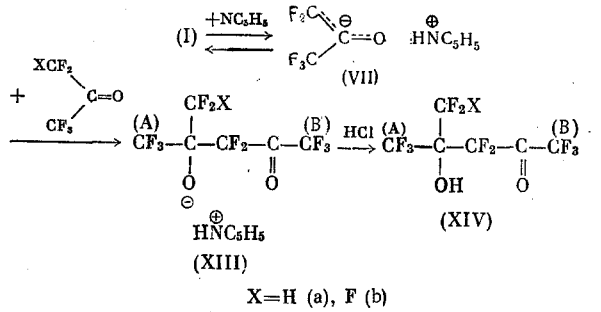
The pyridinium salt of the β-hydroxyketone (XIIIa) was obtained when (I) is heated in the presence of pyridine at 100°, from which the free pentafluoroacetone dimer, namely 4-hydroxy-4-difluoromethylperfluoro-2-pentanone (XIVa), can be isolated by acidification. In order to accomplish this reaction it is

*A lower reaction rate in the presence of salt (X) can also be caused by the heterogeneity of the medium (see Experimental Method).

†The possibility of such a reaction for (I) is mentioned in the patent [22].

‡See [22, 23, 25] for the thermal and hydrolytic stability of esters of type $(CF_3)_2CFOCOR$ and $(CF_3)_2CFOSO_2R$.

necessary to use not a catalytic, but rather an equivalent amount of pyridine [0.5 mole per mole of (I)]. Evidently hydroxyketone (XIVa) is a comparatively strong acid, and consequently the pyridine is bound as the salt (XIIIa) so firmly that it can no longer activate (I) and convert it to the anion (VII). Under analogous conditions, the reaction of (I) with excess hexafluoroacetone in the presence of pyridine gives salt (XIIIb), from which perfluorohydroxyketone (XIVb) was isolated



X=H (a), F (b)

As a result, we were the first to accomplish the reaction of pentafluoroacetone involving a proton-labile H atom.

EXPERIMENTAL METHOD*

The NMR spectra were taken on a Perkin–Elmer R-12 spectrometer (60 MHz), while the ^{19}F NMR spectra were taken on either a Hitachi or a Hitachi–Perkin–Elmer R-20 instrument (56.46 MHz). The chemical shifts are given in parts per million respectively from the external standards TMS or CF_3COOH. The IR spectra were taken by L. P. Volkova on a UR-20 spectrophotometer (as a thin film). The mass spectra were taken by A. P. Pleshkova on an MX-1303 spectrometer (the energy of the ionizing electrons was 12 and 30 eV).

Ethyl Ester of α-Hydroxyhexafluoroisobutyric Acid (VI) (cf. [10]). With stirring, 26.2 g of $KMnO_4$ was gradually added at ~20° to a solution of 53.8 g of the ethylperfluoroisobutenyl ester (V) and 5 ml of water in 110 ml of acetone, the mixture was stirred vigorously for 3 h, SO_2 was passed in until decolorization was achieved, and 150 ml of water was added. The lower layer was separated and washed with water. We obtained 55.9 g of crude ester (VI), which, based on the NMR and GLC data, contained ~10% of acetone; the yield of the pure ester (VI) was ~50 g (~87%). NMR spectrum: δ_{CH_3} 1.09 (triplet), δ_{CH_2} 4.25 (quadruplet), δ_{OH} 4.65 (singlet), $J_{CH_3-CH_2}$ 7.3 Hz [$\delta_{CH_3COCH_3}$ 1.82 (singlet). ^{19}F NMR spectrum: −1.9 (CF_3, singlet).

The product was used without further purification to obtain salt (II).

Sodium Salt of α-Hydroxyhexafluoroisobutyric Acid (II). a) Acid (III) [8, 9] (34 g) was neutralized with an equimolar amount of 10% NaOH solution until alkaline to phenolphthalein, after which the solution was evaporated at 100°, and the residue was dried in a vacuum-desiccator over P_2O_5. We obtained 35 g (93%) of the crude salt (II). Found: C 19.76; H 0.58; F 45.35%. $C_4HF_6NaO_3$. Calculated: C 20.53; H 0.43; F 48.71%. ^{19}F NMR spectrum (in water): −4.1 (CF_3, singlet).

b) A mixture of the crude ethyl ester of α-hydroxyhexafluoroisobutyric acid [containing 29.2 g of pure (VI)] and 100 ml of water was heated, with vigorous stirring, up to 70° and an equivalent amount of 5% NaOH solution was added in 4-6 h up to a pH of ~9; then the mixture was stirred for 1 h at 70°, CO_2 was passed in to pH ~8, and the mixture was evaporated at 100°. The residue contained 25.2 g (88%) of crude salt (II).

