DIRECT FUSION OF A TRIAZINE TO A PYRAZINE RING.
SYNTHESIS OF DERIVATIVES OF [1,2,4]TRIAZINO[5,6-b]QUINOXALINE*

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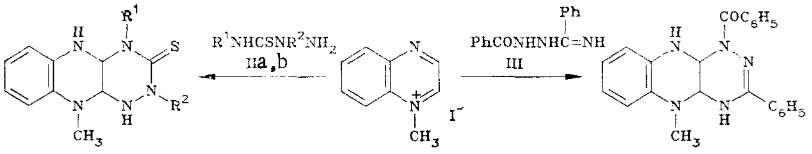
Derivatives of heterocyclic systems containing condensed triazine and pyrazine rings are known — pyrazino[1,2-*a*][1,3,5]triazines [2] and [1,2,3]triazino[3,4-*a*]quinoxalines [3], a nitrogen atom being common to the two condensed hetero rings in both cases. Systems in which the triazine and pyrazine rings have two carbon atoms in common were not described in the literature until very recently. Only at the end of 1983 did a communication appear on the formation of [1,2,4]triazino[5,6-b]quinoxalines in the thermolysis of formazans [4].

In the present investigation we have performed a directed synthesis of [1,2,4]triazino[5,6-b]quinoxaline derivatives based on the cyclization of the N-methylquinoxalinium cation (I) with 1,4-bifunctional nucleophiles. As the synthons for the fusion of the triazine ring we used the substituted thiosemicarbazides (IIa, b), and also the benzamidrazone (III).

The reaction of cation (I) with the 2-substituted thiosemicarbazides (IIa, b) in ethanol at room temperature in the presence of triethylamine led to the formation of the 10-methyl-1,2,3,4*a*,5,10,10*a*-octahydro[1,2,4]triazino[5,6-b]quinoxaline-3-thiones (IVa, b). In the reaction of the 1-benzoyl-substituted benzamidrazone (III), 5-methyl-1,4,4*a*,5,10,10*a*-hexahydro-[1,2,4]triazino[5,6-b]quinoxaline (V) with the opposite orientation of the triazine ring relative to the N-methyltetrahydropyrazine ring was formed.



IVa,b

II, IV a) $R^1=C_6H_5$, $R^2=CH_2C_6H_5$; b) $R^1=H$, $R^2=CH_3$

The structures of compounds (IVa, b) and (V) were established on the basis of their ^1H and ^{13}C NMR spectra. The fusion of the triazine ring to a quinoxaline ring was shown, primarily, by the chemical shifts (CSs) of the nodal carbon atoms of compound (IVb) at 59.0 and 65.3 ppm, these values being close to those for 5-methyl-5,5*a*,6,11,11*a*,12-hexahydroquinoxalino[2,3-b]quinoxaline (58.1 and 63.9 ppm) in which two hydrogenated pyrazine rings are joined [1]. The CSs of the nodal carbon atoms of compounds (IVa) (66.5 and 66.7 ppm) and (V) (53.3 and 63.5 ppm) also correspond to structures with a fused-on six-membered 1,2,4-triazine ring, and not to a 5-membered imidazole ring, for which weaker-field CSs in the region of 72-79 ppm are characteristic [5]. Furthermore, the lower values of the vicinal constants between the nodal protons, $^3J_{4a,10a}$ 3.5-4 Hz in the PMR spectra of compounds (IVa, b) and (V), are also characteristic for tetrahydropyrazines condensed with 6-membered heterocycles [1]. The mutual orientation of the triazine and pyrazine rings follows from the fact that, in the PMR spectra of compounds (IVa) and (V), the signals of both nodal protons undergo splitting on the protons of the neighboring NH groups.

All the compounds had satisfactory elementary analyses.

We give: compound, mp, °C, yield, %: (IVa), 152-154, 71; (IVb), 173-175, 90; (V), 194-196, 48.

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*Communication 13 of the series "Cyclization of N-alkylazinium cations with bifunctional nucleophiles." For communication 12, see [1].

