REACTIONS OF FLUORO OLEFINS

COMMUNICATION 11. REACTIONS OF COMPOUNDS OF THE PERFLUOROISOBUTENE SERIES WITH AMINES AND AMMONIA

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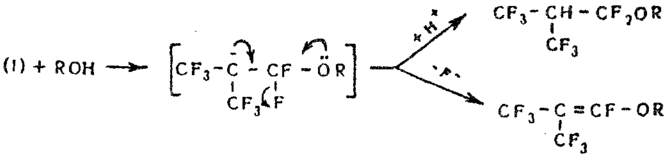
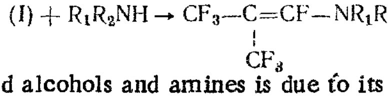
Perfluoroisobutene [pentafluoro-2-(trifluoromethyl) propene] $CF_3-\underset{CF_3}{\underset{|}{C}}=CF_2$ (I) is a compound in which the specific properties of fluoro olefins are most strongly manifested. Thus, we showed previously that, even in absence of alkaline catalysts, (I) readily reacts with alcohols and, apart from addition products, unsaturated ethers are formed which correspond in structure to the replacement of a vinyl fluorine atom of (I) by an alkoxy group [1]:



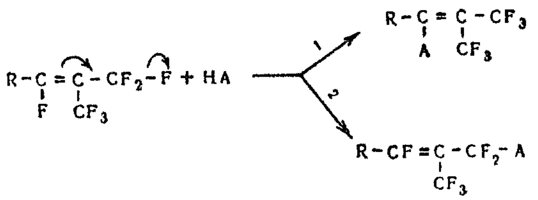
(I) reacts extremely vigorously with amines with exclusive formation of perfluoroisobutenylamines [tetrafluoro-2-(trifuloromethyl) propenylamines]:



$$(I) + R_1R_2NH \rightarrow CF_3-\underset{CF_3}{\underset{|}{C}}=CF-NR_1R_2$$

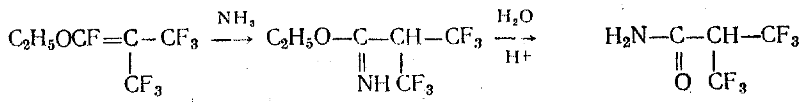
The high reactivity of (I) toward alcohols and amines is due to its very marked electrophilic character, which is caused by the powerful electron-attracting effect of two trifluoromethyl groups and also the lack of symmetry of the molecule. These properties enable us to obtain compounds in which a 1-fluorine of perfluoroisobutene is replaced by an alkoxy or dialkylamino group. We considered it to be of interest to study the character of the reaction of 1-alkyl- and 1-aryl-heptafluoroisobutenes with nucleophilic reagents, in particular with ammonia and amines. For the introduction of alkyl and aryl groups in the 1-position, in the present investigation we carried out reactions of (I) with Grignard reagents, which proceed as follows: $(I) + RMgBr \rightarrow CF_3-\underset{CF_3}{\underset{|}{C}}=CF-R$ This reaction has already been carried out with other fluoro olefins by Tarrant and Warner [2].

For the reactions of 1-alkyl- and 1-aryl-heptafluoroisobutenes with nucleophiles two probable courses can be suggested: 1) replacement of the vinyl fluorine atom; 2) attack at a trifluoromethyl group with replacement of an allyl fluorine atom, the mobility of which is due to hyperconjugation:



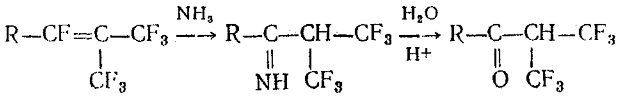
Experiment showed that reactions actually proceed in both of the possible directions and that the place of attack depends both on the character of the olefin and on the character of the attacking reagent.

The action of anhydrous ammonia on 1-alkoxy-, 1-alkyl-, and 1-aryl-heptafluoroisobutenes proceeds only by Scheme 1. Thus, from 1-ethoxyheptafluoroisobutene we obtained ethyl 3,3,3-trifluoro-2-(trifluoromethyl) propionimidate, which under the action of concentrated hydrochloric acid was converted into the corresponding amide:



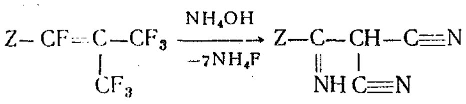
$$C_2H_5OCF{=}\underset{CF_3}{\underset{|}{C}}-CF_3 \xrightarrow{NH_3} C_2H_5O-\underset{NH}{\underset{\|}{C}}-\underset{CF_3}{\underset{|}{CH}}-CF_3 \xrightarrow[H^+]{H_2O} H_2N-\underset{O}{\underset{\|}{C}}-\underset{CF_3}{\underset{|}{CH}}-CF_3$$

