REACTION OF 3-AMINOFURAZANS WITH ELEMENTAL FLUORINE

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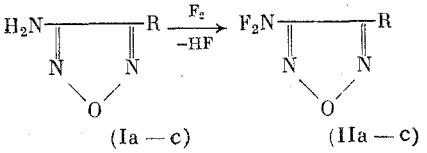
UDC 542.91:547.793.2:546.16

The reactions of fluorine with aliphatic nitrogen-containing compounds have been studied sufficiently extensively [1], but those with heterocyclic amines have been studied very insufficiently.

In the framework of an investigation of fluorination of NH compounds [2], we studied aminofurazans, which previously were not used in this reaction. A series of 3-amino-4-R-furazans (Ia-c) were fluorinated under conditions close to those described in [3] by passing gaseous fluorine diluted with helium (1:5) at reduced temperature through a solution of furazan in acetonitrile. Sodium fluoride was added to bind the HF formed in the reaction.

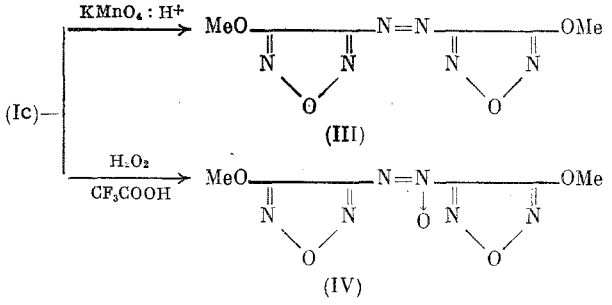
It was ascertained that under these conditions the furazan fragment is quite resistant to the action of F_2, and as a result of selective fluorination of the amino group 3-(difluoroamino) derivatives (IIa-c) were formed



(Ia — c) (IIa — c)

R = Me (a), CO_2H (b), MeO (c).

Compounds (IIa) and (IIb) were obtained as the only reaction products. But, in the fluorination of (Ic), not only (IIc) was obtained, but also a crystalline compound not containing fluorine, the amount of which increased significantly as the reaction temperature was increased from −40 to 0°C. On the basis of its high molecular mass, it could be the product of oxidative dimerization of (Ic), i.e., either azo- (III) or azoxyfurazan (IV). For identification of the resulting product, (III) was obtained by the oxidation of (Ic) by $KMnO_4$ according to [4], and (IV) was obtained by the reaction with H_2O_2 in the presence of CF_3COOH.



By comparison of the physicochemical and spectral characteristics, we showed that the crystalline fluorination product of (Ic) was azo compound (III). Difluoroaminofurazans (IIa-c) are quite stable compounds; therefore, it can be assumed that (III) was formed from monofluoroaminofurazan via the corresponding nitrene according to the scheme given below.

It is known [3] that monofluoroamino derivatives are intermediate fluorination products of amines. As a rule, they are compounds with low stability, tending to undergo further reactions. Thus, monofluorourea easily forms azodicarbamide [5], and during fluorination

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2086-2088, September, 1986. Original article submitted April 3, 1985.

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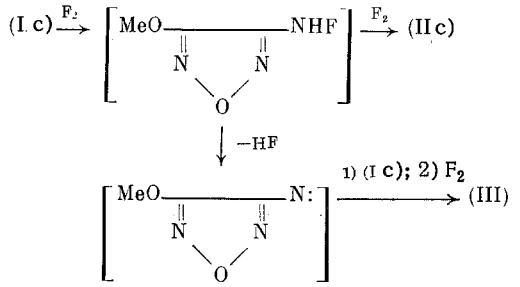

of cyclohexanecarbamide the isocyanate is formed, as Grakauskas and Baum assume [6], via the corresponding monofluoro amide. The instability of the monofluoroamino derivatives is apparently due to facile abstraction of the HF elements from the NHF group with nitrene formation. In this framework, the formation of (III) in the fluorination of (Ic) can be compared with the behavior of (Ic) in reactions with oxidizing agents of "nitrenium" type ($KMnO_4$ in an acid medium and solutions of halogens in alkalis [2]). However, the reason for the differences in the behavior of furazans (Ia-c) during fluorination is not completely clear. It is probably related to the nature of the substituent R in the starting furazan. Thus, unlike Me and CO_2H, the MeO group is capable of n-donor bonding with the furazan ring [7].

