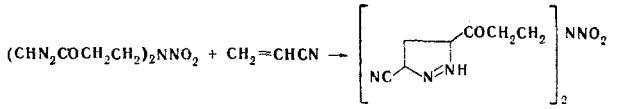
REACTION OF BISDIAZO KETONES WITH ACRYLONITRILE

A. L. Fridman, G. S. Ismagilova,
V. S. Zalesov, N. A. Kolobov,
and V. V. Larikov

UDC 547.776

Diazomethane and ethyl diazoacetate react with acrylonitrile to give the corresponding pyrazolines [1-3]. We have studied the behavior in this reaction of bisdiazo ketones, particularly the previously synthesized nitro-substituted bisdiazo ketones [4].

Diazo ketones that contain an N-nitramine group in the γ position relative to the diazo group could not be made to react with acrylonitrile. This is evidence for lowering of the electron density on the carbon atom in the conjugated CNN system under the influence of the nitramine group. Removal of the nitramine fragment to the δ position facilitates the normal occurrence of the reaction to give the previously unknown bispyrazolines.



EXPERIMENTAL

1,7-Bis(3-cyano-Δ^2-pyrazolin-5-yl)-4-nitro-4-aza-1,7-heptanedione (I). A solution of 1.0 g (3.94 mmole) of 1,9-bisdiazo-5-nitro-5-azo-2,8-nonanedione in 10 ml of acrylonitrile was held at room temperature for 48 h, after which the crystalline precipitate was squeezed and washed with cold acrylonitrile and ether to give 0.97 g (68%) of a product with mp 154-155° (dec., from dichloroethane). IR spectrum: ν_{NO_2} 1520, 1300, 1290; $\nu_{C=O}$ 1705, 1670; $\nu_{C\equiv N}$ 2260; $\nu_{N=N}$ 1565; ν_{NH} 3370 cm^{-1}. Found: C 44.7; H 4.4; N 27.4%. $C_{14}H_{16}N_8O_4$. Calculated: C 46.5; H 4.6; N 31.1%.

1,10-Bis(3-cyano-Δ^2-pyrazolin-5-yl)-4,7-dinitro-4,7-diaza-1,10-decanedione (II). This compound was similarly obtained in 70% yield from 1,12-bisdiazo-5,8-dinitro-5,8-diaza-2,11-dodecanedione and had mp 157-158.5° (dec.). IR spectrum: ν_{NO_2} 1520, 1295, 1280; $\nu_{C=N}$ 1705, 1675; $\nu_{C\equiv N}$ 2260; ν_{N-N} 1560; ν_{NH} 3350 cm^{-1}. Found: C 42.8; H 4.6; N 31.2%. $C_{16}H_{20}N_{10}O_6$. Calculated: C 42.6; H 4.5; N 31.3%.

1,7-Bis(1-acetyl-3-cyano-Δ^2-pyrazolin-5-yl)-4-nitro-4-aza-1,7-heptanedione (III). A 1.0-g (2.78 mmole) sample of I was held in 15 ml of acetyl chloride for 30 days, after which the oily product was dissolved in acetone and precipitated carefully with water to give 0.12 g (10%) of a crystalline substance with mp 139-140° (dec., from aqueous acetone). IR spectrum: ν_{NO_2} 1515, 1290; $\nu_{C=O}$ 1695; $\nu_{C\equiv N}$ 2255 cm^{-1}. Found: C 48.6; H 4.5; N 25.2%. $C_{18}H_{10}N_8O_6$. Calculated: C 48.6; H 4.4; N 25.2%.

LITERATURE CITED

1. K. Auwers and O. Ungemach, Ber., 66, 1198 (1933).
2. S. M. Gurvich and A. P. Terent'ev, Zh. Obshch. Khim., No. 1, 409 (1953).
3. V. I. Ivanskii, A. I. D'yakonov, and A. L. Kuleshov, Zh. Organ. Khim., 7, 2108 (1971).
4. A. L. Fridman, G. S. Ismagilova, and F. A. Gabitov, USSR Author's Certificate No. 308,010 (1968); Byull. Izobr., No. 21 (1971).

Perm State Pharmaceutical Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, p. 424, March, 1973. Original article submitted May 11, 1972.