Similarly, under the action of ammonia, 1-alkyl- and 1-aryl-heptafluoroisobutenes gave imines, which were then converted into the corresponding ketones:



$$R-CF{=}\underset{CF_3}{\underset{|}{C}}-CF_3 \xrightarrow{NH_3} R-\underset{NH}{\underset{\|}{C}}-\underset{CF_3}{\underset{|}{CH}}-CF_3 \xrightarrow[H^+]{H_2O} R-\underset{O}{\underset{\|}{C}}-\underset{CF_3}{\underset{|}{CH}}-CF_3$$

Heptafluoro-1-phenylisobutene (II) can be converted into hexafluoroisobutyrophenone by direct hydrolysis under the action of concentrated sulfuric acid. Concentrated aqueous ammonia acts on 1-substituted heptafluoroisobutenes with formation of compounds which do not contain fluorine:

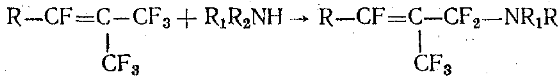


$$Z-CF{=}\underset{CF_3}{\underset{|}{C}}-CF_3 \xrightarrow[-7NH_4F]{NH_4OH} Z-\underset{NH}{\underset{\|}{C}}-\underset{C\equiv N}{\underset{|}{CH}}-C\equiv N$$

in which Z = OR, alkyl, or aryl.

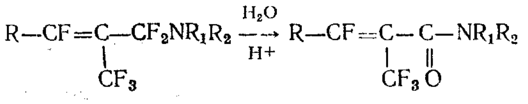
The reaction of 1-ethoxyheptafluoroisobutene with dialkylamines proceeds in just the same way as with anhydrous ammonia [1].

A quite different picture is observed in the reaction of secondary amines with 1-alkyl- and 1-aryl-heptafluorobutenes. Here reaction proceeds exclusively in accordance with Scheme 2:



$$R-CF{=}\underset{CF_3}{\underset{|}{C}}-CF_3 + R_1R_2NH \rightarrow R-CF{=}\underset{CF_3}{\underset{|}{C}}-CF_2-NR_1R_2$$

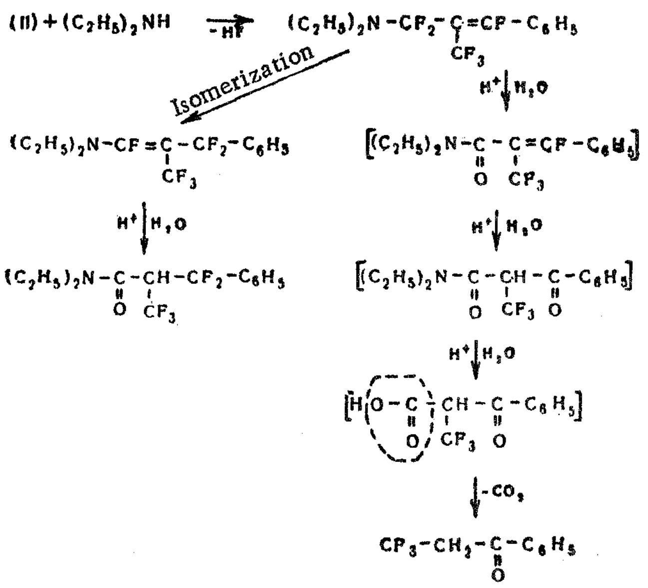
The hydrolysis of the tertiary amines formed (R = alkyl) proceeds smoothly with formation of amides of the corresponding α, β-unsaturated acids:



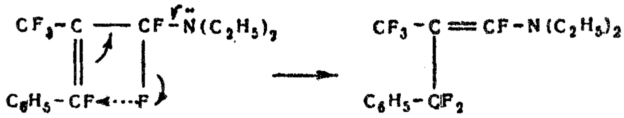
$$R-CF{=}\underset{CF_3}{\underset{|}{C}}-CF_2NR_1R_2 \xrightarrow[H^+]{H_2O} R-CF{=}\underset{CF_3}{\underset{|}{C}}-\underset{O}{\underset{\|}{C}}-NR_1R_2$$

When diethylamine reacts with (II), a fluorine atom of the trifluoromethyl group is again replaced, but according to thermographic analysis the reaction product is a mixture of two isomers melting at −64° and −92°.

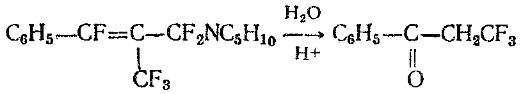
Hydrolysis of this mixture gives trifluoropropiophenone and N,N-diethyl-3,3-difluoro-3-phenyl-2-(trifluoromethyl) propionamide. The most probable scheme of transformations is as follows:



The mechanism of the isomerization is evidently analogous to that of the anionotropic rearrangement previously proposed by us for fluoropropenes [3]:

