5. J. H. Beynon, R. M. Caprioli, and T. Ast, Int. J. Mass Spectrom. Ion Phys., 7, 88 (1971).
6. A. Maquestiau, Y. van Haverbeke, R. Flammang, and A. Menu, Bull. Soc. Chim. Belg., 88, 53 (1979).
7. A. Atmani, J. L. Aubagnac, and V. Pellegrin, Org. Mass Spectrom., 15, 533 (1980).
8. M. A. Baldwin, J. Gilmore, and M. N. Mruzek, Org. Mass Spectrom., 18, 127 (1983).
9. N. S. Kulikov and M. S. Bobyleva, Abstracts of Papers of the IVth All-Union Conf. on Mass Spectrometry, Sumy (1986), p. 118.
10. R. A. Khmel'nitskii and P. B. Terent'ev, Ust. Khim., 48, 854 (1979).
11. S. I. Bobrovskii, E. V. Babaev, and E. G. Bundel', Vestn. Mosk. Univ., Ser. 2: Khim. 25, 222 (1985).
12. P. M. Draper and D. B. Maclean, Can. J. Chem., 46, 1487 (1968).
13. G. H. Lord and B. S. Milard, Org. Mass Spectrom., 2, 547 (1969).
14. E. V. Babaev, "Synthesis of Nitroindolizines, Study of Their Structure and Ambiphilic Reactivity," Dissertation, MGU, Moscow (1987).
15. S. I. Bobrovskii, E. V. Babaev, and Yu. G. Bundel', Khim. Geterotsikl. Soedin., No. 2, 203 (1987).

SYNTHESIS OF 4-NITROSOPYRAZOLES FROM N-SUBSTITUTED N-NITROSOHYDRAZINES

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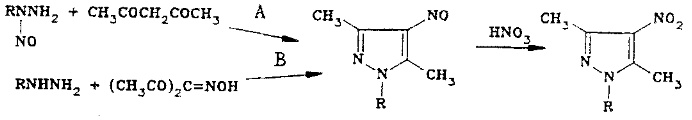
UDC 547.773

Reaction of N-nitrososubstituted propyl- and benzylhydrazines with acetylacetone gives the corresponding 4-nitrosopyrazoles.

The reaction of nitrosohydrazines, $RN(NO)NH_2$ with carbonyl compounds is known to form N-nitrosohydrazones [1, p. 70].

Study of the reaction of N-nitrososubstituted propyl- and benzylhydrazines with acetylacetone showed that besides the expected hydrazones, 1-propyl- and 1-benzyl-3,5-dimethyl-4-nitrosopyrazoles (Ia, b) are formed. The structure of Ia, b was confirmed by physicochemical and spectral properties identical to those of characteristic nitrosopyrazoles obtained by known methods from isonitrosoacetylacetone and propyl- or benzylhydrazine by analogy to the synthesis of 3,5-dimethyl-4-nitroso-1-phenylpyrazole [2].



I, II a $R=C_3H_7$; b $R=C_6H_5CH_2$ Ia, b IIa,b

Nitrosopyrazoles Ia, b are yellow liquids and a mixture of monomeric and dimeric forms. The monomeric forms of Ia, b could not be separated although for some nitrosopyrazoles the monomeric forms have been obtained [3, p. 236]. The structure of the reaction products of nitrosohydrazines with acetylacetone also was confirmed by oxidation with nitric acid of Ia to 3,5-dimethyl-4-nitro-1-propylpyrazole (IIa) by the method of [2].

Formation of nitrosopyrazoles from nitrosohydrazines and acetylacetone can be viewed as a result of intramolecular 1,4-migration of the nitroso group in the nitrosohydrazone which is formed in the initial step. The possibility of such rearrangement was shown earlier for the reaction of isonitrosopyrazolones from nitrosohydrazines and acetoacetic ester

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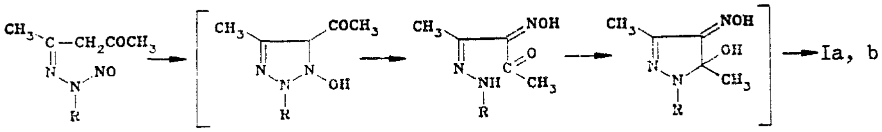
[4]. It can be assumed that 1,4-migration of the nitroso group occurs through a 5-centered complex with participation of the carbon atom of the activated methylene group. Cyclization with elimination of water from the vicinally located oxy- and isonitroso group, known in the chemistry of pyrazoles, leads to nitrosopyrazoles [5, p. 77].



