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DEHYDROFLUORINATION WITH TRIETHYLAMINE–BORON TRIFLUORIDE ADDUCT. NEW SYNTHESIS OF PERFLUOROMETHACRYLIC ACID DERIVATIVES AND RELATED COMPOUNDS

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SUMMARY

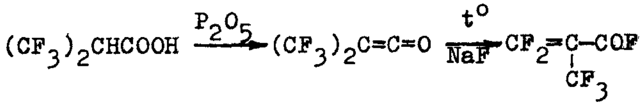
Adduct $(C_2H_5)_3N{\cdot}BF_3$ has proved to be a suitable dehydrofluorinating reagent for preparing highly reactive fluoroolefines through dehydrofluorination of corresponding monohydro derivatives. Its advantage over other dehydrofluorinating agents are demonstrated by the synthesis of a number of perfluoromethacrylic acid derivatives.

INTRODUCTION

Dehydrofluorination of hydroperfluoroalkanes and related compounds through the action of bases is a widespread method of synthesizing fluoro-organic compounds containing a C=C bond. However, the application of this method often involves difficulties which are associated with a high reactivity of the resulting unsaturated compound. The latter can react further with the reagent base; moreover, dehydrofluorination may at times be reversible in view of the fluoride anion readily adding to an electrophilic C=C bond. Perfluoromethacrylic acid (PFMA) derivatives are typical examples of such highly reactive compounds.

METHODS OF SYNTHESIZING PFMA DERIVATIVES

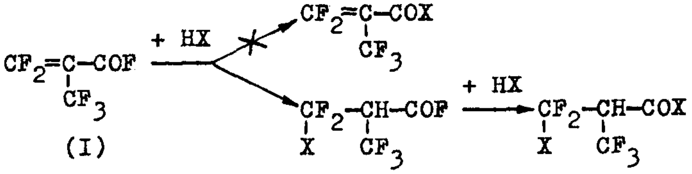
Until recently the possibilities of synthesizing PFMA derivatives were rather limited [*]. Perfluoromethacryloyl fluoride (I) may be conveniently prepared from available α-hydrohexafluoroisobutyric acid (HFIBA) (II); this acid is easily converted into bis(trifluoromethyl)ketene (III) [7,8] which may be isomerized into fluoride (I) [7,9] (cf. [10]).



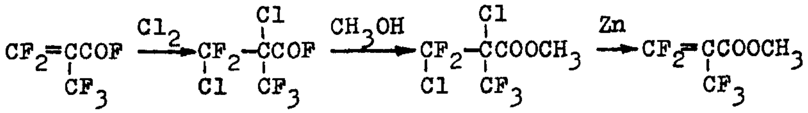
$$(CF_3)_2CHCOOH \xrightarrow{P_2O_5} (CF_3)_2C{=}C{=}O \xrightarrow[NaF]{t^o} CF_2{=}\underset{\displaystyle CF_3}{\underset{|}{C}}{-}COF$$

(II) (III) (I)

Unfortunately, it is impossible to prepare other PFMA derivatives directly from fluoride (I) since in reactions with nucleophiles the active C=C bond of the fluoride comes into play first and only then the fluorocarbonyl group (COF) enters into reaction [1].



PFMA derivatives can be prepared only through protecting the C=C double bond in (I) followed by the action with a nucleophile and removing the protective groups. Methyl perfluoromethacrylate (IVa) was prepared in that way, chlorination being used to protect the double bond [11].



$$CF_2{=}\underset{\displaystyle CF_3}{\underset{|}{C}}COF \xrightarrow{Cl_2} \underset{\displaystyle Cl}{\underset{|}{CF_2}}{-}\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle CF_3}{\underset{|}{C}}}}COF \xrightarrow{CH_3OH} \underset{\displaystyle Cl}{\underset{|}{CF_2}}{-}\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle CF_3}{\underset{|}{C}}}}COOCH_3 \xrightarrow{Zn} CF_2{=}\underset{\displaystyle CF_3}{\underset{|}{C}}COOCH_3$$