Pentafluoroacetone (I). a) With stirring, a mixture of 27.7 g of crude salt (II) and 100 ml of dry nitrobenzene was heated under reflux up to 200°, and the crude (I) was collected in a trap (−78°). After purification by passage through conc. H_2SO_4 we obtained 8 g (45%) of pure (I), bp 14-15°. NMR spectrum: δ_H 5.60 (triplet); J_{H-CF_2} 52.0 Hz. ^{19}F NMR spectrum: +0.6 (CF_3, triplet), +54.7 (CF_2, doublet of quadruplets), $J_{CF_3-CF_2}$ 6.6 Hz, J_{CF_2-H} 52.0 Hz.

*Carried out with the participation of G. S. Kaitmazova and T. B. Moraleva.

b) The crude salt (11.0 g) was mixed thoroughly with 10 g of ignited pure sand and the mixture was heated in an oil bath (up to 300°). We obtained 6.2 g (90%) of pure (I) in the trap (−78°).

Bis-Anilinium Salt of Pentafluoroacetone Hydrate. Compound (I) (0.8 g) was passed into an ether solution of 0.3 g of aniline, the solution was evaporated in the air, and from the residue we obtained 0.5 g (87%) of the salt $HCF_2C(CF_3)(OH)_2 \cdot 2C_6H_5NH_2$, mp 42-43° (from hexane). Found: C 51.25; H 4.92; F 27.01%. $C_{15}H_{17}F_5N_2O_2$. Calculated: C 51.14; H 4.86; F 26.96%.

O-Benzoyl-1-hydro-2-chloropentafluoro-2-propanol (IXa). A mixture of 2.63 g of BzCl, 3.73 g of (I), and 0.05 g of pyridine in a sealed ampul was gradually heated from −78 up to 20°; after the start of exothermic reaction the ampul was cooled, maintaining the temperature at ~20°. The formed homogeneous mixture was kept at 20° for 1 h, and the excess (I) was distilled off. The residue was dissolved in ether, washed with water, and dried over $MgSO_4$. Distillation gave 3.47 g (64%) of ester (IXa), bp 49-51° (2 mm), 185-190° (750 mm). Found: C 41.56; H 2.09; F 33.43; Cl 13.29%. $C_{10}H_6ClF_5O_2$. Calculated: C 41.61; H 2.09; F 32.91; Cl 12.28%. NMR spectrum: δ_{HCF_2} 6.54 (triplet of quadruplets), $\delta_{C_6H_5}$ 6.7-7.6 (multiplet), J_{H-CF_2} 53.4 Hz, J_{H-CF_3} 2.0 Hz. ^{19}F NMR spectrum: −2.1 (CF_3, doublet of doublets), +45.3 (F_A, left portion of AB system, with additional splitting into doublets of quadruplets), +54.7 (F_B, right portion of AB system, with additional splitting into doublets of quadruplets), $J_{CF_3-F_A}$ 8.5 Hz, $J_{CF_3-F_B}$ 14.9 Hz, J_{CF_3-H} 2.0 Hz, $J_{F_A-H} = J_{F_B-H}$ 53.4 Hz, $J_{F_A-F_B}$ 282 Hz. Infrared spectrum: 1770 cm^{-1} (C=O). Mol. wt. 288 and 290 (mass spectrometry).

Ester (IXa) is also formed from (I) and BzCl when an equimolar amount of pyridine is used.