An alternative mechanism, the formation of nitrosohydrazone, its denitrosation, and subsequent nitrosation of the active methylene group, can be proposed. For verification of this possibility, the syntheses of nitrosopyrazoles Ia, b in alcoholic media in the presence or in the absence of urea (urea upon contact with nitric acid decomposes to CO_2 and N_2) were done. In the syntheses with urea, the reaction flasks were connected to gas-measuring burettes, but evolution of gas was not noticed. In experiments with benzylnitrosohydrazine, the yields of nitrosopyrazole Ib were similar (after 3 days, 60% without urea and 57% with urea). The reactions with propylnitrosohydrazine in aqueous alcohols proceeded more slowly than in the presence of solvents. Urea also had an inhibiting effect, the reaction mixture in its presence became green markedly slower by comparison with the parallel experiment. After 7 days, the yields of nitrosopyrazoles Ia were 48% without urea and 30% with urea. From the syntheses with benzylnitrosohydrazine, urea was recovered quantitatively, with propylnitrosohydrazine, 90%. Such results indicate the absence of intermolecular transnitrosation with separation of free nitric acid.

EXPERIMENTAL

IR spectra were taken on a Specord IR-75 (in CCl_4), UV spectra were recorded on a SF-26 instrument (in ethanol). Elemental analyses for the compounds obtained corresponded to those calculated.

3,5-Dimethyl-4-nitroso-1-propylpyrazole (Ia, $C_8H_{13}N_3O$). A. A solution of 2.06 g (20 mmole) N-nitroso-N-propylhydrazine [6] in 20.5 ml (200 mmole) acetylacetone was left at room temperature for 5 days. After removal of acetylacetone in vacuum, the green oily liquid which remained (3.38 g) consisted of a few substances by TLC. Nitrosopyrazole was separated using a chromatographic column (SiO_2, L40/100μ, eluent CCl_4–$CHCl_3$, 1:1). Upon chromatographing Ia, b, a blue band with a yellowish-green tail developed. After removal of solvent from the blue fraction, a green liquid again was obtained. Yield 1.97 g (59%). A sample for analysis was obtained after repeated chromatography; d_4^{20} 1.0483; R_f 0.74 (Silufol UV-254, eluent was ethylacetate). UV spectrum, λ_{max}, nm (log ε): 207 (3.86), 306 (4.16), 670 (1.76).

B. A mixture of 2.06 g (20 mmole) N-nitroso-N-propylhydrazine, 20.5 ml (200 mmole) acetylacetone, 1.2 g (20 mmole) urea, 10 ml 96% ethanol, and 10 ml water was left at room temperature for 7 days. After removal of ethanol, water, and acetylacetone in vacuum, the residue was treated with methylene chloride. The crystals (1.05 g, 87%) were filtered and identified as urea. From the solution after removal of CH_2Cl_2 and chromatographic purification, 1.0 g (30%) of nitrosopyrazole Ia was separated. Carrying out the reaction under these same conditions but without urea, the yield of nitrosopyrazole Ia was 1.6 g (48%).

C. To 5.55 g (75 mmole) propylhydrazine in 15 ml water with cooling by ice and stirring was added a solution of 9.7 g (75 mmole) isonitrosoacetylacetone in 15 ml water at 5-8°C. After 30 min the reaction mixture was extracted with hexane, then ether. The extracts were dried over $MgSO_4$. A yellow liquid was separated from the extracts (Ia), 7 g from hexane, 2.96 g from ether. Total yield 80%.