(I) (IVa)

Not long ago PFMA derivatives were found to form on

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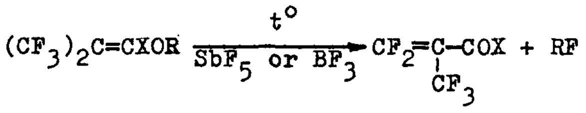
[*] These derivatives are interesting since they may be used for synthesizing various fluoro-organic compounds [1 - 5] and also as being potential monomers [1,6].

electrophilic elimination of alkyl fluorides from substituted alkoxyperfluoroisobutylenes (V) [12,13] .



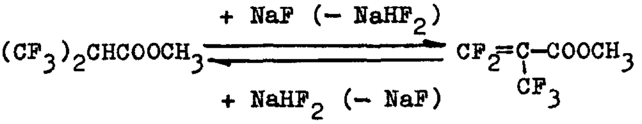
$$(CF_3)_2C{=}CXOR \xrightarrow[SbF_5\ \text{or}\ BF_3]{t^o} CF_2{=}\underset{CF_3}{C}{-}COX + RF$$

(V) X = F (I)
OR (IV)
NR_2 (VII)

This method allows preparing pure alkyl perfluoromethacrylates (IV) and N,N-dialkyl-perfluoromethacrylamides (VI) with high yields. However, a weak point of this method is that sometimes the starting ethers (V) are not sufficiently available.

DEHYDROFLUORINATION OF HFIBA DERIVATIVES

Dehydrofluorination of available HFIBA derivatives at first sight seems to be the most convenient way of preparing PFMA derivatives. Yet, the so far reported attempts to carry out this reaction failed to give good results. Thermal dehydrofluorination of methyl ester (VIIa) over NaF yielded a mixture of PFMA ester (IVa) and the starting saturated ester (VIIa), which is difficult to separate [1]*. This can apparently be accounted for by the fact that dehydrofluorination is reversible because of an exceptionally high reactivity of ester (IVa) with respect to the nucleophilic attack.



$$(CF_3)_2CHCOOCH_3 \underset{+\ NaHF_2\ (-\ NaF)}{\overset{+\ NaF\ (-\ NaHF_2)}{\rightleftarrows}} CF_2{=}\underset{CF_3}{C}{-}COOCH_3$$

(VIIa) (IVa)

An original way of dehydrofluorination in the presence of tertiary amine and acyl chloride [14] proved to be of no

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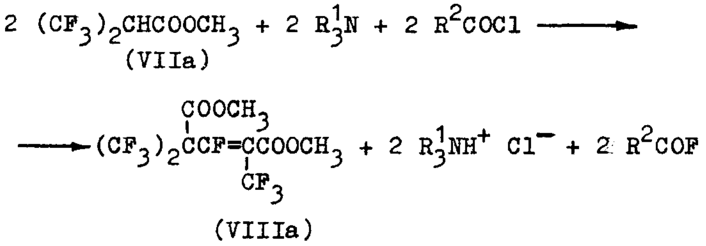
[*] Similar reaction of fluoride $(CF_3)_2CHCOF$ gave a mixture of unsaturated fluoride (I) and ketene (III) [1].

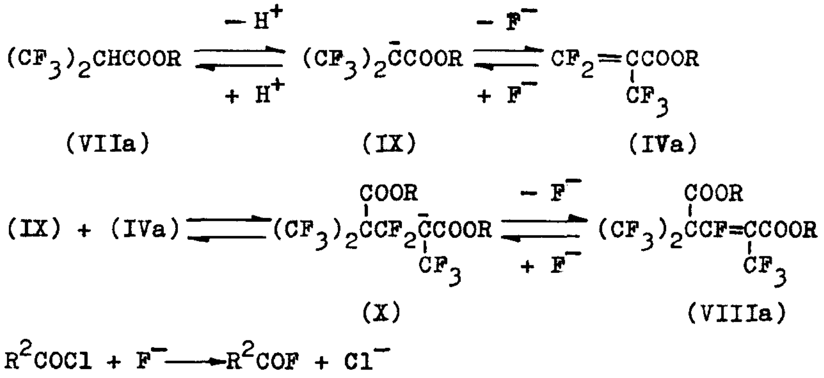
success in the case of HFIBA ester (VIIa); this reaction resulted in "dimeric" ester (VIIIa) rather than in alkyl perfluoromethacrylate (IVa) [15].



