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REVERSIBLE DEHYDROFLUORINATION OF 2-MONOHYDROPERFLUOROISOBUTANE AND OF ESTERS OF α-HYDROHEXAFLUOROISOBUTYRIC ACID

It is known that the presence of perfluoroalkyl groups in a molecule facilitates protonation of the C—H bond, as a result of which monohydroperfluoroalkanes exhibit the properties of weak acids (^{1}) (for example, for 2-monohydroperfluoroisobutane $pK_a \approx 11$ (^{1})). The proton mobility of hydrogen atoms promotes the easy mineralization of fluorine atoms in compounds containing hyperconjugated C—H and C—F bonds under the action of alkaline agents ($^{1-4}$).

$$\mathrm{F_3{\equiv}C{-}C{-}H \xrightarrow[HO^-]{H_2O} H{-}O{-}C(=O){-}C{-}H + F^-}$$

In accordance with this, 2-monohydroperfluoroisobutane (I) readily eliminates fluorine atoms as ions under the action of alkalis (^{1}). Fluorine atoms in α-hydrohexafluoroisobutyric acid and its derivatives are mineralized just as readily (^{5,6}). At the same time, when triethylamine was allowed to act on 2-monohydroperfluoroisobutane, the starting I was obtained (after treating the evolved gas with alcohol) (^{7}).

In the present work it is shown that 2-monohydroperfluoroisobutane is practically unchanged upon prolonged heating with triethylamine. However, it proved that in the presence of equimolar amounts of triethylamine and benzoyl chloride it is readily converted into perfluoroisobutylene (II); triethylamine hydrochloride and, after hydrolysis, benzoic acid were isolated from the reaction mixture.

This result indicates that triethylamine is nevertheless capable of eliminating hydrogen fluoride from monohydroperfluoroisobutane, but that the dehydrofluorination reaction is reversible and the equilibrium is shifted almost completely toward the formation of I owing to nucleophilic hydrofluorination of perfluoroisobutylene (cf. (^{8})). Indeed, perfluoroisobutylene, on interaction with triethylamine hydrofluoride (or even with hydrofluoric acid in the presence of catalytic amounts of triethylamine hydrofluoride), gives 2-monohydroperfluoroisobutane in good yield.* If benzoyl chloride is present in the mixture, however, it enters into an exchange reaction with triethylamine hydrofluoride, which shifts the equilibrium toward the formation of perfluoroisobutylene.

By removing perfluoroisobutylene from the reaction, the equilibrium can likewise be shifted toward dehydrofluorination of 2-monohydroperfluoroisobutane. Indeed, in the presence of triethylamine and methanol, 2-monohydroperfluoroisobutane gives a mixture of esters III and IV, which are formed through inter— of the reaction of perfluoroisobutylene with methanol (cf. (10)):

$$\underset{\text{(I)}}{(CF_3)_2CHCF_3} + (C_2H_5)_3N \rightleftharpoons \underset{\text{(II)}}{(CF_3)_2C{=}CF_2} + (C_2H_5)_3N \cdot HF$$

$$\begin{array}{c} (CF_3)_2CHCF_2OCH_3 \\ \text{(III)} \\ + \\ (CF_3)_2C{=}CFOCH_3 \\ \text{(IV)} \end{array} \xleftarrow{+CH_3OH} (CF_3)_2C{=}CF_2$$

$$(CF_3)_2C{=}CF_2 \xleftarrow{+C_6H_5COCl} [C_6H_5COF] + (C_2H_5)_3N \cdot HCl$$

$$[C_6H_5COF] \xrightarrow{H_2O} C_6H_5COOH$$

The esters of α-hydrohexafluoroisobutyric acid (V) also enter into an analogous reaction with alcohols in the presence of triethylamine (in the absence of alcohol they do not react with triethylamine); the intermediately formed esters of perfluoromethacrylic acid (VI) smoothly add alcohol, being converted into the corresponding esters of alkoxyperfluorocarboxylic acids (VII) (cf. (5)), which upon saponification give esters of trifluoromethylmalonic acid (VIII)

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* This reaction, along with other methods (^{8,9}), may serve as a convenient preparative method for obtaining 2-monohydroperfluoroisobutane.

