BIS-(N^2-HYDROXYHEXAFLUOROISOPROPYL-N^1,N^1-SUBSTITUTED)TEREPHTHALAMIDINES AND THEIR REACTION WITH PERFLUOROHEXANECARBONITRILE

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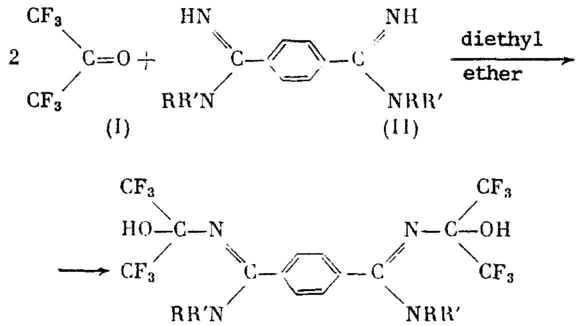
Bis(N^2-hydroxyhexafluoroisopropyl-N^1,N^1-substituted)terephthalamidines, which are stable up to their melting points, were obtained by reacting substituted tetraphthalamidines with hexafluoroacetone. The reaction of bis(N^2-hydroxyhexafluoroisopropyl-N^1,N^1-substituted)terephthalamidines with perfluorohexanecarbonitrile results in the formation of 1,4-bis(2,4-perfluorohexyltriazinyl)benzene.

It is known from the literature that in the reaction of hexafluoroacetone with strong nucleophiles (ammonia, primary, and secondary aliphatic amines), adducts are formed which are relatively stable at ~20°C [1]. There are reports on the synthesis of products stable up to 90-100°C of the reaction of hexafluoroacetone with bases containing amidine fragments [2]. Reactions of hexafluoroacetone with N^1-substituted aromatic amidines were studied, which lead to the formation of 2,2,6,6-tetrakis(trifluoromethyl)-5,6-dihydro-1,3,5-oxadiazines [3].

In the present work, we studied the reaction of hexafluoroacetone with bis(N^1,N^1-substituted)terephthalamidines and the reaction of the product formed with perfluorohexanecarbonitrile.

We found that hexafluoroacetone reacts under mild conditions with bis(N^1,N^1-substituted)-terephthalamidines to form bis(N^2-hydroxyhexafluoropropyl-N^1,N^1-substituted)terephthalamidines.



R = R' = CH_3 (a), RR' = $-(CH_2)_5-$ (b), RR' = $-(CH_2)_2-O-(CH_2)_2-$ (c).

These compounds were found to be stable up to their melting points, which is probably due to the existence of a system of conjugation in the molecule of the geminal amidinohydroxy compound.

In the ^{19}F and ^1H NMR investigation of (III), signals were detected in regions characteristic for aromatic protons and CF_3 groups, indicating the formation of a mixture of isomers of varied configuration, whose ratio depends on the nature of the amine substituent. However, this problem is not discussed in the present article, since this subject requires a detailed investigation.

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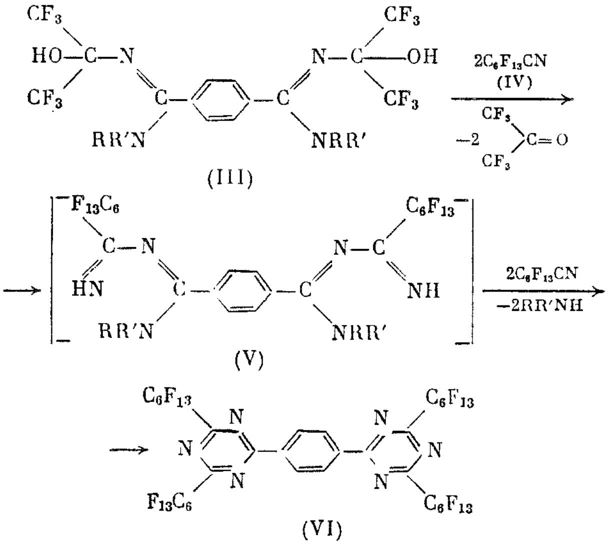
We have previously reported that perfluorohexanecarbonitrile reacts smoothly with bis(N^1,N^1-dimethyl)terephthalamidine to form 1,4-bis(2,4-perfluorohexyltriazinyl)benzene [4].

In the present work, we succeeded in effecting a reaction of the above mentioned bis(N^2-hydroxyhexafluoroisopropyl-N^1,N^1-substituted)terephthalamidines (III) with perfluorohexanecarbonitrile. The end product of this reaction is likewise 1,4-bis(2,4-perfluorohexyltriazinyl)benzene (VI)



One of the possible schemes of this reaction presupposes an initial attack of the perfluorinated nitrile at the N—C bond connecting the amidine and hydroxyhexafluoroisopropyl fragments, the result of which is the elimination of hexafluoroacetone and formation of a highly reactive substituted imidoylamidine (V). An indirect confirmation of this supposition is the reaction of (III) with hydrogen chloride, acetic, and trifluoroacetic acids. In this case, the end products are hexafluoroacetone and a salt of the corresponding bis(N^1,N^1-substituted)terephthalamidine.

