# FLUORINE-CONTAINING AZOLES.

# 4.* 2-PERFLUOROPOLYOXAALKYL-SUBSTITUTED PERIMIDINES

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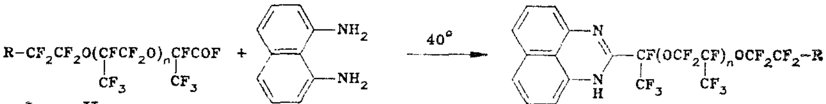
The reaction of 1,8-naphthylenediamine with perfluoropolyoxaalkanoyl fluorides and ω-fluorosulfonylperfluropolyoxaalkanoyl fluorides yielded 2-perfluoropolyoxaalkyl-substituted perimidines. Their basicity and sulfonation by sulfuric acid were studied.

Perimidines containing a perfluorinated substituent at the two position have been very little studied. The first examples of them were obtained comparatively recently by the reaction of 1,8-naphthylenediamine with trifluoroacetic anhydride or the acid chlorides of perfluorinated carboxylic acids [2]. The introduction of a perfluorinated substituent leads to a significant change in the chemical properties of the perimidine ring, and to the appearance of insecticidal and acaricidal activity in the compounds [3]. Very effective antistatic agents were observed among them [4].

We investigated the possible isolation of perimidine derivatives with a higher 2-perfluoropolyoxaalkyl substituent from 1,8-naphthylenediamine and the acid fluorides (I) and (II) of perfluorocarboxylic acids. It was established that 1,8-naphthylenediamine reacts with the ω-fluorosulfonylperfluoropolyoxaalkanoyl fluorides (Ia-c) and the perfluoropolyoxaalkanoyl fluorides (IIa-c) in the medium of boiling absolute diethyl ether with the formation of the 2-(ω-fluorosulfonylperfluoropolyoxaalkyl)perimidines (IIIa-c) or the 2-perfluoropolyoxaalkylperimidines (IVa-c) as the main products respectively with yields of 79-96%.



Ia-c, IIa-c

IIIa-c, IVa-c

I, III R=$FSO_2$; II, IV R=$CF_3$; a n=0, b n=1, c n=2

In contrast to the reaction of 1,8-naphthylenediamine with trifluoroacetic anhydride, the acid chlorides [2], and the acid bromides of fluoroacetic acids [5], the formation of the N,N'-diacyl derivatives of 1,8-naphthylenediamine is not observed in the given case. This can be explained by the larger steric hindrances with the entry of the second bulky ω-fluorosulfonylperfluoropolyoxaalkyl or perfluoropolyoxaalkyl substituent into the 1,8-naphthylenediamine molecule. The absence of monoacyl derivatives in the reaction products indicates the case of their cyclization in the experimental conditions.

Since the reaction of 1,8-naphthylenediamine with the acid fluorides (Ia-c) and (IIa-c) proceeds very regiospecifically, the perimidines (IIIa-c) and (IVa-c), which were isolated directly from the reaction mass, were chromatographically pure. They are readily identified by the doublet of the bands of stretching vibrations of the C=N and C=C bonds in the region

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[*] For communication 3, see [1].

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TABLE 1. Physicochemical Characteristics of the Perimidines (III) and (IV)

| Compound | mp, °C | Color | $R_f$ $Al_2O_3$ / chloroform | $pK_a$* | IR spectrum, ν, cm⁻¹ (in $CCl_4$) | | | | Found C, % | Empirical formula | Calculated, C, % | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | NH | C=N | C=C | $FSO_2$ | | | | |
| IIIa | 89—90 | Orange | 0,93 | 3,31 | 3435 | 1640 | 1600 | 1465 | 38,4 | $C_{15}H_7F_9N_2O_3S$ | 38,6 | 88 |
| IIIb | Oil | Red | 0,91 | 3,18 | 3430 | 1645 | 1600 | 1465 | 34,5 | $C_{18}H_7F_{15}N_2O_4S$ | 34,2 | 92 |
| IIIc | Oil | Dark-red | 0,84 | — | 3440 | 1645 | 1605 | 1470 | 31,8 | $C_{21}H_7F_{21}N_2O_5S$ | 31,6 | 96 |
| IVa | 85—86 | Orange | 0,95 | 3,31 | 3455 | 1640 | 1600 | | 42,8 | $C_{16}H_7F_{11}N_2O$ | 42,5 | 85 |
| IVb | Oil | Red | 0,95 | — | 3440 | 1643 | 1605 | | 35,1 | $C_{19}H_7F_{17}N_2O_2$ | 35,4 | 79 |
| IVc | Oil | Dark-red | 0,90 | 3,29 | 3440 | 1640 | 1600 | | 34,1 | $C_{22}H_7F_{23}N_2O_3$ | 33,7 | 91 |

*The value of the pKa of the compounds (IIIc) and (IVb) was not measured.