$$\underset{(VIIa)}{2\,(CF_3)_2CHCOOCH_3} + 2\,R^1_3N + 2\,R^2COCl \longrightarrow$$

$$\longrightarrow \underset{(VIIIa)}{(CF_3)_2\overset{COOCH_3}{\overset{|}{C}}CF{=}\underset{CF_3}{\underset{|}{C}}COOCH_3} + 2\,R^1_3NH^+\,Cl^- + 2\,R^2COF$$

Evidently, dehydrofluorination conducted in such a manner gives carbanion (IX) as an intermediate; elimination of the F^- anion from the carbanion leads to methyl perfluoromethacrylate (IVa) which immediately reacts with (IX), giving rise to carbanion (X); the latter turns into diester (VIIIa) owing to the elimination of the F^- anion; the whole of the F^- anion being formed reacts irreversibly with acyl chloride.



$$\underset{(VIIa)}{(CF_3)_2CHCOOR} \underset{+\,H^+}{\overset{-\,H^+}{\rightleftharpoons}} \underset{(IX)}{(CF_3)_2\bar{C}COOR} \underset{+\,F^-}{\overset{-\,F^-}{\rightleftharpoons}} \underset{(IVa)}{CF_2{=}\underset{CF_3}{\underset{|}{C}}COOR}$$

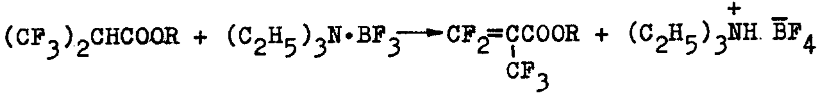
$$(IX) + (IVa) \rightleftharpoons \underset{(X)}{(CF_3)_2\overset{COOR}{\overset{|}{C}}CF_2\underset{CF_3}{\underset{|}{\bar{C}}}COOR} \underset{+\,F^-}{\overset{-\,F^-}{\rightleftharpoons}} \underset{(VIIIa)}{(CF_3)_2\overset{COOR}{\overset{|}{C}}CF{=}\underset{CF_3}{\underset{|}{C}}COOR}$$

$$R^2COCl + F^- \longrightarrow R^2COF + Cl^-$$

Thus, for successful obtaining of PFMA derivatives through dehydrofluorination of HFIBA derivatives at least two conditions are necessary: (1) the F^- anion must be tied up irreversibly; (2) accumulation of an intermediate carbanion such as (IX) should be avoided since the latter is able to react with PFMA derivative and give a "dimeric" product. One could suppose that adducts of tertiary amines with Lewis acids would be suitable reagents for dehydrofluorination[*].Low nucleophilicity of such adducts would lead to a fairly slow heterolysis of the C–H bond in the starting HFIBA derivative. If one selects a suitable Lewis acid with a considerable affinity to the F^- anion, one can anticipate that the carbanion will not be accumulated in the mixture and formation of "dimeric" product will be avoided.

RESULTS AND DISCUSSION

PFMA derivatives turned out to be easily obtainable from corresponding HFIBA derivatives through the action of triethylamine–boron trifluoride adduct [the principal possibility of utilizing $(C_2H_5)_3N\cdot BF_3$ for dehydrofluorination was found by N.B. Kazmina and G.S. Krasnikova who synthesized $CF_2{=}C(CF_3)C(CF_3){=}CF_2$ from $(CF_3)_2CHCH(CF_3)_2$]. This method afforded high yields of alkyl perfluoromethacrylates (IV) from esters (VII) as well as of N,N-dialkyl-perfluoromethacrylamides (VI) from amides (XI) (cf. [17]).

