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SYNTHESIS AND PROPERTIES OF PHENOTHIAZINE DERIVATIVES.

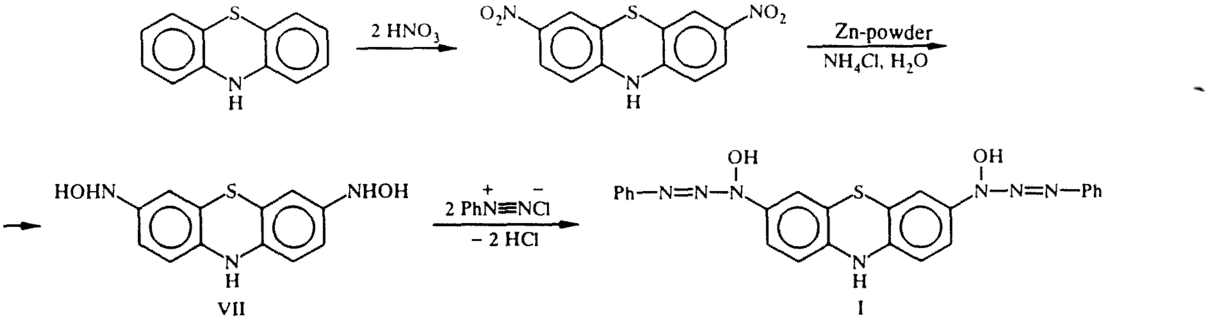
I. SYNTHESIS AND PROPERTIES OF BISOXYTRIAZENES CONTAINING THE PHENOTHIAZINE FRAGMENT

O. B. Tomilin, E. P. Konovalova, É. P. Sanaeva,
A. N. Klyakin, and L. V. Ryabkina

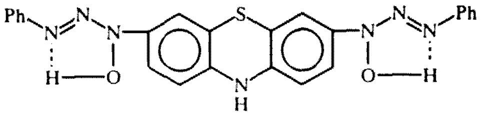
3,7-Bis(1-phenyl-3-hydroxytriazenyl)phenothiazine has been synthesized from phenothiazine. This compound decomposes to phenyl radicals, nitrogen and 3,7-bisnitrosophenothiazine under the influence of nitroso compounds and oxidizing agents (PbO_2, Ag_2O). The reaction of bishydroxytriazenylphenothiazene with 2,4,6-tribromonitrosobenzene has been studied by EPR spectroscopy.

We have previously synthesized and studied some N-substituted derivatives of phenothiazine and their radical forms [1]. The high stability of the cation radicals obtained, demonstrated by both experimental and theoretical investigations, is linked to a considerable extent with delocalization of the unpaired electron into the phenothiazine heterocycle. Condensed aromatic rings on the one hand secure the stability of heterocyclic radical systems and on the other hand create conditions for the introduction of substituents which are independent carriers of unpaired electrons. Thus it is possible to synthesize high spin systems based on phenothiazine and to study the behavior of the intramolecular interactions of the unpaired electrons.

To solve this problem we have synthesized for the first time 3,7-bis-(1-phenyl-3-hydroxytriazenyl)phenothiazine (I) by the following scheme:



The IR spectrum of compound has bands at 1200 and 1248 cm^{-1}, attributable to the –N=N–N–OH group, no OH stretch in the 3300-3600 cm^{-1} range, and an intense ν_{NH} band at 3200 cm^{-1}. The δ_{NH} band at 1600 cm^{-1} indicates the presence of an intramolecular bond, leading to the formation of a stable five-membered ring.



N. P. Ogarev Mordov State University, Saransk 430000. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1284-1287, September, 1996. Original article submitted March 21, 1996.

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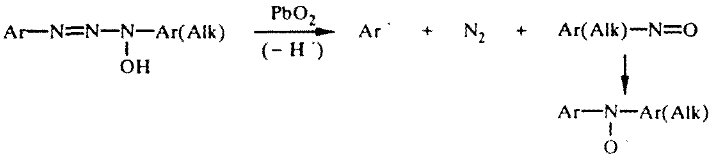
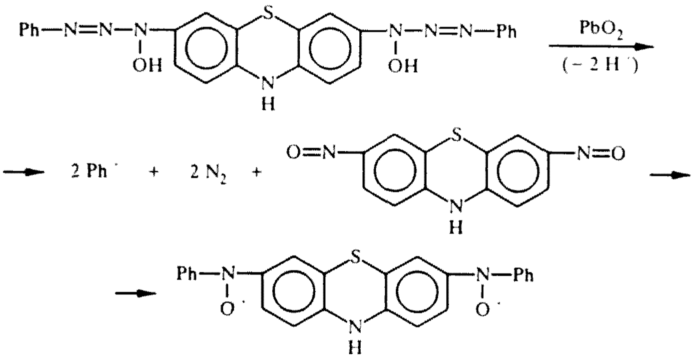
The possibility of forming intramolecular hydrogen bonds in analogous structures has been established previously [2, 3].