At the second stage, the substituted imidoylamidine adds the next molecule of the perfluorinated nitrile and closes into a sym-triazine ring, splitting off an amine.

The successful course of the reaction is promoted by the fact that the hexafluoroacetone and amine by-products react with one another at a high rate producing hexafluoroacetone aminoketal [5]. The formation of the aminoketal is proved by the fact that after treatment of the reaction mixture with ethanol an ammonium salt of bis-trifluoromethylethoxycarbinol was isolated [6, 7]. We obtained a similar compound by the reaction of hexafluoroacetone with piperidine and ethanol (VIII).

EXPERIMENTAL

The ^{19}F and ^1H NMR spectra were run on a Bruker WM-250 spectrometer (235.2 and 250 MHz, respectively), using $CFCl_3$ and HMDS as internal standards and CD_3OD and CF_3COOD as solvents. The IR spectra were recorded on a Specord M-80 spectrophotometer in KBr tablets or in a thin layer. Diethyl ether was distilled over $LiAlH_4$ and was stored over a sodium wire. Chloroform was shaken with water, dried over $CaCl_2$, distilled over P_2O_5, and stored in dark flasks in an N_2 atmosphere.

Bis(N^1,N^1-substituted)terephthalamidines (II) were obtained by Pinner's method [8] from tetraphthaldinitrile and subsequent dehydrochlorination of the amidine salt with a K_2CO_3 solution.

Perfluorohexanecarbonitrile (IV) was obtained by a known method [9] by dehydration of the amide with P_2O_5.

Bis(N^2-hydroxyhexafluoroisopropyl-N^1,N^1-substituted)terephthalamidine (III) (general method). A 6.5 mmoles portion of (II) was added to 40 ml of diethyl ether. Hexafluoroacetone was passed slowly through the reaction mixture for 3 h. The readily volatile compounds were then evaporated under vacuum. After extraction with diethyl ether, the yield of (III) was 75%.

Bis(N^2-hydroxyhexafluoroisopropyl-N^1,N^1-dimethyl)terephthalamidine (IIIa), mp 139-141°C (dec.). Found: C 39.41; H 3.20; F 41.95; N 10.00%. Mol. wt.: 540 (ebullioscopy in $CHCl_3$). $C_{18}H_{18}F_{12}N_4O_2$. Calculated: C 39.27; H 3.27; F 41.46; N 10.18%. M_{theor} = 550. ^1H NMR spectrum (δ, ppm, CD_3OD): 7.74 and AB spectrum with a center at 7.81 and J_{AB} = 8.50 Hz (Ph); 3.25 ($4C\underline{H}_3$—). ^{19}F NMR spectrum (δ, ppm, CD_3OD): 60.7 and 62.5 ($C\underline{F}_3$ — syn and anti-forms). IR spectrum (δ, cm^{-1}): 720 ($C—H_{arom}$); 960 (O—H); 1436 (CH_3); (ν, cm^{-1}): 1100-1200 (C—F); 1632 (C=N); 2984 (CH_3), 3220 (O—H).

Bis(N^2-hydroxyhexafluoroisopropyl-N^1-piperidino)terephthalamidine (IIIb), mp 123-125°C (dec.). Found: C 45.60; H 4.20; F 36.67; N 9.01%. Mol. wt.: 640 (ebullioscopy in $CHCl_3$). $C_{24}H_{26}F_{12}N_4O_2$. Calculated: C 45.71; H 4.13; F 36.19; N 8.89%. M_{theor} = 630. ^1H NMR spectrum (δ, ppm, CD_3OD): 7.86; 7.72 and AB spectrum with a center at 7.81 and J_{AB} = 8.50 Hz (Ph); 3.51; 2.98 and 1.70 ($10\text{-}C\underline{H}_2$—). ^{19}F NMR spectrum (δ, ppm, CD_3OD): 60.9 and 62.9 ($C\underline{F}_3$ — syn and anti-forms). IR spectrum (δ, cm^{-1}): 718 (CH_{arom}); 956 (O—H); 1448 (CH_2); (ν, cm^{-1}): 1100-1200 (CF); 1616 (C=N); 2868, 2956 (CH_2), 3220 (O—H).

Bis(N^2-hydroxyhexafluoroisopropyl-N^1-morpholino)terephthalamidine (IIIc), mp 218-220°C (dec.). Found: C 41.75; H 3.53; F 35.45; N 8.97%. Mol. wt.: 645 (ebullioscopy in $CHCl_3$). $C_{22}H_{22}F_{12}N_4O_4$. Calculated: C 41.64; H 3.47; F 35.96; N 8.83%. M_{theor} = 634. ^1H NMR spectrum (δ, ppm, CD_3OD): 7.86; 7.71; AB spectrum with a center at 7.82 and J_{AB} = 8.50 Hz and AB spectrum with a center at 8.05 with J_{AB} = 8.50 Hz (Ph); 3.75, 3.66, 3.53, and 2.85 ($8\text{-}C\underline{H}_2$—). ^{19}F NMR spectrum (δ, ppm, CD_3OD): 80.6 and 82.7 ($C\underline{F}_3$ — syn and anti-forms). IR spectrum (δ, cm^{-1}): 724 ($C—H_{arom}$); 964 (O—H); 1420 (CH_2); (ν, cm^{-1}): 1056 (C—O); 1100-1200 (CF); 1628 (C=N); 2860, 2908, 2980 (CH_2), 3220 (O—H).

