FLUORINE-CONTAINING HETEROCUMULENES.

COMMUNICATION 22.* SYNTHESIS AND REACTIONS OF FLUORINE-CONTAINING N-ACYLIMIDOYL FLUORIDES

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Perfluoro-tert-butyl anion, produced from perfluoroisobutylene (PFIB) and CsF, alkylates α -chlorohexafluoroisopropyl [2] and perfluoroisopropyl isocyanates [3] to form a stable anion (I). It was found that a stable anion (II) is also formed by perfluoropropyl isocyanate with PFIB in the presence of CsF

$$R_{F}-N=C=O+CF_{2}=C(CF_{3})_{2} \xrightarrow{C_{S}F} R_{F}-N=C \xrightarrow{O} C(CF_{3})_{3}$$

$$R_{F}=CF(CF_{3})_{2} \text{ (I); } n-C_{3}F_{7} \text{ (II).}$$

Like anion (I), anion (II) is stable at 20°C, but on heating to >100°C it decomposes, mainly into the starting products.⁺ The action of BF_3 etherate on anion (II) leads to splitting of ion F⁻ and the formation of a mixture of imidoyl chloride (III) and isocyanate (IV). The formation of isocyanate (IV) in this reaction and the ratio of products depend on the temperature. At -30°C, only imidoyl fluoride (III) is formed. Increase in temperature from 20 to 50°C decreases the imidoyl:isocyanate ratio from 3:1 to 3:2, while further increase in temperature lowers the overall yield of the products because of the decomposition of anion (II) into the starting components. In contrast to anion (II), with BF_3 etherate anion (I) gives only hexafluoroacetone perfluoropivaloylimine at both 0°C [2, 3] and 50°C. It is clear that anion (II) is present in equilibrium with an isomeric anion (V), formed as the result of migration of the perfluoro-tert-butyl group from the carbonyl C atom to the "imidoyl halide" C-atom; this transformation probably includes reversible dissociation of anions (II) and (V), with splitting of the perfluoro-tert-butyl anion to form perfluoropropyl isocyanate or N-fluorocarbonylperfluoropropionylimidoyl fluoride



*For Communication 21, see [1]. +With alcohol, anion (II) gives urethane (VI) and monohydroperfluoroisobutane already at 20°C



It was thus assumed that PFIB does not react with perfluoropropyl isocyanate in the presence of CsF [4].

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The position of the equilibrium is shifted in the direction of anion (II). This is confirmed by analysis of the ¹⁹F NMR spectrum of the reaction mixture containing signals of anion (II) only, and also by the formation of this anion by the action of CsF in diglyme on imidoyl fluoride (III) and on isocyanate (IV).

The addition of perfluoro-tert-butyl anion to perfluoropropyl isocyanate, followed by treatment with BF_3 etherate is thus an available method of synthesis of perfluoroacylimidoyl fluoride (III). We synthesized another two representatives of the little studied class of N-acylimidoyl halides by another scheme, i.e., condensation of PFIB with N-chloro- and N-trimethylsilylacetamides



In the reaction of PFIB with N-chloroacetamide, not only N-acetylimidoyl fluoride (VII), but also an addition product (VIII) is formed, which was isolated after hydrolysis from the reaction mixture in the form of an amide (IX) (the mechanism of these reactions is discussed in [5]). By the action of trimethylsilylacetamide on PFIB, imidoyl fluoride (X) was formed. It should be noted that imidoyl fluoride (X) cannot be obtained in the reaction of PFIB with acetamide. In this case, the ambidentate amide reacts exclusively as an O-nucleophile [6].

Perfluoroimidoyl fluoride (III) readily enters 1,4-cycloaddition reactions with nitriles and carbonyl compounds to form oxadiazines (XI) and dioxazines (XII). In this respect, imidoyl fluoride (III) behaves analogously to acylimines of fluoroketones [2, 7, 8]



Dioxazines (XII) are thermally unstable compounds, which readily decompose into the starting materials. Dioxazine (XIIa) can be isolated by distillation together with a small admixture of benzaldehyde, but the formation of dioxazine (XIIb) was confirmed only spectrally, since on heating it decomposes completely. In contrast to perfluoroimidoyl fluoride (III), N-acetylimidoyl fluorides do not enter cycloaddition reactions. Thus, α -chloroimidoyl fluoride (VII) does not react with MeCN and PhCHO, even on prolonged heating, while α -hydroimidoyl fluoride (X) with ketene gives a substituted imide of acetic acid (XIII) and not a cycloadduct.