O-Benzoyl-1,2-dichloropentafluoro-2-propanol (IXc). A mixture of 5.83 g of BzCl, 7.48 g of chloropentafluoroacetone, and 2 drops of pyridine was kept in a sealed ampul at 20° for 20 h (a homogeneous solution was formed within 10 min), after which it was dissolved in ether, and the ether solution was washed in succession with water, saturated $NaHCO_3$ solution and water, and then dried over $MgSO_4$. Distillation gave 4.30 g (32%) of ester (IXc), bp 54-56° (2 mm). Found: C 36.99; H 1.32; F 29.80; Cl 21.73%. $C_{10}H_5Cl_2F_5O_2$. Calculated: C 37.18; H 1.56; F 29.40; Cl 21.94%. NMR spectrum: $\delta_{C_6H_5}$ 6.8-7.8 (multiplet). ^{19}F NMR spectrum: −7.7 (CF_3, doublet of doublets), −18.3 (F_A, left portion of AB system, with additional splitting into quadruplets), −14.6 (F_B, right portion of AB system, with additional splitting into quadruplets), $J_{CF_3-F_A}$ 11.0 Hz, $J_{CF_3-F_B}$ 13.5 Hz, $J_{F_A-F_B}$ 165 Hz. Infrared spectrum: 1780 cm^{-1} (C=O).

O-Benzoyl-2-chlorohexafluoro-2-propanol (IXb). a) A homogeneous mixture of 4.08 g of BzCl, 6.05 g of hexafluoroacetone, and 6 drops of pyridine was kept in a sealed ampul at 20° for 23 h, after which the excess hexafluoroacetone was distilled off, and the residue was dissolved in ether, washed with water, and dried over $MgSO_4$. Distillation gave 5.60 g (63%) of ester (IXb), bp 41-43° (2 mm), 60-62° (4 mm), 76-79° (10 mm), 186-192° (750 mm). Found: C 40.87; H 1.71; F 36.13; Cl 11.40%. $C_{10}H_5ClF_6O_2$. Calculated: C 39.18; H 1.64; F 37.18; Cl 11.56%. NMR spectrum: $\delta_{C_6H_5}$ 6.8-7.8 (multiplet). ^{19}F NMR −3.06 (CF_3, singlet). Infrared spectrum: 1780 cm^{-1} (C=O). Mol. wt. 306 and 308 (mass spectrometry).

Benzoyl fluoride and benzyl chloride did not react with hexafluoroacetone under analogous conditions.

b) A mixture of 4.07 g of BzCl, 8.16 g of hexafluoroacetone, and 0.10 g of triethylbenzylammonium chloride (X) was kept in a sealed ampul at 20° for 1 month, after which 4.6 g of hexafluoroacetone was distilled off, and the residue was dissolved in ether, washed in succession with saturated $NaHCO_3$ solution and water, and dried over $MgSO_4$. Distillation gave 4.01 g (45%) of ester (IXb).

c) A mixture of 4.8 g of BzCl, 8.4 g of hexafluoroacetone, and 0.4 g of dry triethylbenzylammonium chloride (X) was heated in a sealed ampul from −78 up to 20° (here a part of salt (X) dissolved, but the hexafluoroacetone and BzCl form two immiscible layers). After 1 h (20°) we distilled 7.6 g of the starting hexafluoroacetone into the trap (−78°), while the residue contained BzCl (GLC, NMR). The same results were obtained in the absence of salt (X). Under the same conditions, but using 0.1 g of pyridine instead of salt (X), we obtained a homogeneous solution; after 1 h (20°) we distilled 3.2 g of hexafluoroacetone into the trap, and the residue was dissolved in ether, washed in succession with saturated $NaHCO_3$ solution and water, and dried over $MgSO_4$. Distillation gave 5.9 g (56%) of ester (IXb).

A solution of 2.38 g of O-benzoyl-2-chlorohexafluoro-2-propanol in ether was shaken with saturated $NaHCO_3$ solution, washed with ether, and dried over $MgSO_4$. Distillation gave 1.46 g (61%) of unchanged ester (IXb).

Adduct of 4-Hydroxy-4-difluoromethylperfluoro-2-pentanone with Pyridine (XIIIa). A mixture of 0.92 g of pyridine and 3.65 g of (I) was heated in a sealed ampul at 100° for 7 h. Distillation gave 3.85 g (88%) of adduct (XIIIa), bp 46-49° (4 mm). Found: C 34.77; H 1.79; N 3.79%. $C_{11}H_7F_{10}NO_2$. Calculated: C 35.22; H 1.88; N 3.73%. NMR spectrum: δ_{HCF_2} 5.85 (triplet), $\delta_{C_5H_5}$ 6.8-7.8 (multiplet), δ_{NH} 12.53 (singlet); J_{H-CF_2} 52 Hz. ^{19}F NMR spectrum: −4.6 [CF_3(A), quintet], −2.5 [CF_3(B), triplet], +35.7 (CCF_2C, multiplet), +53.8 (HCF_2, doublet of multiplets), $J_{CF_3(A)-CF_2}$ 10.2 Hz, $J_{CF_3(B)-CCF_2C}$ 8.6 Hz, J_{CF_2-H} 52 Hz.

