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UNUSUAL REACTION OF NITROSO COMPOUNDS WITH THE BIS(AMINOOXY)METHANE/DIBROMOISOCYANURATE SYSTEM

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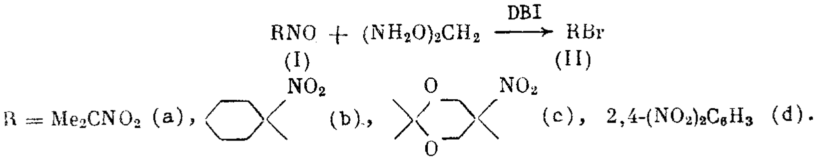
The reaction of nitroso compounds with bis(aminooxy)methane in the presence of dibromoisocyanurate gives the products of the formal replacement of the nitroso group by bromine.

In previous work [1], we have shown that the reaction of various nitroso compounds, including pseudonitrols, with methoxyamine in the presence of dibromoisocyanurate (DBI) gives the corresponding N-methoxydiazene N'-oxides in 10-70% yield.

In an attempt to employ bis(aminooxy)methane (BAM) [2] or its salts instead of methoxyamine, we observed a different pathway for this reaction. Pseudonitrols (Ia)-(Ic) react with BAM to give the products of the formal replacement of the nitroso group by bromine (IIa)-(IIc) in 30-40% yield instead of the expected methylenebis(oxydiazene) oxides.



$$\underset{(I)}{RNO} + (NH_2O)_2CH_2 \xrightarrow{DBI} \underset{(II)}{RBr}$$

The reaction of BAM with 2,4-dinitronitrosobenzene gave the corresponding bromide (IId) in only 4% yield.

These nitroso compounds do not react with DBI to give halogen derivatives in the absence of BAM.

Bromides (IIa)-(IId) were identified by comparison with authentic samples by IR and PMR spectroscopy, melting point, and thin-layer chromatography.

EXPERIMENTAL

The IR spectra were taken neat or for KBr pellets on a Specord spectrophotometer. The PMR spectra were taken for $CDCl_3$ solutions on a Tesla BS-467 spectrometer at 60 MHz relative to HMDS as the internal standard.

2-Bromo-2-nitropropane (IIa). a. A sample of 1 g (3.5 mmoles) DBI and 0.26 g (1.7 mmoles) $CH_2(ONH_2)_2 \cdot 2HCl$ were added to a solution of 0.4 g (3.4 mmoles) 2-nitro-2-nitrosopropane (Ia) in 20 ml CH_2Cl_2 at ~20°C, stirred for 6 h, and left overnight. The precipitate was filtered off and the filtrate was evaporated. The residue was subjected to chromatography on silica gel (R_f 0.66 with chloroform as eluent) to give 0.22 g (39%) (IIa) as an oil.

b. A sample of 1.22 g (4.25 mmoles) DBI was added with stirring to a solution of 0.5 g (4.2 mmoles) (Ia) in 20 ml CH_2Cl_2 at ~20°C and then a solution of 0.17 g (2.1 mmoles) $CH_2(ONH_2)_2$ in 20 ml CH_2Cl_2 was added dropwise. The reaction mixture was maintained for 72 h. The precipitate was filtered off and the filtrate was evaporated. The residue was subjected to chromatography to give 0.28 g (39%) (IIa). IR spectrum (ν, cm^{-1}): 3000, 2850, 1550, 1460, 1410, 1390, 1350, 1160, 1110. PMR spectrum (δ, ppm): 2.16 s (6H, 2Me).

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1-Bromo-1-nitrocyclohexane (Ib). Analogously, 0.37 g (2.4 mmoles) 1-nitro-1-nitrosocyclohexane (Ib), 0.68 g (2.4 mmoles) DBI, and 0.18 g (1.2 mmoles) $CH_2(ONH_2)\cdot 2HCl$ gave 0.27 g (41%) (IIb) as an oil with R_f 0.57 with chloroform as the eluent. IR spectrum (ν, cm^{-1}): 2890, 2850, 1580, 1480, 1370, 1100, 1000.

5-Bromo-2,2-dimethyl-5-nitro-1,3-dioxane (IIc). A sample of 0.83 g (2.9 mmoles) DBI was added to a solution of 0.55 g (Ic) in 20 ml CH_2Cl_2 and then a solution of 0.24 g (2.9 mmoles) $CH_2(ONH_2)\cdot 2HCl$ in 20 ml CH_2Cl_2 was added dropwise at 20°C and stirred for 1 h. The precipitate was filtered off. Chromatography of the filtrate gave 0.21 g (30%) (IIc), mp 77-78°C [3]. IR spectrum (ν, cm^{-1}): 3000, 1560, 1390, 1340, 1260, 1200, 1140, 1080. PMR spectrum (δ, ppm, J, Hz): 1.26 s (3H, Me), 1.45 s (3H, Me), 4.15 (2H, J = 12.5), 4.7 (2H, J = 12.5).

2,4-Dinitrobromobenzene (IId). A sample of 0.23 g (1 mmole) DBI and 0.08 g (0.53 mmole) $CH_2(ONH_2)\cdot 2HCl$ was added with stirring to a solution of 0.2 g (1 mmole) 2,4-dinitronitrosobenzene in 20 ml CH_2Cl_2 at 20°C and stirred for 24 h. An additional 0.23 g DBI and 0.08 g $CH_2(ONH_2)_2\cdot 2HCl$ were added and stirring was continued for an additional 48 h. The reaction mixture was filtered. Chromatography of the filtrate on silica gel (R_f 0.52 with chloroform as the eluent) gave 0.01 g (4%) (IId), mp 70-71°C [4].

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SPIN TRAP STUDY OF THE DISSOCIATION OF THE N—N BOND IN PHENYLHYDRAZONES

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The spin trap method was used to detect the free phenylaminyl radical formed as the result of homolytic cleavage of the N—N bond in the phenylhydrazone of ethyl pyruvate under conditions of the Fischer indole synthesis.

One of the major steps in the indolization of arylhydrazones in the Fischer reaction is dissociation of the N—N bond. The nature of this dissociation has not been studied extensively. In 1949, Pausaker and Schubert [1] proposed that the N—N bond is cleaved homolytically in acid media in light of the formation of cross products from a mixture of two different phenylhydrazones. Mahgoub et al. [2] have recently proposed that the N—N bond is cleaved homolytically in the thermolysis of the phenylhydrazone of acetophenone to give aniline and phenylethylidenimine free radicals. Homolytic dissociation of the N—N bond was also proposed by Kelly et al. [3] but experimental evidence for this process in acid media is not available in the literature.

In order to elucidate the nature of the dissociation of the N—N bond in phenylhydrazones in acid media, we took the ESR spectra of the phenylhydrazone of ethyl pyruvate under conditions of the Fischer reaction in the presence of formic acid as the acid catalyst. Signals from two spin-adducts of radicals with nitrosodurene are found in the ESR spectrum upon the reaction of $PhNHN{=}C(CH_3)CO_2C_2H_5$ with formic acid in the presence of nitrosodurene

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