SOME NITRATION PROPERTIES OF 1-METHYLPYRAZOLES

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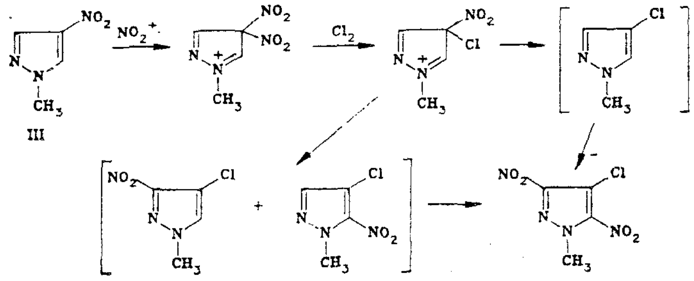
We have nitrated 5-R-1-methylpyrazoles (where R = H, CH_3, COOH) in oleum or monohydrate at temperatures above 100°C to obtain, in turn, 4-nitro- and 3,4-dinitro-1-methylpyrazoles [1, 2].

It has been shown that the single nitration product of 4-bromo-1,5-dimethylpyrazole under the same conditions is 1,5-dimethyl-4-nitropyrazole (I) and that 1,5-dimethyl-3,4-dinitropyrazole (II) is not formed. Even when nitrating 4-nitropyrazole I in oleum in the presence of molecular bromine the dinitro compound II was not formed. In this connection we have carried out the nitration of 1-methyl-4-nitropyrazole (III) in 20% oleum with a five times excess of concentrated nitric acid at 120°C and with passage of chlorine through the reaction mixture. The product was 1-methyl-3,5-dinitro-4-chloropyrazole (IV) in 20% yield. Compound III was unaffected by chlorination in oleum.

The above data suggests that attack of the 1-methyl-4-nitropyrazoles by the nitronium cation involves ipso-dinitro-σ-complexes whose further conversions depends upon the reaction conditions. In the absence of extra electrophiles (bromine, chlorine) rearrangement gives 1-methyl-3,4-dinitropyrazoles. In the presence of a halogen in the reaction mixture it apparently occurs via substitution of one nitro group in the ipso-dinitro complex to form a new σ-complex, the conversion of which is determined by the nature of the halogen. For the bromo containing ipso-σ-complex elimination of halogen can occur (as for nitrodebromination of 4-bromopyrazoles). The nitrochloro-σ-complex can eliminate the nitro group or undergo rearrangement. Subsequent nitration leads to the formation of IV.



IV

Compound III (3.81 g, 0.03 mole) was added at 20°C to a nitrating mixture prepared from nitric acid (99%, 6.5 ml) and oleum (20%, 40 ml). Gaseous chlorine was then bubbled through the reaction mixture for 3 h at 120°C. The product was cooled and poured onto ice. The precipitate was filtered off, washed with water, and dried to give IV (1.25 g, 20%) with mp 99-101°C. The identity of the material was confirmed by the absence of melting point depression when mixed with a known [3] sample and the correspondence of their PMR spectra.

LITERATURE CITED

1. M. A. Andreeva, Yu. A. Manaev, R. Ya. Mushii, V. P. Perevalov, V. I. Seraya, and B. I. Stepanov, Zh. Obshch. Khim., 50, 2106 (1980).
2. V. P. Perevalov, Yu. A. Manaev, M. A. Andreeva, L. I. Baryshnenkova, and B. I. Stepanov, Transactions of the D. I. Mendeleev Chemico-technological Institute, No. 141, 58 (1986).
3. Yu. A. Manaev, M. A. Andreeva, V. P. Perevalov, B. I. Stepanov, V. A. Dubrovskaya, and V. I. Seraya, Zh. Obshch. Khim., 52, 2592 (1982).

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