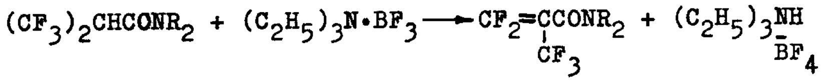


$$(CF_3)_2CHCOOR + (C_2H_5)_3N\cdot BF_3 \longrightarrow CF_2{=}\underset{CF_3}{\underset{|}{C}}COOR + (C_2H_5)_3\overset{+}{N}H\ \overset{-}{B}F_4$$

(VII) a: R = CH_3 (IV)

b: R = C_2H_5

c: R = C_6H_5



$$(CF_3)_2CHCONR_2 + (C_2H_5)_3N\cdot BF_3 \longrightarrow CF_2{=}\underset{CF_3}{\underset{|}{C}}CONR_2 + (C_2H_5)_3\overset{+}{N}H\ \overset{-}{B}F_4$$

(XI) a: R = CH_3 (VI)

b: R = C_2H_5

The reaction is, evidently, irreversible under the conditions we have chosen; therefore, if the time of interaction is sufficiently long, the reaction products contain no starting materials as impurities. This is an important advantage of the method proposed here over that of thermal dehydrofluorination [1]. "Dimers" usually do not arise in the reac-

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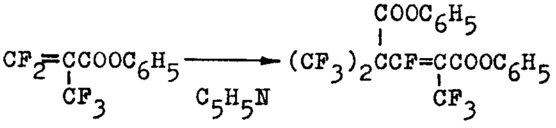
*Adduct $(CH_3)_3N\cdot SiF_4$ was used for dehydrofluorination of $CF_3CHFCOF$ into $CF_3CF{=}C{=}O$ [16].

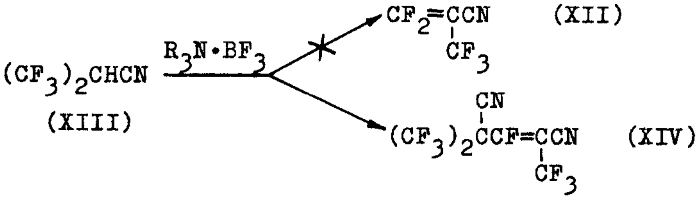
tions. However, the product of dehydrofluorination of phenyl ester (VIIc), phenyl perfluoromethacrylate (IVc), is sometimes dimerized "spontaneously" into diester (VIIIb), perhaps owing to the presence of some impurities. The dimerization takes place through the action of catalytic amounts of pyridine as well.



$$CF_2{=}C(CF_3)COOC_6H_5 \xrightarrow[C_5H_5N]{} (CF_3)_2C(COOC_6H_5)CF{=}C(CF_3)COOC_6H_5$$

(IVc) (VIIIb)

The proposed method is of no use for the synthesis of perfluoromethacrylonitrile (XII); dehydrofluorination of α-hydrohexafluoroisobutyronitrile (XIII) leads to "dimeric" product (XIV) exclusively.



$$(CF_3)_2CHCN \xrightarrow{R_3N\cdot BF_3} CF_2{=}C(CF_3)CN \;\text{(XII)}\quad (CF_3)_2C(CN)CF{=}C(CF_3)CN \;\text{(XIV)}$$

(XIII)

In case of such a strong carbon acid as nitrile (XIII) the equilibrium of C—H bond heterolysis is greatly shifted to the right (cf. [18]), this resulting in sufficient amounts of a carbanion which can react with unsaturated nitrile (XII) to give dinitrile (XIV)*. The same results are obtained when using a less basic pyridine—boron trifluoride adduct.

Dehydrofluorination through the action of $(C_2H_5)_3N\cdot BF_3$ may also be used in case of other compounds containing $(CF_3)_2CH$ group. By means of this reaction α-hydrohexafluoroisopropyl phenyl ketone (XV) has been turned into pentafluoroisopropenyl phenyl ketone (XVI) and N-phenylimido-α-hydrohexafluoroisobutyroyl fluoride (XVII) into bis(trifluoromethyl)-ketene N-phenylimine (XVIII).