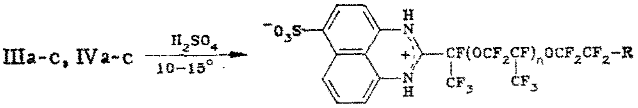
TABLE 2. Characteristics of the Sulfonic Acids (V) and (VI)

| Compound | mp, °C | IR spectrum, ν, cm⁻¹ | | | Found C, % | Empirical formula | Calculated C, % | Yield, % |
|---|---|---|---|---|---|---|---|---|
| | | C=N | $SO_3H$ | $SO_2F$ | | | | |
| Va | 74—75 | 1640—1660 | 1060 | 1445 | 33,4 | $C_{15}H_7F_9O_6N_2S_2$ | 33,0 | 93 |
| Vb | 64—65 | 1645—1665 | 1065 | 1460 | 30,1 | $C_{18}H_7F_{15}O_9N_2S_2$ | 29,8 | 89 |
| Vc | 45—47 | 1640—1670 | 1070 | 1460 | 28,3 | $C_{21}H_7F_{21}O_{12}N_2S_2$ | 27,9 | 94 |
| VIa | 82—84 | 1640—1655 | 1070 | — | 36,4 | $C_{16}H_7F_{11}O_4N_2S$ | 36.1 | 90 |
| VIb | 53—54 | 1640—1670 | 1075 | — | 32,2 | $C_{19}O_7F_{17}O_5N_2S$ | 32,1 | 95 |
| VIc | 51—52 | 1640—1670 | 1065 | — | 28,0 | $C_{21}H_7F_{23}O_6N_2S$ | 28,4 | 88 |

of 1590-1650 cm⁻¹ (Table 1), which is characteristic of 2-substituted perimidines [6]. The presence of the absorption band of the $FSO_2$ group at 1465-1470 cm⁻¹ [7] in the IR spectra of the products of the reaction of 1,8-naphthylenediamine with the ω-fluorosulfonylperfluoropolyoxaalkanoyl fluorides (Ia-c) indicates that the reaction proceeds exclusively at the fluorocarbonyl group of the compounds (Ia-c).

The introduction of the 2-(ω-fluorosulfonylperfluoropolyoxaalkyl) or 2-perfluoropolyoxaalkyl substituents into the molecule of the perimidine of yellow color leads to the deepening of the color of the individual compounds to orange and dark-red. We determined the values of the $pK_a$ of some of the synthesized perimidines by the method of potentiometric titration in a 30% (vol.) aqueous ethanol solution at 22°C (Table 1). For comparison, the value of the basicity of the unsubstituted perimidine was measured under the same conditions; it was equal to 5.91. As was to be expected, the introduction of the 4-fluorosulfonylperfluoro-2-methyl-3-oxabutyl radical at the two position of perimidine [compound (IIIa)] produces a decrease of 2.6 in the basicity. The replacement of the $CF_3$ group by the $SO_2F$ group has practically no effect on the basicity [compounds (IIIa) and (IVa)].

As in the case of the 2-difluoromethyl-, 2-trifluoromethyl-, and 2-perfluorohexylperimidines [8, 9], the sulfonation of the perimidine derivatives (III) and (IV) already proceeds exceptionally readily at the temperature of 10°C. On the basis of the data of the work [3], it can be assumed that the sulfonation reaction proceeds at the position six (seven). The yields of the monosulfonic acids (V) and (VI) reach 85-93%.



Va-c, VI a-c

III, V $R=FSO_2$; IV, VI $R=CF_3$; a n=0, b n=1, c n=2

The absorption bands of the sulfonyl group occur in the region of 1040-1060 cm⁻¹ in the IR spectra of the sulfonic acids (V) and (VI) in mineral oil. The sulfonic acids obtained exist in the form of crystal hydrates and probably as the internal salts; this is indicated by the presence of the band at 1640-1670 cm⁻¹, which is characteristic of the stretching vibrations of the C=N bonds in the perimidinium cations, in the IR spectra.

## EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer. The TLC was performed on aluminum oxide of IV degree of activity in chloroform. The $pK_a$ values were determined according to [10].

The characteristics of the compounds (III)-(VI) are presented in the Tables 1 and 2.

2-(ω-Fluorosulfonylperfluoropolyoxaalkyl)perimidines (IIIa-c) and 2-Perfluoropolyoxaalkylperimidines (IVa-c). To the solution of 0.79 g (5 mmole) of 1,8-naphthylenediamine in 20 ml of absolute diethyl ether are added 5 mmole of the ω-fluorosulfonylperfluoropolyoxaalkanoyl fluoride (Ia-c) or the perfluoropolyoxaalkanoyl fluoride (IIa-c) with intense stirring, at such a rate as to ensure the uniform boiling of the reaction mass. The mixture is maintained at 40°C for 30 min, and filtered. The filtrate is rapidly treated with 20-30 ml of a 5% aqueous solution of $NH_4OH$. The ether layer is separated. The chromatographically pure product, which is well sublimated *in vacuo*, is obtained after the evaporation of the solvent.

2-ω-Fluorosulfonylperfluoropolyoxaalkyl)perimidine-6(7)-sulfonic acids (Va-c) and 2-(Perfluoropolyoxaalkyl)perimidine-6(7)-sulfonic acids (VIa-c). To 10 ml of concentrated sulfuric acid ($d_4^{20}$ 1.82) are gradually added 3.2 mmole of the 2-(ω-fluorosulfonylperfluoropolyoxaalkyl)perimidine (IIIa-c) or the 2-perfluoropolyoxaalkylperimidine (IVa-c) at the temperature of 10-15°C. The dark-red solution obtained is stirred at room temperature for 10 min. Then, the reaction mass is poured onto 20 g of crushed ice with stirring. The dark-red precipitate is filtered off; it is dried at 35-40°C (2 mm of Hg stem) and recrystallized from alcohol.

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