$$\substack{CF_3\\CF_3}>CHCOOR+(C_2H_5)_3N \rightleftharpoons \substack{CF_3\\CF_2}>CCOOR+(C_2H_5)_3N\cdot HF$$

$$\text{(V) a: } R=CH_3 \qquad\qquad \text{(VI)}$$

$$\text{b } R=C_2H_5$$

$$\substack{CF_3\\R'OCF_2}>CHCOOR \xleftarrow{R'OH} \text{(VI)}$$

$$\text{(VII) a } R=R'=CH_3$$

$$\text{(VII)} \xrightarrow{H_2SO_4} CF_3{-}CH\substack{COOR\\COOR'}$$

$$\text{(VIII) a: } R=R'=CH_3$$

$$\text{b: } R=CH_3,\ R'=C_2H_5$$

$$\text{c: } R=R'=C_2H_5$$

By the same method the second trifluoromethyl group can also be converted into a carboalkoxy group; in this case an ester of methanetricarboxylic acid (IX) is formed.

$$\underset{\text{(VIIIa)}}{CF_3CH\substack{COOCH_3\\COOCH_3}} \xrightarrow[\text{2) } H_2SO_4]{\text{1) } (C_2H_5)_3N+CH_3OH} HC\substack{COOCH_3\\-COOCH_3\\COOCH_3} \quad \text{(IX)}$$

This sequence of reactions essentially represents a convenient general method for the partial saponification of trifluoromethyl groups in monohydroperfluoroalkanes and related compounds. This method was applied to obtain previously unknown compounds—derivatives of trifluoromethylmalonic acid—from readily available (11) derivatives of α-hydrohexafluoroisobutyric acid.

Experimental Part

Gas-chromatographic analysis was carried out on packed columns with detection by thermal conductivity. Infrared spectra were recorded on an IKS-14 spectrophotometer. NMR spectra were recorded by E. I. Fedin and P. V. Petrovskii on a TsLA 55-35 spectrometer with hexamethyldisiloxane as internal standard.

2-Monohydroperfluoroisobutane (I). A mixture of 21 g of 95% perfluoroisobutylene, 2 g of anhydrous hydrogen fluoride, and 1.4 g of abs. triethylamine was shaken in a steel ampoule for 10 hours; the gas obtained was passed through aqueous methanol, then through concentrated sulfuric acid, and condensed in a trap (~ −70°). Distillation gave 19 g of 95% 2-monohydroperfluoroisobutane, b.p. 10–11° (lit. b.p. 10–11° (8)); yield of pure I* 18 g (81% of theory). Similar results

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* NMR spectrum of I: $\delta_{>CH-}$ 3.5 (multiplet); J_{HF} 7.0 Hz.

obtained by the interaction of equimolar amounts of perfluoroisobutylene, hydrogen fluoride, and triethylamine.

Reaction of 2-monohydroperfluoroisobutane with triethylamine. a) In the absence of a third component. 3.4 g of I and 1.4 g of anhydrous triethylamine were heated in a sealed ampoule for 20 h on a boiling water bath; after cooling and opening the ampoule, 3 g (88% of theory) of monohydroperfluoroisobutane, containing no perfluoroisobutylene, was collected in a trap.

b) In the presence of benzoyl chloride. A mixture of 3.4 g of I, 1.6 g of triethylamine, 2.2 g of benzoyl chloride, and 4 ml of anhydrous ether in a sealed glass ampoule was heated, after the exothermic reaction had ended, for 0.5 h on a boiling water bath; after opening the ampoule, 3.3 g of a mixture of 2-monohydroperfluoroisobutane (33%) and perfluoroisobutylene (67%) was collected in a trap. The yield of perfluoroisobutylene was 2.2 g (70% of theory). The residue in the ampoule was treated with anhydrous ether; 1.8 g of triethylamine hydrochloride was obtained as a precipitate, mp 249-250°; a mixture with an authentic sample gave no depression of the melting point. Benzoic acid was obtained from the ether filtrate after treatment with water.

c) In the presence of methanol. A mixture of 1.70 g of I, 0.25 g of anhydrous methanol, and 0.78 g of anhydrous triethylamine was heated in a sealed ampoule for 36 h on a boiling water bath, treated with hydrochloric acid, and the ether extract was washed with water and dried with magnesium sulfate; distillation gave 0.6 g (33% of theory) of 1-methoxy-2-hydroperfluoroisobutane (III), bp 68-74° (lit. bp 69.5-70° (10)), and 0.2 g (12% of theory) of 1-methoxyperfluoroisobutylene (IV), bp 98-104° (lit. bp 101-102° (10)). Compounds III and IV were chromatographically identical with authentic samples.