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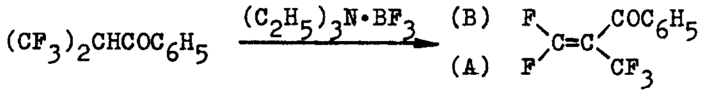
* It may also be essential here that nitrile (XII) is especially reactive with regard to nucleophiles.



(XV) (XVI)

$$(CF_3)_2CHCF{=}NC_6H_5 \xrightarrow{(C_2H_5)_3N\cdot BF_3} (CF_3)_2C{=}C{=}NC_6H_5$$

(XVII) (XVIII)

Preliminary experiments showed that dehydrofluorination of N,N-dimethyl-perfluoromethacrylamide (XIa) through the action of $(C_2H_5)_3N\cdot BF_3$ is accelerated in the presence of triethylamine and slowed down in the presence of boron trifluoride etherate. This fact, evidently, indicates that heterolysis of C–H bond is the slowest stage which determines the rate of the entire dehydrofluorination process.

Preparation of allenes (XIX) by dehydrofluorination of dialkyl fluoroalkylidenemalonates (XX) is one more example of using adduct $(C_2H_5)_3N\cdot BF_3$. These esters (XX) are obtained in condensation reaction of perfluoroisobutylene with dialkyl malonates, adduct $(C_2H_5)_3N\cdot BF_3$ catalyzing this reaction as well [19].

$$(CF_3)_2C{=}CF_2 + CH_2(COOR)_2 \xrightarrow{(C_2H_5)_3N\cdot BF_3} (CF_3)_2CHCF{=}C(COOR)_2$$

(XX)

$$\xrightarrow{(C_2H_5)_3N\cdot BF_3} (CF_3)_2C{=}C{=}C(COOR)_2$$

(XIX)

It should be noted in conclusion that the possibilities of synthesizing unsaturated compounds through the use of adduct $(C_2H_5)_3N\cdot BF_3$ are by no means limited to the examples considered in the present communication.

EXPERIMENTAL

^1H NMR spectra have been recorded on a "Perkin-Elmer R-12" spectrometer at 60 MHz; ^{19}F NMR spectra have been recorded on a "Hitachi" instrument at 56.46 MHz; IR spectra have been recorded in a thin layer or in KBr pellets on an "UR-20" spectrometer; and mass spectra have been recorded on a "Varian-MAT CH-8" mass spectrometer at an ionizing energy of 70 eV. The IR spectra have been obtained by L.P.Volkova and the mass spectra by E.I. Mysov. Chemical shifts in the NMR spectra are given in ppm from $(CH_3)_4Si$ (for ^1H) or CF_3COOH (for ^{19}F) as external standards. Stretching frequencies in the IR spectra are expressed in cm^{-1}. For the mass spectra m/e values, relative abundance and supposed ion composition (for most intensive signals) are presented.

Methyl perfluoromethacrylate (IVa)

A mixture consisting of $(C_2H_5)_3N{\cdot}BF_3$ [20] (11.73 g) and methyl α-hydrohexafluoroisobutyrate (VIIa) [1,21] (9.88 g) was refluxed for 2 h. After cooling, distillation at room temperature in vacuo (3 mmHg) into a trap (−78°) gave 7.25 g (81%) of (IVa) containing about 98% of the desired substance and about 2% of the starting material (VIIa) (GLC). B.p. 92 - 94°, n_D^{20} 1.3390. As reported in the literature, b.p. is 90 - 92° [11] or 94 - 95° [12]; n_D^{20} is 1.3288 [11]. The product is identical with an authentic sample of (IVa) [12] (GLC, ^{19}F NMR spectrum).