4-Hydroxy-4-difluoromethylperfluoro-2-pentanone (XIVa). Adduct (XIIIa) (3.64 g) was treated with excess cold dilute HCl solution, extracted with ether, the ether solution was dried over $MgSO_4$, the ether was distilled off (up to 130° in the bath), and the crude hydroxyketone hydrate (XIVa) was obtained in the residue; ^{19}F NMR spectrum: −7 [CF_3(A)], +4 [CF_3(B)], +41 (CCF_2C), +55 (HCF_2). The crude hydrate was refluxed with an equal volume of conc. H_2SO_4 for 1.5 h, and distillation gave 1.69 g (59%) of the dimer (XIVa), bp 105-106°. Found: C 23.72; H 0.57; F 63.12%. $C_6H_2F_{10}O_2$. Calculated: C 24.34; H 0.68; F 64.16%. NMR spectrum: δ_{HCF_2} 5.95 (triplet), δ_{OH} 3.78 (singlet), δ_{H-CF_2} 52.2 Hz. ^{19}F NMR spectrum: −3.8 [CF_3(A), quintet], −1.9 [CF_3(B), triplet], +36.2 (CCF_2C, multiplet), +54.0 (HCF_2, doublet of multiplets), $J_{CF_3(A)-CF_2}$ 9.9 Hz, $J_{CF_3(B)-CCF_2C}$ 9.3 Hz, J_{CF_2-H} 52.2 Hz. Infrared spectrum: 1792 (C=O) and 3600 cm^{-1} (OH).

The addition of a small amount of water to an ether solution of the dimer (XIVa) gave the corresponding hydrate (the ^{19}F NMR spectrum was identical with the spectrum of the crude hydrate that was obtained by the decomposition of (XIIIa) with dilute HCl solution, see above).

Adduct of 4-Hydroxy-4-trifluoromethylperfluoro-2-pentanone with Pyridine (XIIIb). A mixture of 3.2 g of (I), 10 g of hexafluoroacetone, and 1.52 g of pyridine was heated in a sealed glass ampul for 6 h at 100°. Distillation gave 1.93 g (22%) of adduct (XIIIb), bp 80-81° (20 mm). NMR spectrum: $\delta_{C_5H_5}$ 6.7-7.8 (multiplet), δ_{NH} 13.20 (singlet). ^{19}F NMR spectrum: −4.1 [$(CF_3)_2C$, triplet], −3.2 (CF_3CO, triplet), +36.0 (CF_2, multiplet), $J_{(CF_3)_2C-CF_2}$ 11.2 Hz, $J_{CF_4CO-CF_2}$ 8.9 Hz.

4-Hydroxy-4-trifluoromethylperfluoro-2-pentanone (XIVb). Adduct (XIIIb) (1.58 g) was treated with excess dilute HCl solution, extracted with ether, the ether solution was dried over $MgSO_4$, the ether was distilled off, and the residue was refluxed for 1.5 h with an equal volume of conc. H_2SO_4 solution. Distillation gave 0.55 g (43%) of hydroxyketone (XIVb), bp 96-102°. Found: C 24.36; H 0.74; F 64.20%. $C_6HF_{11}O_2$. Calculated: C 22.95; H 0.32; F 66.54%. NMR spectrum: δ_{OH} 2.31 (singlet), ^{19}F NMR spectrum: −3.7 [$(CF_3)_2C$, triplet], −2.0 (CF_3CO, triplet), +36.8 (CF_2, multiplet), $J_{(CF_3)_2C-CF_2}$ 10.2 Hz, $J_{CF_3CO-CF_2}$ 9.7 Hz.

CONCLUSIONS

1. Fluoroketones easily add benzoyl chloride in the presence of catalytic amounts of pyridine to give the benzoates of fluoro-substituted chloroisopropanols.

2. When pentafluoroacetone is heated with fluoroketones in the presence of equivalent amounts of pyridine, the labile hydrogen atom is replaced and the pyridinium salts of the corresponding β-hydroxyketones are formed.

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