Reaction of methyl α-hydrohexafluoroisobutyrate (Va)* with triethylamine. Equimolar amounts of ester Va (10) and triethylamine were mixed; after 2 h the mixture was distilled under vacuum, the distillate was treated with dilute hydrochloric acid, washed with water, and dried with magnesium sulfate. The starting ester Va was obtained, chromatographically identical with an authentic sample. The yield of Va was 90% of theory.

Methyl α-trifluoromethyl-β-methoxy-β,β-difluoropropionate (VIIa). To a mixture of 14.48 g of methyl ester Va and 7.4 g of anhydrous triethylamine, cooled with ice, an excess of anhydrous methanol was added dropwise. After the end of the exothermic reaction the mixture was poured into dilute hydrochloric acid, and the separated oil was washed with water and dried with magnesium sulfate. Distillation gave 7 g of a fraction with bp 56-71°/8 mm, containing 25% of ester VIIa (chromatographically identical with an authentic sample (5)) and 75% of ester VIIIa; the yield of VIIa was 1.75 g (11% of theory), and the yield of VIIIa was 5.25 g (38% of theory).

Dimethyl trifluoromethylmalonate (VIIIa). To 78 g of ester VIIa (5)** 30 ml of concentrated sulfuric acid was added. After 2 h the mixture was poured into water; the separated oil was washed with saturated sodium bicarbonate solution, then with water, and dried with magnesium sulfate. Distillation gave 46.51 g (66% of theory) of ester VIIIa, bp 72.5-73°/9 mm, n_D^{20} 1.3739.

Found, %: C 36.18; H 3.71; F 28.47
$C_6H_7F_3O_4$. Calculated, %: C 36.00; H 3.50; F 28.50

IR spectrum: $\nu_{\max}$ 1780 and 1765 cm^{-1} (doublet of the CO group); NMR spectrum: δ_{CH_3} 3.76; $\delta_{>CH-}$ 4.40 (quartet), J_{HF} 8 Hz.

Methylethyl trifluoromethylmalonate (VIIIb). To a mixture of 9.5 g of anhydrous triethylamine and 20 g of methyl ester

* NMR spectrum of Va: δ_{CH_3} 3.84; $\delta_{>CH-}$ 4.20 (septet), J_{HF} 7.6 Hz.

** IR spectrum of VIIa: $\nu_{\max}$ 1765 cm^{-1} (CO group).

Va was carefully treated with 20 g of absolute ethanol. After completion of the exothermic reaction, the mixture was boiled with a reflux condenser for 0.5 h, cooled, and poured into water. The solution of the oil obtained was poured, after 20 min, into an equal volume of concentrated sulfuric acid. It was poured into ice water. The ethereal solution of the lower layer was dried over magnesium sulfate; distillation gave 16.5 g (81% of theory) of ester VIIIb, b.p. 64-66°/6 mm, n_D^{20} 1.3748.

Found, %: C 39.28; H 4.26; F 26.52
$C_7H_9F_3O_4$. Calculated, %: C 39.25; H 4.20; F 26.63

IR spectrum: $\nu_{\max}$ 1780 and 1762 cm^{-1} (doublet of the CO group).

Diethyl ester of trifluoromethylmalonic acid (VIIIb). Ester VIIIb was obtained analogously to ester VIIIb, yield 64% of theory, b.p. 77°/8 mm, n_D^{20} 1.3773.

Found, %: C 41.96; H 4.84; F 24.74
$C_8H_{11}F_3O_4$. Calculated, %: C 42.10; H 4.82; F 25.00

IR spectrum: $\nu_{\max}$ 1778 and 1760 cm^{-1} (doublet of the CO group).

Trimethyl ester of methanetricarboxylic acid (IX). Ester IX was obtained from dimethyl ester of trifluoromethylmalonic acid (VIIIa), triethylamine, and methanol, analogously to the preparation of VIIIb from Va. The sulfuric acid solution was poured onto ice; the precipitate was washed with water and dried. 2.0 g (21% of theory) of ester IX was obtained, m.p. 42-44° (from methanol) (lit. m.p. 45-46° (12)).

Found, %: C 44.07; H 5.22
$C_7H_{10}O_6$. Calculated, %: C 44.21; H 5.26

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Note: Figure translations are in progress. See original paper for figures.