Ethyl perfluoromethacrylate (IVb)

In a manner similar to that described above, reaction of ethyl α-hydrohexafluoroisobutyrate (VIIb) [21] (7.00 g) with $(C_2H_5)_3N{\cdot}BF_3$ (7.16 g) yielded ester (IVb) (5.42 g, 85%) containing about 2% of the starting ester (VIIb). B.p. 107 - 109°. B.p., as reported in Ref. [12] , is 106 - 107°. The product is identical with an authentic sample of (IVb) [12] (GLC, ^{19}F NMR spectrum).

Phenyl α-hydrohexafluoroisobutyrate (VIIc)

Bis(trifluoromethyl)ketene (III) [8] (~105 g) was introduced under cooling into a mixture consisting of phenol (38.84 g) and absolute ether (110 ml); distillation gave 82.57 g (74%) of ester (VIIc) (nc), b.p. 82 - 83°/20 mmHg. Analysis: Found: C, 43.83; H, 2.06; F, 41.67%. $C_{10}H_6F_6O_2$ requires C, 44.11; H, 2.20; F, 41.81%.

^{1}H NMR spectrum: δ (CH), 3.76 (septet); δ (C_6H_5), 6.6 - 7.1 (multiplet); J(CH—CF_3), 7.4 Hz. ^{19}F NMR spectrum: a doublet at −13.2 (CF_3); J(CF_3—CH), 7.8 Hz.

Phenyl perfluoromethacrylate (IVc)

A mixture consisting of phenyl α-hydrohexafluoroisobutyrate (VIIc) (5.62 g), $(C_2H_5)_3N{\cdot}BF_3$ (4.91 g) and absolute ether (4 ml) was heated in a sealed tube at 70° for 10 h. The precipitate was filtered off and washed with absolute ether; distillation of the filtrate gave 1.44 g (28%) of ester (IVc) (nc), b.p. 52 - 55°/4 mmHg, 76°/11 mmHg. Analysis: Found: C, 47.18; H, 1.87; F, 38.08%. $C_{10}H_5F_5O_2$ requires C, 47.62; H, 1.98; F, 37.69%.

^{1}H NMR spectrum: δ(C_6H_5), ~6.6 (multiplet). ^{19}F NMR spectrum: complicated multiplet at −20 to −23 (CF_3, CF_2). IR spectrum: 1720 (C=O), 1760 (C=C). Mass spectrum: 252, 12%, M^+; 224, 6%, M^+ − CO; 159, 100%, M^+ − C_6H_5O.

Phenyl 4-carbophenoxy-2,4-bis(trifluoromethyl)perfluoro-2-pentenoate

(a) A mixture consisting of phenyl α-hydrohexafluoroisobutyrate (VIIc) (7.15 g) and $(C_2H_5)_3N{\cdot}BF_3$ (7.76 g) was heated at 100 - 110° for 3.5 h, then an extra amount (3.56 g) of $(C_2H_5)_3N{\cdot}BF_3$ was added and the mixture was heated at 100 - 110° for another 2.5 h. Then it was cooled and treated with absolute ether; the precipitate was filtered off and washed with absolute ether. Distillation of the filtrate gave 6.48 g of crude perfluoromethacrylate (IVc), b.p. 70 - 79°/8 mmHg, which changed spontaneously into "dimer" (VIIIb) in about ten minutes (crystallizing while growing warm). Repeated distillation gave a pure sample of diester (VIIIb) (nc), b.p. 155 - 158°/8 mmHg, m.p. 82 - 84°. Analysis: Found: C, 47.63; H, 2.05; F, 37.76%. $C_{20}H_{10}F_{10}O_4$ requires C, 47.62; H, 1.98; F, 37.69%.

^{1}H NMR spectrum (in CCl_4): δ (C_6H_5), 6.9 - 7.4 (multiplet). ^{19}F NMR spectrum (in ether): a doublet at −13.7 [$(CF_3)_2C$], a doublet at −18.8 ($CF_3C=$), and a multiplet at +11.2 (CF=);

J[CF–$(CF_3)_2C$], 12.9 Hz; J(CF–CF_3C=), 23.4 Hz. IR spectrum: 1680 (C=C), 1750 (C=O), 1770 (C=O). Mass spectrum: 504, 1%, M^+; 411, 14%, $M^+ - C_6H_5O$; 77, 100%, $C_6H_5{}^+$.

