FLUORINE-CONTAINING IMINES.

5.* REACTIONS OF ACYLIMINES OF HEXAFLUOROACETONE AND PERFLUOROALKYL ISOCYNATES WITH METHYLENEBISDIMETHYLAMINE

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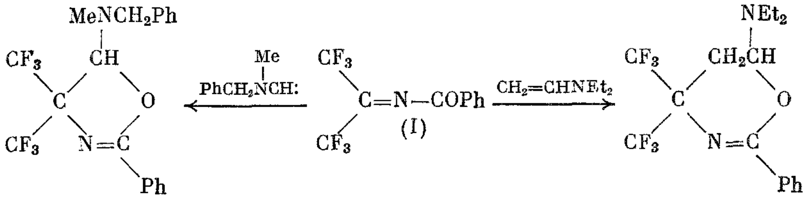
It has already been found that hexafluoroacetone (HFA) benzoyl imine (I) dehydrogenates tertiary amines: Et_3N to $Et_2NCH{=}CH_2$ [2], and $PhCH_2NMe_2$ to $PhCH_2(Me)NCH$: [3]; these intermediates were isolated in the form of cycloadducts



The first stage of these reactions is transfer of the hydride ion from tertiary amine to (I).

In the present work we studied the reactions of HFA acylimines with methylenebisdimethylamine (II). The hydride rearrangement reactions for (II) have not yet been studied, but it can be expected that, as in the case of the cyclic analog 1,3-dimethylbenzylimidazoline [4, 5], the methylene group in (II) will have an increased hydride mobility. A characteristic property of (II) is splitting by the action of electrophiles, whereby the dimethylaminomethyl cation formed becomes bound to an anion derived from the electrophile [6, 7].

It was found that in the reaction with (I), compound (II) may serve as a source of both a hydride ion and the dimethylaminomethyl cation. In the dark or at weak illumination, the hydride ion transfer products are mainly formed: the immonium salt (III) and the addition products of (II) to (I)-(IV), which are characterized by ^{19}F NMR spectra [a broad signal at −12 ppm for (III) and a singlet at −5.1 for (IV)], and also by transformation reactions by the action of excess alcohol into benzamides (V) and (VI), respectively (see [3]). Entirely different results are obtained in light (sunlight in the presence of C_5H_5N or UV irradiation). Under these conditions, a substituted benzamide (VII) and dimethylaminooxazoline (VIII) are finally formed. It is clear that the intermediate adduct of (I) with (II) dissociates into an anion and dimethylmethyleneimmonium cation, which in the dark gives an addition product (IV), and in light is deprotonated into dimethylaminomethylene which, as the result of a [1 + 4]-cycloaddition, forms the oxazoline (VIII) with (I).

In contrast to dimethylbenzylamine, which with (I) forms methylbenzylaminocarbene as the result of splitting of two H atoms [3], compound (II) does not give bisdimethylaminocarbene but converts into dimethylaminomethylene due to splitting of dimethylamine (the two reactions proceed only in light). The structure of aminooxazoline (VIII) is confirmed by the spectral data, and also by hydrolysis into the known hydroxyoxazoline (IX) and by alcoholysis into benzamide (V) (cf. [3]).

An attempt to detect dimethylaminomethylene in the reaction with HFA N-perfluoropivaloylimine was unsuccessful. In this case the dimethylaminomethyl cation does not deprotonate into aminocarbene, but adds to the perfluoro-tert-butyl anion that splits from the inter-

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*For Communication 4, see [1].

