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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UDC 541.127:547.04

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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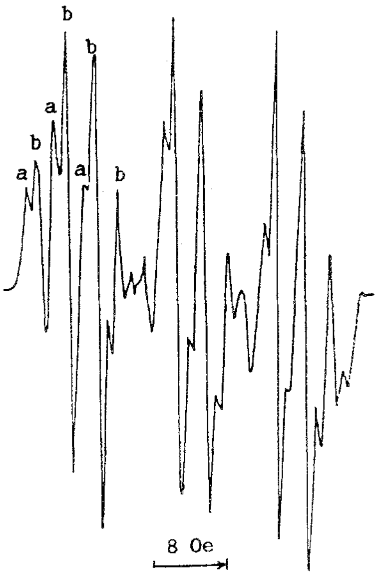
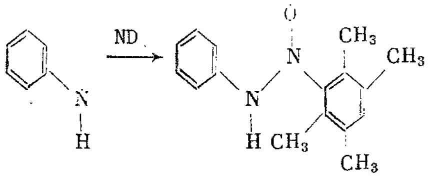


Fig. 1. ESR spectrum of the product (II) of the reaction of PhṄH (I) with nitrosodurene.

in CH_2Cl_2 at 50-60°C (Fig. 1). The triplet of triplets (1:1:1 intensity ratio in each individual triplet) (lines a) with coupling constants $a_{N_\alpha} = 13.3$ and $a_{N_\beta} = 3.5$ Oe were assigned to the spin-adducts of radicals with the unpaired electron on the nitrogen atom with nitrosodurene. Signals b were assigned to the spin-adducts of the PHṄH radicals (I) with the trap. These radicals have $a_{N_\alpha} = 12.8$ and $a_{N_\beta} = a_H = 3.7$ Oe.

Thus, ESR spectroscopy indicates that the product of the reaction of the phenylhydrazone of ethyl pyruvate with nitrosodurene under conditions of the Fischer reaction is the aniline free radical (I). Hence, the N—N bond in phenylhydrazones is homolytically cleaved.



(I) (II)

EXPERIMENTAL

A sample of 0.2 ml formic acid and 0.05 g $PhNHN{=}C(CH_3)CO_2C_2H_5$ were added to a solution of 0.001 g nitrosodurene in 0.3 ml CH_2Cl_2. A sample of 0.2 ml of this solution was transferred to a glass ampul, which was attached to a vacuum system. The solution was degassed by several cycles of the standard freeze—thaw procedure. The ampul was sealed and placed in the probe of an RÉ-1306 spectrometer maintained at low temperature. No ESR signals were observed upon the reaction of $PhNHN{=}C(CH_3)CO_2C_2H_5$ or formic acid with nitrosodurene (except for weak signals from a triplet with $a_N = 14.2$ Oe, which, apparently, arise due to decomposition of the trap).

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