Perfluoro isocyanate (IV) also does not enter into cycloaddition reactions with nitriles and carbonyl compounds, so that the isomers (III) and (IV) can be readily separated by removing imidoyl fluoride (III) from the mixture by its cycloaddition to acetophenone. The ready dissociation of the cycloadduct after distillation of isocyanate (IV) leads to the regeneration of imidoyl fluoride (III). The structure of isocyanate (IV) is confirmed by reaction with alcohol, leading to addition product (XIV), which is readily dehydrofluorinated into N-carboethoxyimine of a perfluoroketone (XV)



EXPERIMENTAL

The ¹H and ¹⁹F NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer (¹H, 90 MHz, ¹⁹F, 84.6 MHz) with reference to TMS and CF₃COOH external standards (δ , ppm; J, Hz); the IR spectra were taken on a UR-20 spectrophotometer and the mass spectra on a "Varian MAT CH-8" spectrometer (energy of ionizing electrons 70 eV). Given are m/z, intensity, %, suggested assignments of intense peaks. The GLC analysis and preparative separation were carried out on a column with 20% FS-1265 chromosorb W.

<u>Preparation of Salt (II)</u>. a) Equimolar amounts of perfluoroisobutylene and perfluoropropyl isocyanate were passed simultaneously, with stirring and cooling, into freshly calcined CsF (0.01 mole) in 10 ml of absolute diglyme. A solution of salt (II) was obtained. IR spectrum (ν , cm⁻¹): 1640. ¹⁹F NMR spectrum: -15.9 s [(CF₃)₃C], 2.1 t (CF₃), 4.2 t.q. (CF₂N), 50.5 t (CF₂), JCF₂N-CF₃ = 7.5, JCF₂-CF₂ = 10.3.

b) An equimolar solution of imidoyl fluoride (III) was added to a suspension of freshly calcined CsF in diglyme. Salt (II) was obtained in the solution (¹⁹F NMR data).

A solution of salt (II) was obtained under the same conditions from equimolar amounts of CsF and isocyanate (IV) in diglyme (¹⁹F NMR data).

<u>Reaction of Salt (II) with Alcohol.</u> A 0.5-ml portion of absolute alcohol was added to a freshly prepared solution of salt (II) in diglyme, prepared from 1 g of imidoyl fluoride (III). According to ¹⁹F NMR data, the mixture contains $(CF_3)_3CH$ and urethane (VI) that is identical with an authentic sample [4].

<u>Pyrolysis of Salt (II)</u>. A solution of salt (II) in diglyme, obtained from 1.8 g of imidoyl fluoride (III), was heated at 130-170°C for 30 min. Thus, 1 g of a mixture was condensed in the trap (-78°C), consisting mainly of perfluoroisobutylene and perfluoro-propyl isocyanate (¹⁹F NMR data).

Action of $\text{Et}_2 0.8F_3$ on Salt (II). A 5.5 g portion of $\text{BF}_3.\text{Et}_2 0$ was added dropwise, with stirring (20°C), to a solution of salt (II) in diglyme, obtained from 8 g of perfluoropropyl isocyanate and 7.5 g of perfluoroisobutylene. After 1 h (20°C), the volatile products were distilled in vacuo (3-5 mm) into a trap (-78°C) and the residue was fractionated. Yield, 13.6 g (88%) of a mixture, bp 103-110°C, containing 75% of imidoyl fluoride (III) and 25% of isocyanate (IV), which were separated by preparative GLC.