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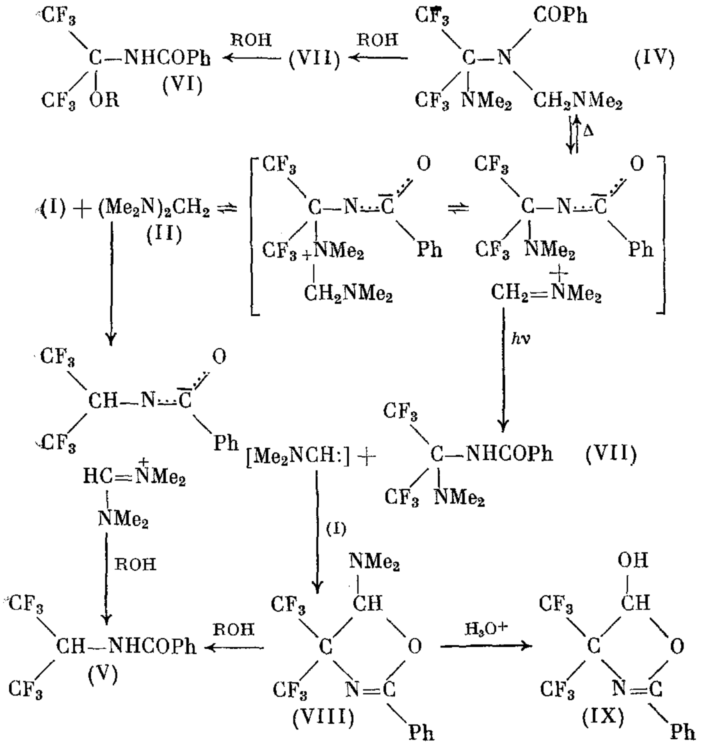
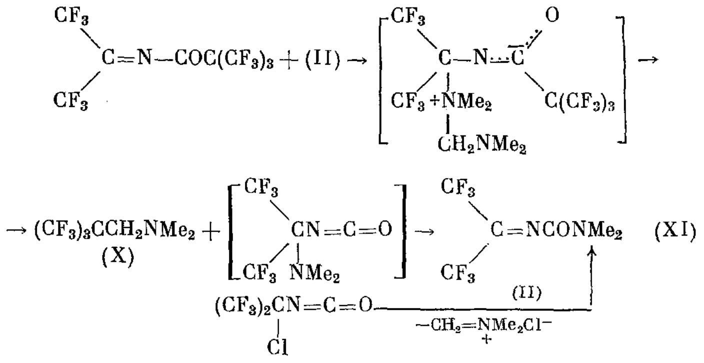
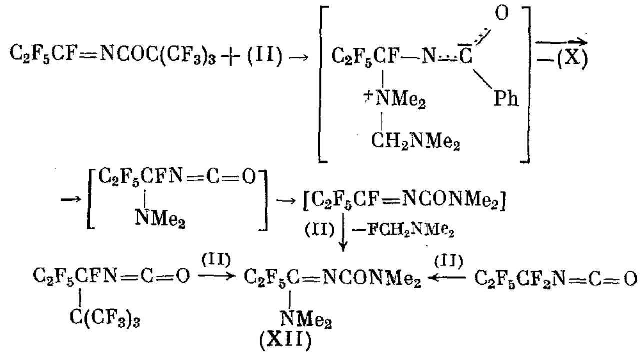


mediate adduct to form tertiary amine (X), identical to an authentic compound [8]. The intermediate α-dimethylaminoisocyanate thus obtained isomerizes into HFA N,N-dimethylcarbamoylimine (XI) [9, 10], synthesized also by the reactions of α-chlorohexafluoroisopropyl isocyanate with (II)



In the reaction of N-perfluoropivaloylpropimidoyl fluoride with (II), not only the perfluoro-tert-butyl group, but also an α-fluorine atom, is replaced by the dimethylamino group to form alkylideneurea (XII), which is also obtained by reactions of (II) with perfluoropropyl isocyanate and perfluoro-α-tert-butylpropyl isocyanate.*



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*Ureas of this type were previously obtained by the action of perfluoroalkyl isocyanates with secondary amines [11].

In reactions with highly electrophilic unsaturated fluororganic compounds, compound (II) may thus serve as a source of not only the dimethylamino group, but also of dimethylaminomethylene and hydride ion.