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0009-3122/84/2009-1057$08.50

LITERATURE CITED

1. O. N. Chupakhin, V. N. Charushin, M. G. Ponizovskii, and L. M. Naumova, Khim. Geterotsikl. Soedin., No. 5, 706 (1984).
2. W. T. Flowers, R. Franklin, R. N. Haszeldine, and R. J. Perry, J. Chem. Soc., Chem. Commun., No. 14, 567 (1976).
3. Yu. S. Andreichikov, S. G. Pitirimova, and T. N. Tomakova, USSR Inventors' Certificate No. 809,848; Byull. Izobret., No. 7, 281 (1982).
4. L. V. Shmelev, M. N. Stopnikova, and A. V. Kessenikh, in: Advances in the Chemistry of Nitrogen Heterocycles [in Russian], Rostov-on-Don (1983), p. 220.
5. V. N. Charushin, V. G. Baklykov, O. N. Chupakhin, N. N. Vereshchagina, L. M. Naumova, and N. N. Sorokin, Khim. Geterotsikl. Soedin., No. 12, 1684 (1983).

β-PERFLUOROALKYLIMIDOCARBOCYANINES

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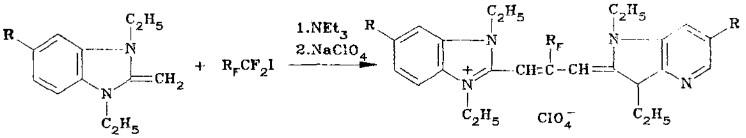
We have found that, in contrast to other nitrogen heterocycles [1], the methylene bases obtained from quaternary salts of benzimidazole [2] react with perfluoroalkyl iodides without irradiation. This forms β-perfluoroalkylimidocarbocyanines containing one CF_2 group less than in the initial perfluoroalkyl iodides. A solution of 10 mmole of the appropriate methylene base, 7 mmole of perfluoroalkyl iodide, and 5 mmole of anhydrous triethylamine in 10 ml of anhydrous acetonitrile was stirred at 20°C for 4 h. Then 20 mmole of $NaClO_4$ in 2 ml of water was added to the mixture. The dye was extracted with dichloroethane, and the extract was washed with 200 ml of water and dried with $MgSO_4$. The solvent was evaporated off in vacuum and the dye was crystallized from ethanol. Imidocarbocyanines substitute in the β position have scarcely been studied.



I R=H, $R_F=CF_3$; II R=H, $R_F=C_2F_5$; III $R=SO_2CF_3$, $R_F=C_2F_5$

It is interesting that, in contrast to the thia-, quino-2-, and indocarbocyanines, the introduction of perfluoroalkyl groups into the β position of an imidocarbocyanine scarcely affects the absorption maximum (shifts of 1-3 nm). The extinctions in the spectra of the dyes (I-III) had lower values, which shows the existence of pronounced steric hindrance.

The following details are given for the dyes synthesized: compound, mp, °C, λ_{max}, $\varepsilon \cdot 10^{-4}$ (ethanol), yield, %: 2-[3-(1,3-diethylbenzimidazolin-2-ylidene)-2-trifluoromethylprop-1-enyl]-1,3-diethylbenzimidazolium perchlorate (I), 167-168 (decomp.), 498, 2.69, 40; 2-[3-(1,3-diethylbenzimidazolin-2-ylidene)-2-perfluoroethylprop-1-enyl]-1,3-diethylbenzimidazolium perchlorate (II), 169-170 (decomp.), 500, 2.33, 33; and 2-[3-(1,3-diethyl-6-trifluoromethylsulfonylbenzimidazolin-2-ylidene)-2-perfluoroethylprop-1-enyl]-1,3-diethyl-6-trifluoromethylsulfonylbenzimidazolium perchlorate (III), 227-228 (decomp.), 526, 4.51, 68. The results of elementary analysis for C, H, and F corresponded to the calculated figures.

LITERATURE CITED

1. L. M. Yagupol'skii, S. V. Pazenok, and N. V. Kondratenko, Zh. Obshch. Khim., 19, 2223 (1983).
2. J. Bourson, Bull. Soc. Chim. Fr., No. 1, 158 (1971).

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