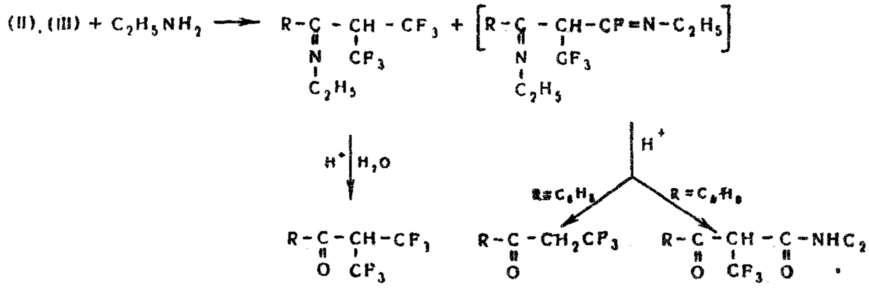


In the case of piperidine this rearrangement is not observed, and the acid hydrolysis of 1-[1,1,3-trifluoro-3-phenyl-2-(trifluoromethyl) allyl] piperidine leads only to 3,3,3-trifluoropropiophenone:



$$C_6H_5-CF=\underset{\substack{|\\ CF_3}}{C}-CF_2NC_5H_{10}\xrightarrow[H^+]{H_2O}C_6H_5-\underset{\substack{\|\\ O}}{C}-CH_2CF_3$$

In its reactions with 1-substituted heptafluoroisobutenes, ethylamine occupies a position intermediate between ammonia and dialkylamines; as well as replacement of a vinyl fluorine atom, the fluorine of a trifluoromethyl group is replaced, which is confirmed by the isolation from the hydrolyzate of trifluoropropiophenone in the case of (II) and of $C_2H_5NH-\underset{\substack{\|\\ O}}{C}-\underset{\substack{|\\ CF_3}}{CH}-\underset{\substack{\|\\ O}}{C}-C_4H_9$ in the case of 1-butylheptafluoroisobutene (III):



In order to compare the reactivities of 1-substituted heptafluoroisobutenes with those of the corresponding compounds of the unbranched propene series, pentafluoro-1-phenylpropene was prepared by the action of phenylmagnesium bromide on hexafluoropropene; it was found that this substance did not react with amines and ammonia, but reacted with concentrated sulfuric acid with formation of 2,3,3,3-tetrafluoropropiophenone.

EXPERIMENTAL

Heptafluoro-1-phenylisobutene (II).

A solution of 0.2 mole of phenylmagnesium bromide (31.4 g of C_6H_5Br and 5 g of Mg) was prepared in the usual way in 300 ml of dry ether and was cooled to 0° and stirred continuously while 30 g (0.15 mole) of (I) was introduced over a period of one hour. The reaction mixture was then left overnight at room temperature. On the next morning the ethereal solution was decanted from the resinous precipitates and carefully poured into a mixture of crushed ice and dilute hydrochloric acid. The ether layer was separated, and the aqueous layer was extracted with three 150-ml portions of ether; the ether layer was combined with the ether extracts, washed with sodium bicarbonate solution and then with water, and dried over calcium chloride. Solvent was distilled off, and distillation then gave 30 g (0.116 mole; 77% yield) of (II); b.p. 75.5-76.5° (45 mm); n_D^{20} 1.4275; d_4^{20} 1.3966; found MR 47.50; calculated $C_{10}H_5F_7F_4$ MR 45.29. λ_{max} 6.90; 6.76; 5.95 μ. Found: C 46.27; H 2.17%. $C_{10}H_5F_7$. Calculated: C 46.52; H 1.95%.

Hydrolysis of (II).

A mixture of 6.6 g (0.0256 mole) of (II), 10 ml of concentrated sulfuric acid, and 0.5 g of silica gel was heated at 80-100° for six hours with vigorous stirring. There was a vigorous evolution of hydrogen fluoride. When cool, the reaction mixture was extracted with methylene chloride (five 15-ml portions). The extract was washed with water and dried over magnesium sulfate. Solvent was distilled off, and the residue was vacuum-distilled. This gave 2.6 g (0.01 mole) of unchanged (II) (b.p. 75-78°; n_D^{20} 1.4280) and 1.7 g (42% on the olefin that reacted) of hexafluoroisobutyprophenone; m.p. 35.5-36° (from octane); λ_{max}: 6.29; 5.85 μ. Found: C 46.89; H 2.32; F 44.80%. $C_{10}F_6H_6O$. Calculated: C 46.88; H 2.36; 44.50%.

Oxidation of (II).

Over a period of one hour 10 g (0.039 mole) of (II) was added dropwise to a stirred mixture of 100 ml of water and 30 g of potassium permanganate at 35-40°. During the addition, carbon dioxide was continuously passed through the reaction mixture. The mixture was then stirred further for 12 hours. The reaction mixture was then cooled to 0°, and sulfur dioxide was passed until the solution was decolorized. The mixture was extracted with ether in a continuous extractor for three days. The ether extract was dried over magnesium sulfate. Ether was carefully distilled off, and the residue was vacuum-distilled. This gave 4.9 g (68%) of hexafluoroacetone hydrate; b.p. 49-50° (800 mm); n_D^{20} 1.3160. The literature [4] gives: b.p. 55-56° (80 mm); n_D^{20} 1.3179. From the residue remaining after distillation of the liquid part we obtained 4.7 g (99%) of crystals of m.p. 119° (from water). A mixture with benzoic acid melted without depression (m.p. 120°).