EXPERIMENTAL

The IR spectra were run on a UR-20 spectrophotometer and the ^1H and ^{19}F NMR spectra (δ, ppm) on a Perkin–Elmer R-32 spectrometer (^1H 90, ^{19}F 84.6 MHz) relative to TMS and $CF_3 \cdot COOH$ used as external standards. A DRT-230 mercury lamp served as the light source.

2-Phenyl-4,4-bis(trifluoromethyl)-5-dimethylamino-2-oxazoline (VIII). a) Under UV irradiation. A mixture of 2.6 g of (I) and 1 g of (II) was irradiated for 17 h by UV light. According to the ^{19}F NMR data, compounds (VII) (18%), V (8%), (VIII) (43%), and (IV) (30%), are formed. Hexane was added to the mixture, and the solution was decanted from the precipitate and distilled. Yield, 0.6 g (37%) of oxazoline (VIII), bp 91-93°C (1 mm). Found, %: C 47.03, H 3.61, F 35.61. $C_{13}H_{12}F_6N_2O$. Calculated, %: C 47.85, H 3.68, F 34.96. PMR spectrum: 2.2 s (CH_3), 5.6 s (CH), 7.1-7.8 m (C_6H_5), ^{19}F NMR spectrum −9.9 q (CF_3), −1.5 q (CF_3), $J_{FF} = 11.3$ Hz. Mass spectrum: M^+ m/z 326.

b) Influence of the addition of pyridine. A mixture of 0.3 g of (I) and 0.17 g of (II) was divided into two parts and left to stand in sealed ampuls with slight illumination (0.2 g of pyridine was preliminarily introduced into one of the ampuls). According to ^{19}F NMR spectra, the formation of the following compounds is observed after 6 days (without pyridine): salt (III) (30%) [broad signal at −12 ppm; EtOH converts it completely into (V)], oxazoline (VIII) (6.7%) and amides (V) (8.3%) and (IV) (55%) [singlet at −5.1 ppm; on heating with EtOH for 20 h at 55°C, it converts into (VI)]; (with pyridine): oxazoline (VIII) (27%) and amides (V) (36%), (IV) (32%), and (VII) (3%).

c) Influence of illumination. A mixture of 3.6 g of (I) and 1.3 g of (II) was held in sunlight or in the dark. The content of the reaction products was determined from the ^{19}F NMR spectra after 11 days. The following compounds are formed in light: salt (III) (11%), oxazoline (VIII) (25%) and amides (V) (13%), (IV) (40%), and (VII) (8%). In the dark: salt (III) (30%), oxazoline (VIII) (8%) and amides (V) 11%, (IV) (45%), and (VII) (2.3%).

Hydrolysis and Alcoholysis of Oxazoline (VIII). A mixture of 0.5 g of (VIII) and 1.5 g of concentrated HCl was stirred for 5 min, then poured onto ice, and the precipitate was filtered. Yield: 0.27 g (59%) of crystals, mp 156-157°C, which is not lowered in a mixture with authentic (IX) [3].

Equal volumes of oxazoline (VIII) and absolute EtOH were heated for 7 h in a sealed ampul at 70°C. According to the ^{19}F NMR data, the mixture consists of oxazoline (VIII) (70%) and benzamide (V) (30%). The alcoholysis is complete after 20 h at 75-80°C. The mp (148°C) of the crystals isolated from the mixture is not lowered in a mixture with benzamide (V).

N,N-Dimethyl-N'-benzoyl-2,2-diaminohexafluoropropane (VII). An excess of dimethylamine was passed through a solution of 0.3 g of (I) in 1.5 ml of absolute ether. After evaporation of ether, 0.32 g (91%) of (VII) was obtained, mp 74-75°C. Found, %: C 45.45, H 3.89, F 36.1, N 8.9. $C_{12}H_{12}F_6N_2O$. Calculated, %: C 45.86, H 3.8, F 36.3, N 8.9. PMR spectrum (in MeCN): 2.3 s (CH_3), 6.8 br. s (NH), 7.2-7.7 m (C_6H_5). Mass spectrum: M^+ m/z 314.