(b) One drop of pyridine was added to 0.2 g of phenyl perfluoromethacrylate (IVc). The whole mixture grew solid in a few days, ester (IVc) being found to have turned totally into "dimer" (VIIIb) (^{19}F NMR spectrum of ether solution).

N,N-Diethyl-α-hydrohexafluoroisobutyramide (XIb)

A solution consisting of $(C_2H_5)_2NH$ (200 g) in absolute ether (500 ml) was placed into a three-necked flask fitted with a stirrer, a reflux condenser (–78°) and a gas inlet tube. Crude perfluoroisobutylene (275 g) containing about 85% of pure $(CF_3)_2C=CF_2$ was passed over the surface of the solution with stirring and cooling (~–5°). On completion of the passing, a Liebig condenser was substituted for the reflux one and volatile products (b.p. up to 30°) were distilled off from the mixture. After that the Liebig condenser was replaced by a water-cooled reflux one and water was added to the residue to dissolution of the solid; subsequently dilute (15%) hydrochloric acid was carefully added to the mixture with vigorous stirring to bring the pH value down to 1. An exothermic reaction being over, the mixture was stirred for another 4 h; the organic layer was separated, washed with water, and dried over $MgSO_4$. After removal of the ether the residue was distilled *in vacuo* using an air-cooled condenser. This gave 244 g (~83%) of amide (XIb), b.p. 77 - 78°/5 mmHg, m.p. 51.5- - 52°. M.p., as reported in Ref. [21], is 51 - 51.5° (from heptane).

^{19}NMR spectrum (in CH_3CN): a doublet at –13.7 (CF_3); J(CF_3–CH), 7.7 Hz.

N,N-Dimethyl-perfluoromethacrylamide (VIa)

A mixture consisting of $(C_2H_5)_3N \cdot BF_3$ (109.4 g) and N,N-dimethyl-α-hydrohexafluoroisobutyramide (XIa) [22] (117.0 g) was heated at 145 - 150° for 3.5 h, cooled and treated with absolute ether. The solid was filtered off and washed with absolute ether. Distillation of the filtrate gave 91.1 g (85%) of amide (VIa), b.p. 61 - 62°/17 mmHg. B.p., as reported in Ref. [12], is 78 - 80°/39 mmHg, or 40 - 41°/5 mmHg. The product is identical with an authentic sample of (VIa) [12] (^{19}F NMR spectrum).

N,N-Diethyl-perfluoromethacrylamide (VIb)

In a manner similar to that described above, reaction of N,N-diethyl-α-hydrohexafluoroisobutyramide (XIb) (38.42 g) with $(C_2H_5)_3N{\cdot}BF_3$ (34.81 g) at 150 - 160° yielded amide (VIb) (27.10 g, 76%), b.p. 52 - 53°/6 mmHg. B.p., as reported in Ref. [12], is 75 - 76°/12 mmHg. The product is identical with an authentic sample of (VIb) [12] (^{19}F NMR spectrum).

4-Cyano-2,4-bis(trifluoromethyl)perfluoro-2-pentenonitrile (XIV)

α-Hydrohexafluoroisobutyronitrile (XIII) [21] (3.90 g) was carefully added dropwise to $(C_2H_5)_3N{\cdot}BF_3$ (6.17 g). The mixture was heated on a steam bath for 1 h, then cooled; the volatile product was distilled in vacuo at 20° into a trap (−78°). This gave 2.98 g (43%) of dinitrile (XIV) (nc), b.p. 116 - 118°, n_D^{20} 1.3295. Analysis: Found: C, 30.44; F, 60.45; N, 8.18%. $C_8F_{10}N_2$ requires C, 30.60; F, 60.48; N, 8.92%.