Pentafluoro-1-phenylpropene.

Hexafluoropropene (30 g; 0.2 mole) was passed into a continuously stirred solution of 0.3 mole of phenylmagnesium bromide (47.1 g of C_6H_5Br and 8 g of Mg) in 300 ml of ether at room temperature. The reaction mixture was treated in the usual way. Fractionation gave 17 g (0.082 mole; 42% yield) of pentafluoro-1-phenylpropene; b.p. 77-78° (65 mm); n_D^{20} 1.4482; d_4^{20} 1.3210; found MR 42.19, calculated for $C_9H_5F_5F_4$ MR 40.39. The literature [5] gives b.p. 148°. Found: C 52.11; H 2.45%. $C_9H_5F_5$. Calculated: C 52.43; H 2.42%.

2,3,3,3-Tetrafluoropropiophenone.

A mixture of 10 g of pentafluoro-1-phenylpropene, 10 ml of concentrated sulfuric acid, and 5 g of silica gel powder was heated at 125-135° for 3.5 hours. The reaction mixture was cooled, diluted with methylene chlorides, washed with water, and dried over magnesium sulfate. Solvent was distilled off, and the residue was vacuum-distilled. This gave 8.3 g (84%) of 2,3,3,3-tetrafluoropropiophenone; b.p. 41-42° (from hexane). Found: C 52.71; H 2.86; F 36.82%. $C_9H_6F_4O$. Calculated: C 52.43; H 2.93; F 36.87%.

The 2,4-dinitrophenylhydrazone had m.p. 172.5-173.5° (from alcohol). Found: N 14.72%. $C_{15}H_{10}F_4N_3O_4$. Calculated: N 14.50%.

1-2-Dibromopentafluoro-1-phenylpropane.

Pentafluoro-1-phenylpropene (5.9 g) was treated with excess of a solution of bromine in methylene chloride at 40°. This gave 7.6 g (74%) of 1,2-dibromopentafluoro-1-phenylpropane; b.p. 106-107° (22 mm); n_D^{20} 1.4993; d_4^{20} 1.9168; Found MR 55.43; calculated for $C_9H_5F_5Br_2F_3$ MR 56.39. Found: C 29.02; H 1.44%. $C_9H_5F_5Br_2$. Calculated: C 29.37; H 1.37%.

1-Butylheptafluoroisobutene.

With vigorous stirring and cooling to 0°, 20 g (0.1 mole) of (I) was introduced into a solution of 0.2 mole of butylmagnesium bromide in 30 ml of ether. After four hours the mixture was treated in the usual way. This gave 16.3 g (70%) of (III); b.p. 113-114° (750 mm); m.p. –70°; n_D^{20} 1.3390; d_4^{20} 1.2769; found MR 38.99; calculated for $C_8H_9F_7F$ MR 39.66; λ_{max} 5.88; 5.68 μ. Found: C 40.33; H 3.69%. $C_8H_9F_7$. Calculated C 40.34; H 3.81%.

Heptafluoro-1-styrylisobutene.

Excess of perfluoroisobutene was passed into a stirred solution of 0.1 mole of styrylmagnesium bromide (from 16.3 g of β-bromostyrene and 3 g of Mg) in 200 ml of ether at 0°. The mixture was then left for three days at room temperature. The ether solution was then separated from the resinous precipitate, either was distilled off, and the residue was vacuum-distilled. This gave 9.6 g (32%) of heptafluoro-1-styrylisobutene; b.p. 87-87.5° (12 mm); n_D^{20} 1.4852; d_4^{20} 1.3734). Found: C 50.54; H 2.46%. $C_{12}H_7F_7$. Calculated: C 50.71; H 2.48%.

1-Ethylheptafluoroisobutene.

With vigorous stirring and cooling to 0°, an excess of dry perfluoroisobutene was passed into a solution of 0.13 mole of ethylmagnesium bromide (from 14.2 g of C_2H_5Br and 4 g of Mg) in 150 ml of dibutyl ether. The mixture was left at room temperature for two days. The contents of the reaction flask were then poured into a mixture of dilute hydrochloric acid and ice. The aqueous layer was extracted with dibutyl ether, and the ether extracts were combined and dried over calcium chloride. A fraction of b.p. 44-135° was distilled from the dibutyl ether solution. Further fractionation of this through a column of 18-plate efficiency gave 15.3 g (56%) of 1-ethylheptafluoroisobutene; b.p. 73.5-74° (752 mm); n_D^{20} 1.3122; d_4^{20} 1.3548; found MR 30.08; $C_6H_5F_7F$; calculated MR 30.42. Found: C 34.36; H 2.28%. $C_6H_5F_7$. Calculated: 34.30; H 2.39%.