Alcoholysis of (VII). A solution of VII in absolute EtOH was heated in a sealed ampul for 1 h at 65-70°C. According to the ^{19}F NMR data, the mixture consists of (VII) (24%) and 2-ethoxy-2-benzimidohexafluoropropane (VI) (73%). Further heating (20 h at 75-80°C) does not lead to a change in the composition of the mixture.

Hexafluoroacetone N,N-dimethylcarbamoylimine (XI). a) A 0.2 g portion of (II) was added dropwise to 0.8 g of HFA N-perfluoropivaloylimine, and the mixture was heated for 10 min at 70-80°C. Distillation gave 0.3 g (65%) of (XI), bp 71-72°C (30 mm) [9]. Found, %: C 30.68, H 2.82, N 11.75. $C_6H_6F_6N_2O$. Calculated, %: C 30.50, H 2.54, N 11.86. IR spectrum (ν, cm^{-1}): 1690 (C=N), 1727 (C=O). PMR spectrum: 2.3 s (CH_3), 2.6 s (CH_3). ^{19}F NMR spectrum: −8 m (CF_3). Mass spectrum: M^+ m/z 236. On distillation of (XI), amine (X), identical with an authentic sample [8], condensed in a trap.

b) Excess of (II) was added dropwise, with stirring and ice-cooling to 3.5 g of α-chlorohexafluoroisopropyl isocyanate. Three hours after the end of an exothermal reaction, the product was flash-distilled in vacuo into a trap (−78°C) and then distilled. Yield: 2.5 g (69%) of (XI), bp 74-76°C (32 mm).

N,N'-Dimethyl-N'-(α-dimethylaminopentafluoropropylidene)urea (XII). a) A 0.7 g portion of (II) was added dropwise to 1.4 g of N-perfluoropivaloylpropimidoyl fluoride. Three hours after the end of the exothermal reaction, the mixture was heated for 10 min at 100°C and the volatile products were distilled in vacuo (10 mm) into a trap (−78°C) to yield 1 ml of a mixture of amine (X) and fluoromethyldimethylamine (according to ^{19}F NMR). Distillation of the residue gave 0.8 g (90%) of (XII), bp 77-78°C (1 mm), mp 35-37°C (from hexane). Found, %: C 36.21, H 4.70, F 36.71, N 16.77. $C_8H_{12}F_5N_3O$. Calculated, %: C 36.78, H 4.59, F 36.39, N 16.09. IR spectrum (ν, cm^{-1}): 1645 (C=N), 1670 (C=O). PMR spectrum: 2.8 s (CH_3), 2.9 s (CH_3). ^{19}F NMR spectrum: 2.8 s (CF_3), 34.1 s (CF_2).

b) A 3.2 g portion of (II) was added dropwise with cooling to 3.2 g of perfluoropropyl isocyanate. The mixture was allowed to stand for 48 h at 20°C, and the volatile products were distilled in vacuo into a trap (−78°C). Thus, 1 g of fluoromethyldimethylamine, bp 39°C, was obtained. Distillation of the residue gave 3.1 g (78%) of (XII), bp 79-83°C (1 mm).

c) Under similar conditions, from 1.2 g of perfluoro-α-tert-butylpropyl isocyanate and 0.6 g of (II), 0.6 g (79%) of (XII), bp 69-72°C (1 mm), was obtained after 20 h. From the trap, 0.6 g of a mixture, bp 85-95°C, was isolated, consisting of amine (X) and fluoromethyldimethylamine (according to ^{19}F NMR).

CONCLUSIONS

In reactions with hexafluoroacetone acylimines, perfluoroalkyl isocyanates and imidoyl fluoride, methylenebisdimethylamine serves a source of dimethylaminomethylene, hydride ion, and dimethylamino group.

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