Perfluoropropionic acid N-perfluoropivaloylimidoyl fluoride (III), bp 105-106°C. Found: C 23.32; F 69.10%. $C_8F_{15}NO$. Calculated: C 23.35; F 69.34%. IR spectrum (v, cm⁻¹): 1760, 1785. ¹⁹F NMR spectrum: -49.5 m (CF), -13.3 s [(CF₃)₃C], 7.3 m (CF₃), 45.3 d (CF₂), JCF₂-CF = 12.7. Mass spectrum: 392(0.2) (M-F)⁺, 345(0.1)(M-F-COF)⁺, 312(0.1)(M-CF₃-NCO)⁺, 276(0.4) (M-CF₃-COF)⁺, 247(18) (M-2CF₃-CN)⁺, 178(10.4) (CF₃)₂CCO)⁺, 159 (13.3) (C₂F₅COO)⁺, 142(2.7)(C₂F₄NCO)⁺, 92(10.4) (CF₂NCO)⁺, 76(0.9) (CF₂NC)⁺, 73(1) CFNCO)⁺, 69(100) (CF₃)⁺, 54(13.3)(CNCO)⁺, 47, (2.7) (COF)⁺, 28(13.3) (CO)⁺. Perfluoro- α -tert-butylpropyl isocyanate (IV), bp 115-116°C. Found: C 23.46; F 69.39%. $C_8F_{15}NO$. Calculated: C 23.35; F 69.34%. IR spectrum (v, cm⁻¹): 2290. ¹⁹F NMR spectrum: -15.5 d. d. d. [(CF₃)₃C], 2.8 d (CF₃), 40.3 m (CF), 41.5 m (CF₂), JCF₃-CF = 16.9, JF-F = 11.2; 13.2; 24.4. Mass spectrum: 392(1.7) (M-F)⁺, 342(0.2) (M-CH₃)⁺, 292(24) (M-C₂F₅)⁺, 254(0.3) (M-C₂H₇)⁺, 247(1.9) (M-2CF₃-CN)⁺, 226(0.25) (M-2CF₃-COF)⁺, 192(55) (M-C₄F₉)⁺, 178(0.4) (C₃F₆CO)⁺, 142(8) (C₂F₄NCO)⁺, 123(1.5) (C₂F₃NCO)⁺, 92(70) (CF₂NCO)⁺, 73(1.6) (CFNCO)⁺, 69(100) (CF₃)⁺, 54(2) (COCN)⁺, 47(1) (COF)⁺, 28(15) (CO)⁺.

Under similar conditions, from salt (II), obtained from 5 g of perfluoropropyl isocyanate, 4.5 g of perfluoroisobutylene, and 3.6 g of CsF in absolute diglyme, but by the action of 3.5 g of BF_3Et_2O at --30°C, 8.3 g (85%) of (III), bp 102-106°C, were obtained, while at 40-50°C, 5.6 g of a mixture bp 105-115°C were obtained, containing 60% of (III) and 40% of isocyanate (IV) (¹⁹F NMR data).

<u>Reaction of Perfluoroisobutylene with N-Chloroacetamide.</u> A 12-g portion of perfluoroisobutylene was passed, with cooling and stirring, into a solution of 5.3 g of N-chloroacetamide in 30 ml of absolute N-methylpyrrolidone. After 1 h (20°C), the fraction bp < 80°C (12 mm) was distilled in vacuo. Repeated fractionation, gave 4.9 g (30%) of α -chlorohexafluoroisobutyric acid N-acetylimidoyl fluoride (VII), bp 58-60°C (50 mm). Found: C 26.54; H 1.18%. C₆H₃ClF₇NO. Calculated: C 26.34; H 1.09%. IR spectrum (v, cm⁻¹): 1735; 1780. ¹⁹F NMR spectrum: -51.6 h (CF), -6.6 d (CF₃), JCF₂-CF = 9.6. After distillation of low-boiling compounds, the residue was poured into water, and the oil that separated was extracted by ether. After distillation of ether, 3 g (34%) of N-(1,1,3,3,3-pentafluoro-2-trifluoropropyl)acetamide (IX), mp 85-87°C (from $CHCl_3$) were obtained. Found: C 27.51; H 2.03%. $C_6H_5F_8NO$. Calculated: C 27.80; H 1.93%. IR spectrum (ν , cm⁻¹): 1700, 3260-3340. PMR spectrum (in MeCN): 1.9 s (CH₃), 4.8 t.h (CH), 8.4 br. s (NH), JCF₃H = 7.7, JCF₂-H = 4. ¹⁹F NMR spectrum (in CH₃CN): -14.2 d. t (CF₃), 1.3 d. H (CF₂), JCF₃-CF₂ = 10.5.