Heptafluoro-1-isopentylisobutene.

With stirring and cooling to 0°, 40 g (0.2 mole) of dry perfluoroisobutene was passed into a solution of 0.2 mole of isopentylmagnesium bromide (from 30.1 g of i-$C_5H_{11}Br$ and 5.2 g of Mg) in 150 ml of dry ether. After the usual treatment we obtained 27.8 g (55%) of heptafluoro-1-isopentylisobutene; b.p. 57° (58 mm); n_D^{20} 1.3500; d_4^{20} 1.2017; found MR 45.15; $C_9H_{11}F_7F$; calculated MR 44.27. Found: C 43.34; H 4.60%. $C_9H_{11}F_7$. Calculated: C 42.86; H 4.40%.

Reactions of Heptafluoro-1-phenylisobutene.

Imine of Hexafluoroisobutyprophenone [α-[2,2,2-trifluoro-1-(trifluoromethyl) ethyl]benzylidenimine]. Dry ammonia was passed for one hour into a solution of 14.1 g (0.054 mole) of (II) in 200 ml of dry ether cooled to 0° After one day the precipitate of NH_4F (2.45 g) was filtered off, ether was distilled off, and the residue was vacuum-distilled. This gave 10 g (72%) of the imine of hexafluoroisobutyprophenone, b.p. 74-75° (3 mm) and n_D^{20} 1.4600; a slightly yellowish liquid which decomposes when kept for a short time. Found: C 47.25; H 2.76; F 44.67%. $C_{10}H_7F_6N$. Calculated C 47.07; H 2.83; F 43.20%.

Hexafluoroisobutyrophenone. Concentrated hydrochloric acid (20 ml) was mixed with 5.6 g (0.022 mole) of the imine of hexafluoroisobutyrophenone. Heat was evolved and a precipitate formed. The mixture was boiled for 15 hours in a water bath and extracted with ether. The extract was dried, and ether was distilled off. The residue came over at 75-85° (11 mm). With cooling the substance crystallized. We obtained 4.5 g (80%) of hexafluoroisobutyrophenone, m.p. 35-36.5° (from octane). A mixture with a known sample melted without depression (m.p. 34°).

(α-Iminobenzyl) malononitrile. A mixture of 3.8 g (0.015 mole) of (II) and excess of aqueous ammonia was shaken for six hours. The crystals formed were filtered off and dried. We obtained 2.46 g (98%) of (α-iminobenzyl) malononitrile; m.p. 180-181° (from xylene); λ_{max}: 6.53; 6.33; 5.97; 4.49 μ. Found: C 70.90; H 4.04; N 24.94%. $C_{10}H_7N_3$. Calculated: C 71.00; H 4.17; N 24.83%.

The same compound was obtained by the action of excess of aqueous ammonia on the imine of hexafluoroisobutyrophenone.

Reaction of (II) with Diethylamine. A solution of 13 g (0.05 mole) of (II) in 30 ml of dry ether was added over a period of 20 minutes to a stirred solution of 17 g of diethylamine in 100 ml of ether. The reaction mixture was left overnight and then filtered from the precipitate of $(C_2H_5)_2$ NH · HF (3.9 g; 84% calculated for the replacement of one fluorine atom). The residue was vacuum-distilled. We obtained 14.2 g of slightly colored viscous liquid; b.p. 115-120° (4 mm); n_D^{20} 1.4790; λ_{max} 5.41; 5.97 μ; melting points of the components of the mixture, determined thermographically: from −63° to −67° and from −90° to −94°. Found: C 53.86; H 4.60; F 37.86%. $C_{14}H_{15}F_6NO$. Calculated: C 54.02; H 4.86; F 36.62%.

A mixture of 7.6 g of the freshly distilled substance and 15 ml of concentrated hydrochloric acid was heated in a water bath. The mixture was cooled and repeatedly extracted with ether. The ether solution was washed with water and dried over magnesium sulfate. Ether was distilled off, and the residue was vacuum-distilled. The bulk of the substance came over at 95-100° (5 mm); when cooled, the distillate crystallized. Recrystallization at −30° gave 3.2 g of 3,3,3-trifluoropropiophenone; m.p. 37-37.5° (from octane); λ_{max}: 6.25; 5.85 μ. Found: C 57.41; H 3.77; F 30.31%. $C_9H_7F_3O$. Calculated: C 57.45; H 3.75; F 30.29%.

The 2,4-dinitrophenylhydrazone had m.p. 190-191° (from alcohol). Found: C 48.79; H 2.98%. $C_{15}H_{11}N_4F_3O_4$. Calculated: C 48.92; H 3.01%.

Crystallization of the residue in the flask gave 0.8 g of N,N-diethyl-3,3-difluoro-3-phenyl-2-(trifluoromethyl propionamide; m.p. 95.5-96° (from octane); λ_{max}: 6.06 μ. Found: C 54.56; H 5.53; F 31.03; N 4.52%. $C_{14}H_{16}F_5ON$. Calculated: C 54.36; H 5.21; F 30.72; N 4.52%.