^{19}F NMR spectrum: a doublet at −12.1 [$(CF_3)_2C$], a doublet at −17.1 ($CF_3C{=}$), and a multiplet at +5.7 ($CF{=}$); J[$CF{-}(CF_3)_2C$], 12.0 Hz; J($CF{-}CF_3C{=}$), 22.2 Hz. IR spectrum: 1670 (C=C), 2270 (C≡N).

"Dimer" (XIV) was also produced when using $C_5H_5N{\cdot}BF_3$ [23] instead of $(C_2H_5)_3N{\cdot}BF_3$.

Pentafluoroisopropenyl phenyl ketone (XVI)

A mixture consisting of α-hydrohexafluoroisopropyl phenyl ketone (XV) [24] (4.90 g), $(C_2H_5)_3N{\cdot}BF_3$ (4.33 g), $(C_2H_5)_2O{\cdot}BF_3$ (several drops), and absolute ether (4.5 ml) was refluxed for

5.5 h and then heated in a sealed tube at about 100° for 3 h. Distillation of the filtrate gave 1.88 g (42%) of ketone (XVI) (nc), b.p. 83 - 84°/20 mmHg. Analysis: Found: C, 50.47; H, 1.92; F, 39.88%. $C_{10}H_5F_5O$ requires C, 50.84; H, 2.11; F, 40.25%.

^1H NMR spectrum: δ (C_6H_5), 6.7 - 7.1 and 7.3 - 7.6 (two multiplets). ^{19}F NMR spectrum: a quartet at −8.3 [CF(A)], a quartet at −10.5 [CF(B)], and a doublet of doublets at −20.2 (CF_3); J [CF_3—CF(A)], 18.3 Hz; J [CF_3—CF(B)], 10.6 Hz; J[F(A)—F(B)], 0. IR spectrum: 1680 (C=O), 1740 (C=C). Mass spectrum: 236, 19%, M^+; 159, 10%, $M^+ - C_6H_5$; 105, 100%, $C_6H_5CO^+$.

With a catalytic quantity of $(C_2H_5)_3N$ ketone (XVI) is readily converted into a mixture of unidentified products.

Bis(trifluoromethyl)ketene N-phenylimine (XVIII)

A mixture consisting of N-phenylimido-α-hydrohexafluoroisobutyroyl fluoride (XVII) [25] (7.85 g), $(C_2H_5)_3N{\cdot}BF_3$ (4.91 g), and absolute ether (4 ml) was heated to boiling, then cooled, and kept for a few days at about 20°. The precipitate was filtered off and washed with absolute ether. Distillation of the filtrate gave 6.02 g (83%) of imine (XVIII), b.p. 69 - - 70°/14 mmHg, n_D^{20} 1.4450. As reported in Ref. [25], b.p. is 70 - 71°/14 mmHg, and n_D^{20} is 1.4462. The product is identical with an authentic sample of (XVIII) [25] (GLC).

The effect of adding $(C_2H_5)_3N$ or $(C_2H_5)_2O{\cdot}BF_3$ on the dehydrofluorination rate of N,N-dimethyl-α-hydrohexafluoroisobutyramide (XIa) under the action of $(C_2H_5)_3N{\cdot}BF_3$

A mixture consisting of amide (XIa) (0.595 g), $(C_2H_5)_3N{\cdot}BF_3$ (0.636 g) and a few milliliters of absolute ether was divided into three equal parts: samples (a), (b), and (c). Sample (b) was treated with a few drops of $(C_2H_5)_3N$, and sample (c) with a few drops of $(C_2H_5)_2O{\cdot}BF_3$. The three samples were heated in sealed tubes at 90 - 95° for 2 h, then

^{19}F NMR spectra were recorded. It was found that sample (a) contained the starting amide (XIa) with a small admixture of N,N-dimethyl-perfluoromethacrylamide (VIa); in sample (b) starting amide (XIa) totally turned into amide (VIa); sample (c) consisted of solution of almost pure amide (XIa) containing no amide (VIa). Further heating (100 - 120°) resulted in that the amounts of unsaturated amide (VIa) in samples (a) and (c) gradually increased [this increase being more rapid in (a) than in (c)].

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