It is known that the NF_2 group is a strong electronegative substituent and, on the basis of pK_a of difluoroamino acids [8], it is comparable with the NO_2 group with respect to the induction effect. It seemed of interest to evaluate the value of the σ constant of the NF group in the furazan series. However, for this purpose, it was not possible to use the known dependence [9] because (IIa) decomposes in strongly acid media, which is probably related to protonation at the nitrogen of the difluoroamino group. The value of the σ_R constant (0.16 + 0.05) was calculated according to a correlation equation [9] on the basis of the chemical shift of the methyl protons of (Ia). The rather large positive value of σ_R indicates that the NF_2 group, as a substituent in the series of 3-methyl-4-R-furazans, does not exhibit n-donor properties and is similar in its effect to other electronegative substituents, e.g., NO_2.

EXPERIMENTAL

The NMR spectra were recorded on a Perkin-Elmer R-20 instrument, ^{19}F spectra (56.45 MHz, from a CF_3COOH external standard) and ^1H spectra (60 MHz, from HMDS), and IR spectra were recorded on a UR-10 instrument (film on NaCl, δ, cm^{-1}). The molecular mass was determined by reverse ebullioscopy. The starting compounds (Ia, b) were obtained according to [10, 11].

Fluorination of 3-Methyl-4-aminofurazan (Ia). A mixture of 7 g (71 mmoles) of (Ia) and 6 g of NaF, as a suspension in 150 ml of acetonitrile, was cooled to −5°C, and at this temperature it was treated for 5 h with a stream of fluorine diluted with nitrogen to 30 vol. % at a rate of 3.2 liters/h. After completion of fluorination, the system was purged with nitrogen, the precipitate was filtered, the filtrate was decanted into 500 ml of water, the precipitated oil was washed with water (3 × 10 ml), and distilled. Obtained: 3 g (31%) of (IIa), bp 82-84°C, n_D^{20} 1.3797, d_4^{20} 1.228. Found, %: F 29.6. $C_3H_3N_3F_2O$. Calculated, %: F 28.2. NMR spectrum (δ, ppm): ^{19}F +136.8 singlet (NF_2); ^1H 2.66 singlet (CH_3).

Fluorination of 3-Aminofurazan-4-carboxylic Acid (Ib). We fluorinated similarly 2 g (15 mmoles) of (Ib) (see above). After completion of fluorination, the system was purged with nitrogen and filtered, the solvent was evaporated, and the residue was distilled in vacuo. Obtained: 0.8 g (40%) of (IIb), bp 68°C (1 mm), n_D^{20} 1.4300, d_4^{20} 1.606. Found, %: C 21.5, H 0.65, N 24.2. $C_3HN_3F_2O_3$. Calculated, %: C 21.8, H 0.61, N 25.5. Fluorine-19 NMR spectrum: −136.5 singlet (NF_2). IR spectrum (ν, cm^{-1}): 1760 singlet (C=O), 1090 singlet (furazan ring), 980, 923, 840 singlet (NF).

Fluorination of 3-Amino-4-methoxyfurazan (Ic). a) We fluorinated 3.5 g (31 mmoles) of (Ic) similarly at −30 to −25°C. After completion of fluorination, the system was purged with nitrogen and filtered, the filtrate was decanted into 300 ml of water, the precipitated oil was extracted with Freon-113, the extract was washed with water (3 × 50 ml) and dried with $MgSO_4$, the solvent was driven off, and the residue was distilled in vacuo. Obtained: 2 g (42%) of (IIc), bp 55° (60 mm), n_D^{20} 1.3835, d_4^{20} 1.453. Found, %: F 28.0. $C_3H_3N_3F_2O_2$. Calculated, %: F 25.2. NMR spectra: ^{19}F −135.1 singlet (NF_2); ^1H 4.21 singlet (OCH_3).

b) We fluorinated 2.0 g (18 mmoles) of (Ic) similarly at −5°C. After completion of fluorination, the system was purged with nitrogen and filtered, and the filtrate was decanted into 200 ml of water. The precipitated solid substance was filtered and washed with water. Obtained: 0.8 g of (IV), mp 176-177°C (from acetone). It was identified with a known sample according to the IR and proton NMR spectra. A mixed sample did not give a depression of the melting point.