Treatment of an ethereal solution of 7.7 g of $C_{14}H_{15}F_6N$ with dilute hydrochloric acid at 0° gave 3.24 g of N,N-diethyl-3,3-difluoro-3-phenyl-2-(trifluoromethyl) propionamide, m.p. 95°, undepressed by admixture of a previously prepared sample (m.p. 95.5°). N,N-Diethyl-3,3-difluoro-3-phenyl-2-(trifluoromethyl) propionamide is stable to the action of concentrated hydrochloric acid.

1-[1,1,3-Trifluoro-3-phenyl-2-(trifluoromethyl) allyl] piperidine.

The substance (II) (17.3 g; 0.067 mole) was gradually added to piperidine (15 g) in dry ether (50 ml). To avoid a violent reaction the mixture was cooled externally with ice water. After one day the reaction mixture was treated with a mixture of dilute hydrochloric acid and ice. The ether layer was separated, the aqueous layer was extracted with ether, and the combined ether extracts were dried over magnesium sulfate. When ether was distilled off, the residue crystallized. We obtained 17.2 g (80%) of 1-[1,1,3-trifluoro-3-phenyl-2-(trifluoromethyl) allyl] piperidine, m.p. 79-81° (from octane). Found: C 55.85; h 4.65; F 35.60; N 4.32. $C_{15}H_{15}F_6N$. Calculated: C 55.73; H 4.68; F 35.25; N 4.32%.

A mixture of 8 g (0.0248 mole) of 1-[1,1,3-trifluoro-3-phenyl-2-(trifluoromethyl) allyl] piperidine and 15 ml of concentrated hydrochloric acid was heated at 60-70° for five hours. There was a vigorous evolution of carbon dioxide. The reaction mixture was diluted with water and extracted with ether, the ether extracts were dried with magnesium sulfate, ether was distilled off, and the residue was vacuum-distilled. We obtained 2.7 g (58%) of 3,3,3-trifluoropropiophenone, m.p. 36.5° (from octane). A mixture with a known sample melted without depression (m.p. 36°).

Reaction of (II) with Ethylamine.

In the course of 30 minutes, 5.75 g (0.1278 mole) of gaseous ethylamine was passed into a solution of 12 g (0.0426 mole) of (II) in 150 ml of dry ether cooled to 0°. There was a voluminous white precipitate of $C_2H_5NH_2$·HF. The mixture was left overnight. On the next day the precipitate was filtered off, ether was distilled off, and the residue was vacuum-distilled. We obtained 11 g of a fraction boiling over the range 59-84° (10 mm). Hydrolysis of this fraction with concentrated hydrochloric acid gave a semicrystalline mass, the fractional crystallization of which gave 4.2 g (35%) of hexafluoroisobutyrophenone, m.p. 35-36° (from octane). A mixture with a known sample melted without depression (m.p. 35°). Strong cooling of the mother liquor gave an oil, from which we obtained the 2,4-dinitrophenylhydrazone of 3,3,3-trifluoropropiophenone, m.p. 190-191° (from alcohol). A mixture with a known sample melted without depression (m.p. 190°).

Reactions of 1-Alkylheptafluoroisobutenes.

Imine of Butyl Hexafluoroisopropyl Ketone. Dry ammonia was passed for one hour into a solution of 16.7 g (0.07 mole) of (III) in 140 ml of dry ether cooled to 0°. On the next day the precipitate of NH_4F was filtered off. Ether was distilled from the filtrate, and the residue was vacuum-distilled. We obtained 10 g of the imine of butyl hexafluoroisopropyl ketone; b.p. 64° (11 mm); n_D^{20} 1.3840; d_4^{20} 1.2770; found MR 43.05; $C_8H_{11}F_6N_F$. Calculated MR 42.93. Found: C 40.91; H 4.71; F 48.87%. $C_8H_{11}NF_6$. Calculated: C 40.86; H 4.71; F 48.47%.

The benzoyl derivative had m.p. 106-107° (from aqueous alcohol). Found: C 52.59; H 4.44; F 34.30%. $C_{15}H_{15}F_6NO$. Calculated: C 53.10; H 4.45; F 33.60%.

Butyl Hexafluoroisopropyl Ketone. The imine of butyl hexafluoroisopropyl ketone (4.1 g; 0.0174 mole) was hydrolyzed by treatment with concentrated hydrochloric acid (7 ml) at 80° for three hours. The reaction mixture was extracted with ether, ether was distilled off, and the residue was vacuum-distilled. We obtained 3 g (72%) of butyl hexafluoroisopropyl ketone; b.p. 64-65° (52 mm); n_D^{20} 1.3465; d_4^{20} 1.2569; found MR 40.06; $C_8H_{10}F_6O$. Calculated MR 39.99; λ_{max} 5.75 μ. Found: C 40.69; H 4.32; F 48.35%. $C_8H_{10}F_6O$. Calculated: C 40.68; H 4.27; F 48.26%.

