REACTION OF SUCCINONITRILE WITH ANHYDROUS HYDRAZINE

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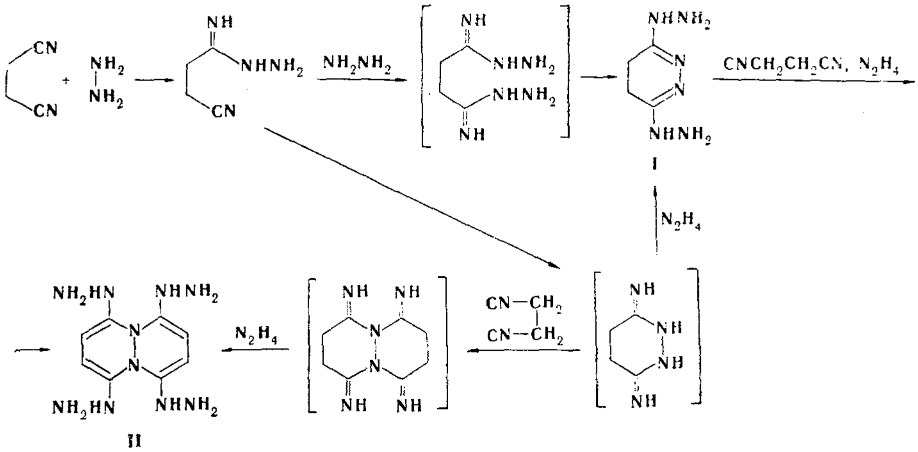
3,6-Dihydrazino-4,5-dihydropyridazine and 1,4,5,8-tetrahydrazino-pyridazino[1,2-*a*]pyridazine were obtained by the reaction of succinonitrile with anhydrous hydrazine.

It is known that amidrazones are formed in the reaction of nitriles with hydrazine, but up until now it was impossible to isolate a diamidrazone in the reaction of malononitrile [1] and succinonitrile with hydrazine [2].

In the present study we have investigated the reaction of succinonitrile with anhydrous hydrazine at various temperatures and a reagent molar ratio of 1:2. The scheme of the formation of the possible reaction products can be represented as follows:



Pyridazines I and II were identified among the reaction products. The linear diamidrazone of succinic acid cannot be isolated, although the IR spectra of the reaction products at 80°C, recorded 15, 30, 45, and 60 min after the start of the reaction, contain an absorption band at 1690 cm^{-1} that characterizes a noncyclic C=N bond [3]. The reaction mechanism was not studied in detail.

The mass spectrum* of I contained an intense $[M]^+$ molecular ion peak with m/e 142, which coincides with the value calculated for $C_4H_{10}N_6$. Absorption with a maximum at 265-275 nm, which characterizes ring conjugation, is observed in the UV spectrum. Compound I reacts with polyethyleneimine with the liberation of ammonia, i.e., it contains the fragment of an amidine grouping; it also reacts with methyl iodide in absolute ethanol to give a monomethiodide, i.e., it contains a tertiary nitrogen atom.

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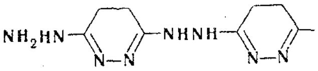
The mass spectrum of II contains an intense $[M]^+$ molecular ion peak with m/e 252, which corresponds to $C_8H_{16}N_{10}$. An absorption maximum at 310 nm is observed in the UV spectrum of an aqueous solution of II, while the absorption maximum is lowered (275 nm) in solution in 5% hydrochloric acid; this is characteristic for aromatic amino compounds.

In contrast to I, II does not react with polyethyleneimine. The  $NHNH_2$ structure is possible for the compound with molecular ion 252, but the spectral and chemical properties of this compound should be similar to those of I. The presence of hydrazine groups in I and II is confirmed by the formation of a hydrazone with m-nitrobenzaldehyde.

By varying the reaction conditions it was shown that excess hydrazine in the reaction mixture favors the production of dihydropyridazine I. Thus the yield of I was 20% after 170 h for a succinonitrile–hydrazine ratio of 1:2, and the yield was 50% after 120 h (at 20°) for a ratio of 1:4. The yield of II under these conditions does not exceed 5%. An increase in the temperature promotes the formation of pyridazino[1,2-*a*]pyridazine: the yield of II after 5 h at 80° is 25%.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer. The UV spectra of aqueous solutions (c $1 \cdot 10^{-3}$ M) were recorded with an EPS-3T spectrophotometer. The mass spectra were recorded with an MKh-1309 spectrometer. Succinonitrile was obtained by the method in [4].

A mixture of 0.1 mole of succinonitrile and 0.2 mole of anhydrous hydrazine was maintained at 20, 60, and 80° for various times in a reactor sealed with a ground-glass stopper. The reaction mixture was treated with ether in order to dissolve the unchanged nitrile, after which dihydropyridazine I was extracted with hot absolute ethanol. Alcohol-insoluble pyridazino[1,2-*a*]pyridazine was found in the residue.

3,6-Dihydrazino-4,5-dihydropyridazine (I). This compound was obtained as a slightly pinkish powder with mp 151-152° (decomp. from absolute ethanol). It was quite soluble in water, poorly soluble in methanol, and dissolved in absolute ethanol on heating; it was in ether, benzene, chloroform, acetone, and n-hexane. On standing in air, it decomposed with nitrogen evolution, but it did not change for several months when it was stored in vacuo. UV spectrum, λ_{max} 265-275 nm (log ε 4). IR spectrum: 3330, 3300, 3230, and 1630 cm^{-1}. Found: C 34.0; H 7.0; N 58.4%. $C_4H_{10}N_6$. Calculated: C 33.8; H 7.0; N 59.2%. The monopicrate had mp 152-153° (decomp. from ethanol). The dipicrate had mp 176-177° (decomp. from ethanol). Found: C 32.3; H 2.9; N 28.0%. $C_4H_{16}N_6 \cdot 2C_6H_3N_3O_7$. The dihydrochloride had mp 155° (decomp. from water). The monomethiodide had mp 134° (decomp. from absolute ethanol). m-Nitrobenzaldehyde monohydrazone had mp 221-222° (from water).

1,4,5,8-Tetrahydrazinopyridazino[1,2-*a*]pyridazine (II). This compound was obtained as shiny yellow crystals with mp 186° (from water). UV spectrum: λ_{max} 310 nm (log ε 4.4); in solution in 5% hydrochloric acid λ_{max} 275 nm (log ε 4.4). IR spectrum: 3300, 3200, and 1610 cm^{-1}. Found: C 38.1; H 6.5; N 55.4%. $C_8H_{16}N_{10}$. Calculated: C 38.0; H 6.4; N 55.6%. The dipicrate had mp 136° (from ethanol containing water; sublimed). Found: C 34.5; H 4.1; N 37.4%. $C_8H_{16}N_{10} \cdot 2C_6H_3N_3O_7$. Calculated: C 34.9; H 3.9; N 37.8%. m-Nitrobenzaldehyde dihydrazone had mp 164-165° (from water).

LITERATURE CITED

1. Todashi Sato, J. Org. Chem., 24, 963 (1959).
2. T. Kauffmann, and L. Ban, Ber., 99, 2600 (1966).
3. H. Brown and D. Pilipovich, J. Amer. Chem. Soc., 82, 4700 (1960).
4. A. P. Terent'ev and A. M. Kost, Zh. Obshch. Khim., 21, 1867 (1951).