<u>a-Hydrohexafluoroisobutyric Acid N-Acetylimidoyl Fluoride (X).</u> A 58-g portion of perfluoroisobutylene was added, with stirring and cooling, to a solution of 37 g of trimethylsilylacetamide in 100 ml of absolute ether. The mixture was stirred for 6 h, and after 20 h, trimethylfluorosilane and ether were distilled. From the residue, by fractionation, 33 g of fraction bp 40-80°C (30 mm) were obtained. By repeated fractionation, 27 g (40%) of imidoyl fluoride (X), bp 40-43°C (20 mm), were isolated. Found: C 30.12; H 1.66; F 55.70%. $C_6H_4F_7NO$. Calculated: C 30.10; H 1.68; F 55.61%. IR spectrum (ν , cm⁻¹): 1740, 1780. ¹⁹F NMR spectrum: -12.6 t (CF₃), -57.1 d. h (CF), JCF₃-CF = JCF₂-H = 8, JCF-H = 5.

<u>Reactions of Imidoyl Fluoride (III) with Nitriles.</u> A 0.1-g portion of absolute MeCN was added, with stirring, to 0.7 g of imidoyl fluoride (III), and the mixture was left to stand at 20°C. After 3 h, the mixture was distilled to yield 0.7 g (88%) of 2-methyl-4-fluoro-4-pentafluoroethyl-6-perfluoro-tert-butyl-1,3,5-oxadiazine (XIa), bp 71-73°C (25 mm). Found: C 26.58; H 0.64; N 6.18%. $C_{10}H_3F_{15}N_2O$. Calculated: C 26.54; H 0.66; N 6.19%. IR spectrum (ν , cm⁻¹): 1740. ¹⁹F NMR spectrum: -14.1 s [(CF₃)₃C], 3.1 d (CF₃), +9.1 t. q (CF), 52.1 d (CFa), 52.2 d (CFb), JCF₃-CF = 8.5, JCF₂-CF = 5.7, JF^a-F^b = 0.

A 0.55-g portion of PhCN was added, with stirring, to 3 g of a mixture consisting of imidoyl fluoride (III) and isocyanate (IV) (\sim 2:1), and the mixture was left to stand at 20°C. After \sim 20 h, the unreacted isocyanate (IV) was distilled in vacuo (2-5 mm) into a trap (-78°C), and the residue was fractionated to yield 1.9 g of 2-phenyl-4-fluoro-4-penta-fluoroethyl-6-perfluoro-tert-butyl-1,3,5-oxadiazine (XIb), bp 85-87°C (1 mm). Found: C 35.06; H 1.06; F 55.42; N 5.96%. C₁₅H₅F₁₅N₂O. Calculated: C 35.01; H 0.97; F 55.44; N 5.44%. IR spectrum (\vee , cm⁻¹): 1640, 1725. ¹⁹F NMR spectrum: -14.2 s [(CF₃)₃C], 3.1 d (CF₃), 9.2 t. q. (CF), 54.8 d (CF^a), 54.9 (CF^b), JCF₃-CF = JCF₂-CF = 9.4, JF^a-F^b = 0.