Imine of Valerylmalononitrile. The substance (III) (3.85 g; 0.016 mole) was treated with excess of aqueous ammonia. The mixture was shaken for one day. The crystals formed were filtered off. We obtained 1.83 g (75%) of the imine of valerylmalononitrile, m.p. 110-110.5° (from benzene); λ_{max} 6.49; 5.95; 4.44 μ. The substance was dissolved by 50% KOH solution and was reprecipitated on acidification. Found: C 64.58; H 7.48; N 28.35%. $C_8H_{11}N_3$. Calculated: C 64.41; H 7.43; N 28.35%. Analogously, from the corresponding olefins we obtained the imine of propionylmalononitrile in 32% yield; m.p. 164-165° (from xylene); found: C 59.71; H 5.86%. $C_6H_7N_3$. Calculated: C 59.49; H 5.82%; the imine of (4-methylvaleryl)malononitrile in 54% yield; m. p. 100-101° (from xylene); λ_{max} 6.45; 5.95; 4.48 μ. Found: C 66.59; H 8.04; N 25.96%; $C_9H_{13}N_3$. Calculated: C 66.23; H 8.03; N 25.73%.

Reaction of (III) with Diethylamine.

A solution of 22 g (0.32 mole) of diethylamine in 50 ml of dry ether was added with stirring to a solution of 19.3 g (0.08 mole) of (III) in 175 ml of dry ether in an apparatus protected from atmospheric moisture and carbon dioxide. The mixture was left for two days. The ethereal solution was then filtered from the precipitate of diethylamine hydrofluoride (6.97 g; 0.075 mole). Ether was distilled from the filtrate, and the residue was vacuum-fractionated. We obtained 16 g (68%) of N,N-diethyl-1,1,3-trifluoro-2-(trifluoromethyl)-2-heptenylamine, b.p. 100-101° (6.5 mm) and n_D^{20} 1.4293, a viscous liquid which decomposes when kept for a short time. Found: C 49.24; H 6.49%. $C_{12}H_{19}F_6N$. Calculated: C 49.47; H 6.57%.

The freshly distilled amine (2.6 g; 0.0093 mole) was mixed with dilute hydrochloric acid (10 ml) in a flask fitted with a reflux condenser. Heat was evolved. The mixture was left at room temperature for three days, diluted with 25 ml of water, and extracted with three 15-ml portions of ether. The ether extracts were washed with water and dried over magnesium sulfate. Ether was distilled off, and the residue was vacuum-fractionated. We obtained 1.6 g (57%) of N,N-diethyl-3-fluoro-2-(trifluoromethyl)-2-heptenamide; b.p. 110° (4 mm); n_D^{20} 1.4261; d_4^{20} 1.1298; λ_{max}: 5.99; 5.68 μ; found MR 61.28; $C_{12}H_{19}F_4NOF$. Calculated: MR 61.62. Found: C 53.53; H 7.07; N 5.50%. $C_{12}H_{19}F_4NO$. Calculated: C 53.52; H 7.11; N 5.19%.

The nuclear magnetic resonance spectrum of F^{19} consisted of two sharply defined resonance peaks with a ratio of amplitudes of 3 : 1, and the higher peak was in the region of absorption of the CF_3 group.

Reaction of (III) with Piperidine.

A solution of 25 g (0.22 mole) of piperidine in 20 ml of ether was added to a solution of 11.6 g (0.0487 mole) of (III) in 40 ml of ether. After a few minutes an exothermic reaction set in, and this was controlled by external cooling. On the next day the precipitate of piperidine hydrofluoride was filtered off (3.15 g; 0.3 mole) and the ether and most of the excess of piperidine were vacuum-distilled off. The viscous residue was treated with excess of dilute (1 : 1) hydrochloric acid. The mixture was left overnight, and the crystals formed were then filtered off. We obtained 10.3 g (75 %) of the piperidide of 3-fluoro-2-(trifluoromethyl)-2-heptenoic acid; m.p. 64.5-65° (from aqueous alcohol); λ_{max}: 6.04; 5.80 μ. Found: C 56.32; H 6.92; N 5.06; F 27.38%. $C_{13}H_{19}F_4NO$. Calculated: C 55.50; H 6.81; N 4.98; F 27.02%.

By an analogous procedure we obtained the following from the corresponding olefins: The piperidide of 3-fluoro-2-(trifluoromethyl)-2-pentenoic acid; m.p. 88-88.5° (from aqueous alcohol); λ_{max} 6.02; 5.80 μ; yield 64%. Found: C 52.13; H 5.90; F 30.38 N 5.88%. $C_{11}H_{15}F_4NO$. Calculated: C 52.17; H 5.97; F 30.01; N 5.53 %. The piperidide of 3-fluoro-2-(trifluoromethyl)-2-octenoic acid; m.p. 75-76° (from aqueous alcohol); λ_{max} 6.02; 5.80 μ; yield 69%. Found: C 56.97; H 7.14; F 25.77; N 4.74%. $C_{14}H_{21}F_4NO$. Calculated: C 56.97; H 7.17; F 25.73; N 4.74%.