1,4-Bis(2,4-perfluorohexyltriazinyl)benzene (VI) (general method). A 0.5 mmole portion of (III) was added to 15 ml of chloroform and then 2.1 mmoles of (IV) was added and the mixture was boiled for 8 h. At the end of the reaction, the solvent was evaporated under vacuum and 100 ml of ethanol was added to the reaction mixture. The precipitate that separated out was filtered off, and dried. The yield of (VI) was 92-96%. The physicochemical constants and the absorption spectra of compound (VI) are similar to those given in [4].

Reaction of (III) with Hydrogen Chloride. A 0.7 mmole portion of (III) was dissolved in 50 ml of ethanol. Then dry hydrogen chloride was led in with stirring up to saturation. At the end of the reaction, the readily volatile compounds were evaporated under vacuum. The solid end product was a hydrochloride salt of bis(N^1,N^1-disubstituted)-terephthalamidine (II).

Preparation of Piperidylammonium Salt of Bis-trifluoromethylethoxycarbinol (VII). Hexafluoroacetone was led in slowly in the course of 4 h into 2.5 g (29.4 mmoles) of piperidine in 10 ml of diethyl ether. At the end of the reaction the readily volatile compounds were evaporated under vacuum and 50 ml of ethanol was added to the reaction mixture. The mixture was stirred for 30 min, and ethanol was evaporated under vacuum. The yield of (VII) was 8.07 g (92.4%), mp 102-104°C (dec.). Found: C 40.52; H 5.66; F 38.90; N 4.52%. Mol. wt.: 285 (ebullioscopy in $CHCl_3$). $C_{10}H_{17}F_6NO_2$. Calculated: C 40.40; H 5.72; F 38.39; N 4.71%. M_{theor} = 297. PMR spectrum (δ, ppm, CD_3OD): 3.55 ($—C\underline{H}_2—CH_3$); 2.98 and 1.68 ($5\text{-}C\underline{H}_2$—); 1.13 ($C\underline{H}_3$—). ^{19}F NMR spectrum (δ, ppm, CD_3OD): 81.1 ($C\underline{F}_3$—). IR spectrum (δ, cm^{-1}): 956, 1632 (O—H); 1460 (CH); (ν, cm^{-1}): 1052 (C—O); 1100-1200 (CF); 2876, 2976 (CH); 3180 (O—H).

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SPLITTING OF PERFLUORINATED TERTIARY CYCLIC AMINES BY THE ACTION OF SbF_5

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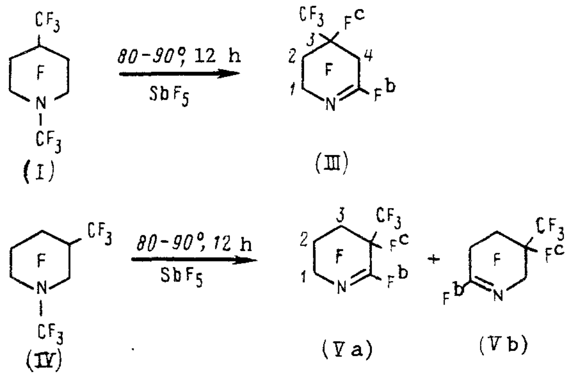
It was shown that perfluorinated tertiary cyclic amines are dealkylated by the action of SbF_5 with the formation of cyclic azomethines. The presence of a perfluoroalkyl substitutent in the α-position to the nitrogen atom in the amine molecule considerably decreases its stability to the action of antimony pentafluoride.

Perfluorinated tertiary amines undergo dealkylation by the action of SbF_5 [1-3] and amines containing the $\rangle N{-}CF_3$ fragment in particular are readily split [3].

It was found that perfluoro-1,4-dimethylpiperidine (I), like perfluoro-1,2-dimethylpiperidine (II) [3] is capable of undergoing dealkylation on heating with SbF_5 with the formation of perfluoro-1-aza-4-methyl-1-cyclohexene (III). Under comparable conditions, perfluoro-1,3-dimethylpiperidine (IV) becomes dealkylated with the formation of two isomeric compounds (Va) and (Vb) in a 70/30 ratio (overall yield 76%).



(I)
(III)
(IV)
(Va)
(Vb)

The structure of the azomethines (Va, b) was determined from the ^{19}F NMR and mass spectroscopy data. In the mass spectra of compounds (III), (Va), and (Vb), peaks of molecular ions were observed as well as peaks corresponding to the elimination of a fluoroolefin molecule from the molecular ion (the retro Diels—Alder reaction). The mass spectrum of compound (Vb) shows a $M^{+}{-}C_3F_6$ ion, the considerable intensity of which is explained by its secondary origin: it is obtained as a result of the decomposition of the $M^{+}{-}C_2F_4$ ion (elimination of CF_2).

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