<u>Reactions of Imidoyl Fluoride (III) with Carbonyl Compounds.</u> A 0.5-g portion of PhCHO was added, with cooling, to 3 g of a mixture of (III) and (IV) (\sim 2:1), and the mixture was left to stand at 20°C. After 30 min, the unreacted (IV) was distilled in vacuo (2-5 mm) into a trap (-78°C), and the residue was fractionated to yield 0.9 g 2-phenyl-4-fluoro-4-pentafluoroethyl-6-perfluoro-tert-butyl-1,3,5-dioxazine (XIIa), bp 55-57°C (5 mm). Found: N 2.79. C₁₅H₆F₁₅NO₂. Calculated: N 2.70%. IR spectrum (\vee , cm⁻¹): 1670, 1705. ¹⁹F NMR spectrum: -14.4 s [(CF₃)₃C], 3.2 d (CF₃), 13.8 t. q (CF), 51.3 d (CF₂), JCF₃-CF = 8.4, JCF₂-CF = 5.9.

A 0.6-g portion of acetophenone was added, with stirring, to 3 g of a mixture of (III) and (IV) (\sim 2:1), and the mixture was left to stand at 20°C. After 1 h, the unreacted (IV) was distilled in vacuo (2-3 mm) into a trap (-78°C). From the residue, 2-methyl-2-phenyl 4-fluoro-4-pentafluoroethyl-6-perfluoro-tert-butyl-1,3,5-dioxazine (XIIb) was obtained. IR spectrum (\vee , cm⁻¹): 1680, 1690. ¹⁹F NMR spectrum: -14.4 s [(CF₃)₃C], 3.3 d (CF₃), 12.6 m (CF), 51.7 m (CF₂), JCF₃-CF = 9. In an attempt to purify dioxazine (XIIb) by fractionation in vacuo (1 mm), the latter decomposed completely into imidoyl fluoride (III) and acetophenone.

<u>Reaction of Imidoyl Fluoride (X) with Ketene.</u> An equimolar mixture of imidoyl fluoride (X) and ketene in absolute ether was left to stand in a sealed ampule at 20°C. After ~ 20 h, the unreacted compounds were distilled, and the residue was fractionated to yield N,N-diacetylaminoperfluoroisobutylene (XIII), bp 60-62°C (16 mm). Found: C 34.31; H 2.22; F 47.5%. C₈H₆F₇NO₂. Calculated: C 34.19; H 2.14; F 47.42%. IR spectrum (ν , cm⁻¹): 1695, 1710, 1740. PMR spectrum (in CCl₄): 2.18 s (CH₃). ¹⁹F NMR: -24.0 q. q (CF), -18.0 d. q (cis-CF₃), -17.1 d. q. (trans-Cf₃), J_{cis}-CF₃ = 22.5, J_{trans}-CF₃ = 12.2, J_CF₃-CF₃ = 7.5.

<u>Reaction of Isocyanate (IV) with Alcohol.</u> A 0.2-g portion of absolute alcohol was added, with cooling and stirring, to 0.9 g of isocyanate (IV). The reaction mixture containing urethane (XIV) according to the ¹⁹F NMR data [-16.1 m [(CF_3)₃C], 2.4 g (CF_3), 41.8 m (CF_2), 82.8 m (CF), J CF_3 -CF = 17.8], was heated at 100°C for 30 min, and fractionated to yield 0.5 g (53%) of pentafluoroethyl perfluoro-tert-butyl ketone N-carboethoxyimine (XV),

bp 62-63°C (10 mm). Found: C 27.38; H 1.14; F 61.04; N 3.57%. $C_{10}H_5F_{14}NO_2$. Calculated: C 27.45; H 1.14; F 60.86; N 3.20%. IR spectrum (ν , cm⁻¹): 1705, 1775. ¹⁹F NMR spectrum: 15.5 t. q [(CF₃)₃C], -0.9 dec (CF₃), 28.2 dec (CF₂), JCF₃-C(CF₃)₃ = 4.7, JCF₂-C(CF₃)₃ = 9.4.

CONCLUSIONS

1. N-Acylimidoyl fluorides of fluorine-containing carboxylic acids were synthesized for the first time.

2. Perfluoropropionic acid N-perfluoropivaloylimidoyl fluoride enters 1,4-cycloaddition reactions with nitriles and carbonyl compounds, and by the successive action of CsF and boron trifluoride etherate, converts into the isomeric perfluoro- α -tert-butylpropyl isocyanate.

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