Reaction of (III) with Ethylamine.

A solution of 12.1 g (0.051 mole) of (III) in 20 ml of dry ether was added over a period of 30 minutes to a cooled (to 0°) stirred solution of 11.5 g (0.25 mole) of ethylamine in 150 ml of dry ether. The mixture was left for three days. The precipitate of ethylamine hydrofluoride was filtered off, ether was distilled off, and the residue was vacuum-distilled. We obtained 3.5 g (26%) of the ethylimine of butyl hexafluoroisopropyl ketone, which was redistilled, and then had the following constants: b.p. 49-50° (9 mm); n_D^{20} 1.3715; d_4^{20} 1.1626; found: MR 51.40; $C_{10}H_{15}F_6N_F$. Calculated MR 52.34; Found: C 45.68; H 5.92; F 43.85%. $C_{10}H_{15}F_6N$. Calculated: C 45.62; H 5.74; F 49.31%.

The residue in the distillation flask was a straw-yellow thick mass with a pyridinelike odor. Its hydrolysis with concentrated hydrochloric acid gave 1.2 g of N-ethyl-3-oxo-2-(trifluoromethyl) heptanamide; m.p. 95-97° (from octane) λ_{max}: 5.75; 6.02; 6.41 μ. Found: C 49.90; H 6.69; F 23.86; N 5.89%. $C_{10}H_{16}F_3NO_2$. Calculated: C 50.20; H 6.74; F 23.82; N 5.85%.

Hydrolysis of the Ethylimine of Butyl Hexafluoroisopropyl Ketone.

A mixture of 4 g (0.01519 mole) of the ethylimine of butyl hexafluoroisopropyl ketone and 5 ml of concentrated hydrochloric acid was heated at 60° foi 30 minutes. The mixture was then diluted with water and repeatedly extracted with ether. The combined ether extracts were dried over magnesium sulfate. Ether was distilled off, and the residue was vacuum-distilled. We obtained 2.4 g (67%) of butyl hexafluoroisopropyl ketone [1,1,1-trifluoro-2-(trifluoromethyl)-3-heptanone], b.p. 62-64° (52 mm) and n_D^{20} 1.3470. The infrared absorption spectrum was identical with that of known butyl hexafluoroisopropyl ketone.

Reaction of Ethyl Perfluoroisobutenyl Ether with Ammonia.

Ethyl 3,3,3-Trifluoro-2-(trifluoromethyl) propionimidate. Dry ammonia was passed for one hour into a solution of 24.6 g (0.109 mole) of ethyl perfluoroisobutenyl ether in 200 ml of dry ether cooled to 0°. The mixture was left for one hour, the precipitate of ammonium fluoride was filtered off, ether was distilled off, and the residue was vacuum-distilled. We obtained 13.3 g (55%) of ethyl 3,3,3-trifluoro-2-(trifluoromethyl) propionimidate. After redistillation the substance had the following properties: b.p. 48° (111 mm); n_D^{20} 1.3348; d_4^{20} 1.3383; λ_{max} 5.97 μ; found MR 34.45; $C_6H_7F_6NO$. Calculated MR 35.05. Found: C 32.01; H 2.93; F 51.66%. $C_6H_7F_2NO$. Calculated: C 32.39; H 3.16; F 51.09%.

Hydrolysis of the imidic ester with concentrated hydrochloric acid led to 3,3,3-trifluoro-2-(trifluoromethyl) propionamide, m.p. 155-156° (from aqueous alcohol). A mixture with a known sample melted without depression (m.p. 155-156°). Treatment of the imidic ester with aqueous ammonia gave (ethoxyiminomethyl)malononitrile; m.p. 215-223° (decomp.; from water); λ_{max}: 4.54; 6.02; 6.41 μ. The literature [6] gives m.p. 219-220°. Found: C 52.19; H 5.14; N 30.65%. $C_6H_7N_3O$. Calculated: C 52,55; H 5.03; N 30.64%.

The same compound was obtained by the action of concentrated ammonia on ethyl perfluoroisobutenyl ether; m.p. 217-220° (from water). A mixture with a known sample melted without depression (m.p. 215-217°).

SUMMARY

1. A perfluoroisobutene in which the fluorine atom in the 1-position is replaced by an alkoxy, alkyl, or aryl group reacts with amines and ammonia in the 1- or 3-position; the position attacked is determined both by the structure of the fluoro olefin and the character of the attacking reagent.

2. The reaction of such substituted perfluoroisobutenes with excess of aqueous ammonia leads to the complete elimination of fluorine from the molecule and the formation of derivatives of malononitrile.

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