

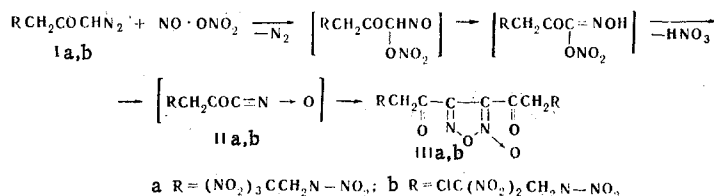
REACTION OF NITRODIAZO KETONES WITH
NITROGEN TETROXIDE

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UDC 547.79.07.543.422.4

It is known that phenylbenzoyldiazomethane forms phenyldinitromethane on reaction with nitrogen tetroxide [1]. We have attempted to extend this reaction to nitrodiazo ketones (Ia, b). The latter also react readily with nitrogen tetroxide. However, disubstituted furoxanes (IIIa,b) rather than gem-dinitromethane derivatives, in analogy with [1], were obtained as final products. All of the structural fragments in the nitroketone molecule were retained after splitting out of a diazo group.

It may be assumed that cyclization to the furoxane ring occurs as a result of dimerization of the intermediate N-oxide (II) [2].



The structures of the furoxanes were confirmed by spectroscopy [IIIa,b, respectively: 1020, 1015 (furoxane ring), 1482, 1470 ($N < \overset{O}{O}$); 1580, 1295 and 1575, 1282 ($N-NO_2$); 1605, 1305 [$C(NO_2)_3$]; 1600, 1315 [$C(NO_2)_2$]; 1635, 1615 ($C=N$); 1740, 1730, 1755 (carbonyl)].

EXPERIMENTAL

Bis(3,5,5,5-tetranitro-3-azavaleryl)furoxane (IIIa). A 1.12-g sample of 1-diazo-4,6,6,6-tetranitro-4-aza-2-hexanone (Ia) was added to a solution of nitrogen tetroxide in 30 ml of dry dichloroethane at -5 to -10°C, and the mixture was stirred at -5 to 0° for 30 min and allowed to stand at room temperature for 1 h. The solvent was removed along with excess nitrogen tetroxide in vacuo at 15-20 mm. The residue was stirred with carbon tetrachloride, squeezed, washed with dichloroethane, dried, and recrystallized from dichloroethane-carbon tetrachloride (4:1) to give 0.81 g (65%) of a product with mp 152.5-153.5° (decomp.). Found %: C 20.2; H 1.3; N 27.7. $C_{16}H_8N_{15}O_{20}$. Calculated %: C 19.4; H 1.3; N 27.1.

Bis(5-chloro-3,5,5-trinitro-3-azavaleryl)furoxane (IIIb). This was similarly obtained in 62% yield from 1-diazo-6-chloro-4,6,6-trinitro-4-aza-2-hexanone (Ib) and had mp 136-138° (decomp.). Found %: C 22.8; H 1.4; Cl 13.6; N 26.8. $C_{10}H_8Cl_2N_{10}O_{16}$. Calculated %: C 22.4; H 1.5; Cl 13.3; N 26.2.

The starting diazo ketones were prepared from the acid chlorides of the appropriate nitrocarboxylic acids [3] and diazomethane in ether by the Arndt-Eistert method [4]; Ia with mp 132-133° (from benzene-chloroform) was obtained in 91% yield. Found %: C 19.6; H 1.3; N 32.0. $C_5H_5N_7O_9$. Calculated %: C 19.5; H 1.6; N 31.9. Compound Ib with mp 87-88° (from methanol) was obtained in 86% yield. Found %: C 20.3; H 1.7; N 28.0. $C_5H_5ClN_6O_7$. Calculated %: C 20.2; H 1.7; N 28.4.

Permsk State Pharmaceutical Institute. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 6, p. 859, June, 1971. Original article submitted November 27, 1970.

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