3,5-Dimethyl-4-nitro-1-propylpyrazole (IIa, $C_8H_{13}N_3O_2$). To 9.75 g (155 mmole) 100% nitric acid were added dropwise 5.2 g (31 mmole) nitrosopyrazole Ia, keeping the temperature near 0°C. After 40 min ice was added to the mixture which was extracted with ether. The ether extract was washed with 2% aqueous sodium bicarbonate until neutral. The extract was dried over $MgSO_4$. After removal of ether, 3.7 g (65%) of a yellow liquid were obtained. Nitropyrazole IIa was purified by distillation, yield 2.2 g (40%); mp 142-144°C (4-5 mm Hg std.); n_D^{20} 1.5220; d_4^{20} 1.1315. UV spectrum, λ_{max} 282 nm (log ε 4.02).

1-Benzyl-3,5-dimethyl-4-nitrosopyrazole (Ib, $C_{12}H_{13}N_3O$). A. This was synthesized analogously to the nitrosopyrazole Ia by method A, but the mixture of N-benzyl-N-nitrosohydrazine [7] and acetylacetone was kept for 3 days. The reaction product was a green liquid, yield after purification on a column 60%; d_4^{20} 1.1218. R_f 0.86 (Silufol UV-254; eluent ethylacetate—chloroform, 1:4). UV spectrum, λ_{max}, nm (log ε): 205 (4.21), 304 (4.14), 670 (1.73).

B. This was synthesized with addition of urea analogously to Ia by method B, but the solvent was ethanol only. Treatment was done for three days. Urea was recovered quantitatively. Yield of nitrosopyrazole Ib, 57% (in the absence of urea, 60%).

C. The synthesis was done as described for Ia by method C, but the temperature during addition of the isonitrosoacetylacetone was kept below 30°C, and it was left for 1 day. From 6.1 g (50 mmole) benzylhydrazine and 6.45 g (50 mmole) isonitrosoacetylacetone, 8.8 g (82%) of green liquid were obtained after chromatographic separation.

LITERATURE CITED

1. B. V. Ioffe, M. A. Kuznetsov, and A. A. Potekhin, Chemistry of Organic Derivatives of Hydrazine [in Russian], Khimiya, Leningrad (1979).
2. L. Wolff, Annalen., 325, 129 (1902).
3. K. Schofield, M. R. Grimmett, and B. R. T. Keene, The Azoles (Heteroaromatic Nitrogen Compounds), Cambridge Univ. Press, London—New York (1975).
4. G. A. Lanovaya, A. S. Mashikhina, V. A. Fedorova, V. P. Mikheeva, and O. D. Bondarenko, Zh. Org. Khim., 23, 2004 (1987).
5. R. Elderfield (ed.), Heterocyclic Compounds, Vol. 5 [Russian translation], IL., Moscow (1961).
6. S. N. Danilov, G. A. Lanovaya, and V. I. Beresneva, Zh. Org. Khim., 44, 2307 (1974).
7. Th. Curtius, Berichte, 33, 2561 (1900).

ELECTRON STRUCTURES OF AZOLOISOINDOLES WITH A NODAL NITROGEN ATOM.

2.* TRIAZOLO- AND TETRAZOLOISOINDOLES

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The electron structures of N-methyl-substituted triazolo- and tetrazoloisoindoles with a modal nitrogen atom were calculated by the Pariser—Parr—Pople (PPP) and CNDO/2 methods. On the basis of an analysis of the canonical and localized MO it was concluded that the examined compounds, to a first approximation, can be regarded as 1,2-disubstituted isoindoles, i.e., 10 π-electron systems rather than 14π-electron systems, as one should have expected on the basis of the structural formulas. It was also established that the degree of conjugation through the nitrogen atoms of the pyrrole type depends on their position. Equalization of the bonds and intensification of the interannular conjugation occur in the first singlet excited state of all of the investigated structures. The calculated data obtained are in good agreement with the known chemical properties and UV spectra of derivatives of triazolo- and tetrazoloisoindoles.

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*See [1] for Communication 1.

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