Preparation of Azomethoxyfurazan (IV). We suspended 1.2 g of (Ic) in 35 ml of 20% hydrochloric acid and added dropwise at ~20°C a solution of 1.8 g of $KMnO_4$ in the minimum amount of water. The whole was stirred for 30 min, several drops of 30% H_2O_2 were added until clarification of the reaction material, and the precipitate was filtered and washed with a 3% H_2O_2 solution and with water. Obtained: 0.7 g (58%) of (IV), mp 177-179°C (from acetone). Found, %: C 32.1, H 2.75, N 37.6. Mol. wt. 221 (acetone). $C_6H_6N_6O_4$. Calculated, %: C 31.7, H 2.65, N 37.2. Mol. wt. 226. Proton NMR spectrum (DMSO-d_6): 4.20 singlet (OCH_3). IR spectrum: 3023 w, 2973 w, 1590 s, 1505 s, 1470 m, 1450 m, 1420 s, 1325 m, 1285 s, 1190 w, 1040 m, 980 s, 935 m, 865 w, and 770 w.

Preparation of Azoxymethoxyfurazan (III). We dissolved 1 g of (Ic) in a mixture of 20 ml of 30% H_2O_2 and 1 ml of CF_3CO_2H, and left it for 72 h at ~20°C. The precipitate was filtered and washed with water. Obtained: 0.45 g (42%) of (III), mp 105-106°C (from CCl_4). Found, %: C 30.0, H 2.60, N 34.9. Mol. wt. 237 (acetone). $C_6H_6N_6O_5$. Calculated, %: C 29.8, H 2.48, N 34.7. Mol. wt. 242. Proton NMR spectrum (DMSO-d_6): 4.25 and 4.20 singlet (OCH_3). IR spectrum: 3025 m, 2970 m, 1590 s, 1525 m, 1510 m, 1475 m, 1460 s, 1430 s, 1415 s, 1280 m, 1210 m, 1170 m, 1040 w, 1025 w, 980 m, 930 w, 875 w, 865 w, 840 w, 790 w, 740 w, and 710 w.

3-Amino-4-methoxyfurazan (Ic). To a solution of 1.3 g of 3-amino-4-nitrofurazan (obtained according to [12]) in 25 ml of ether, a solution of 0.7 g of KOH in 5 ml of methanol was added dropwise at ~20°C, the whole was stirred for 30 min, the KNO_2 precipitate was filtered, and the mother liquor was evaporated to dryness. Obtained: 0.7 g (58%) of (Ic), mp 74-75°C (from CCl_4). Found, %: C 31.2, H 4.16, N 36.7. Mol. wt. 112 (dichloroethane). $C_3H_5N_3O_2$. Calculated, %: C 31.3, H 4.35, N 36.5. Mol. wt. 115. Proton NMR spectrum (acetone): 4.07 singlet (OCH_3), 5.50 singlet (NH_2). IR spectrum: 3390 m, 3260 w, 2950 w, 1590 s, 1470 m, 1435 m, 1325 s, 1285 w, 1130 w, 1015 m, 1000 m, 860 w, and 795 w.

CONCLUSIONS

1. Aminofurazans are fluorinated by elemental fluorine selectively at the amino group with the formation of N,N-difluoroamino derivatives as the main products. The reaction can be accompanied by oxidative dimerization to the corresponding azo compounds.

2. The difluoroamino group in a series of furazans exhibits the properties of an R substituent.

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