According to literature data [3-5] 1-aryl-3-hydroxytriazenes decompose as follows in the presence of oxidizing agents (PbO_2, Ag_2O):



Formation of nitroso compounds during the oxidation makes it possible to trap Ar· radicals or solvent radicals (substrate or additive) as stable nitroxyl radicals (the spin trap method). However, the bisnitroxyl II, which should be formed under these conditions, was not observed by EPR spectroscopy on oxidation of compound I with lead dioxide in benzene solution:

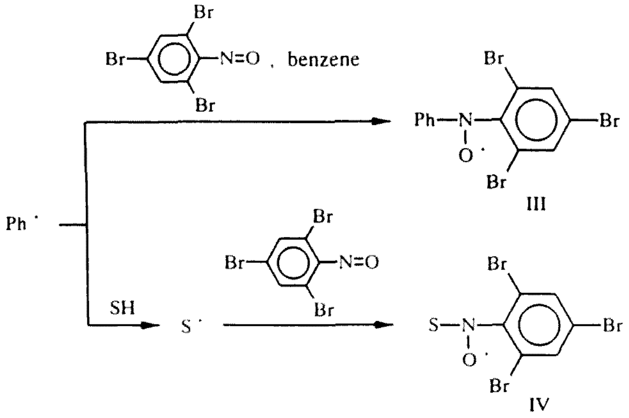


II

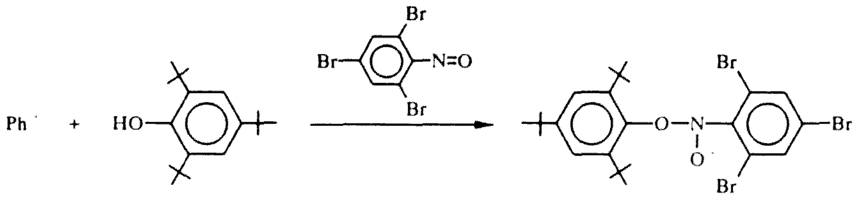
However, the characteristic pattern of decomposition was observed on oxidation: bubbles of nitrogen were evolved and the solution became the reddish-brown color characteristic of nitroxyl radicals. The compound separated from the reaction mixture at the end of the reaction was capable of oxidizing 2,4,6-tri-tert-butylphenol to the phenoxyl radical and diphenylpicrylhydrazine to the diphenylpicrylhydrazyl radical which confirms its free radical nature. Analogous results were obtained when compound I was oxidized by lead dioxide in other solvents. Oxidation in the presence of other nitroso compounds, for example 2,4,6-tribromonitrosobenzene, allowed the trapping of free phenyl radicals formed during decomposition as stable paramagnetic nitroxyl radicals.

In summary, it can be concluded that the bisnitroxyl II, formed by oxidation of compound I, is a low spin compound (S = 0, singlet ground state).

Further study of the properties of 3,7-bis(1-phenyl-3-hydroxytriazenyl)phenothiazine showed that nitroso compounds are capable of inducing its free radical decomposition in solution and in the absence of an oxidant. The fate of the phenyl radicals formed depends on the nature of the solvent or additive (SH) as shown in the following scheme:

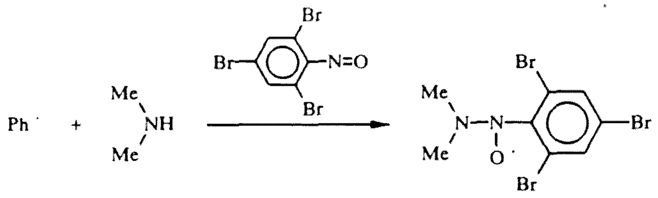


We have observed the EPR spectra of the nitroxyl radicals III and IV in solutions containing compound I and 2,4,6-tribromonitrosobenzene at room temperature immediately on mixing. Solvents (or additives) of various classes have been used: benzene, toluene, methylene bromide, diethyl ether, benzyl alcohol, hexane, diphenol- and dimethylamine, 2,4,6-tri-*tert*-butylphenol. The EPR spectrum of the nitroxyl radical III was observed when the reaction was carried out in benzene; in all the remaining cases the products of trapping the radicals from the solvent or the additive 2,4,6-tribromonitrosobenzene in the form of the stable nitroxyl radicals IV were observed. For example, when 2,4,6-tri-*tert*-butylphenol was used as additive the EPR signal of nitroxyl V with a_N = 15.2 Oe was recorded:



V

When compound I reacted with 2,4,6-tribromonitrosobenzene in benzene in the presence of dimethylamine, the EPR spectrum of radical VI, which is the product of trapping the dimethylnitrogen radical with 2,4,6-tribromonitrosobenzene, was observed:



VI

EXPERIMENTAL

EPR spectra were recorded with an EPA 2M radiospectrometer. The standard used was Mn^{2+} ions in an MgO lattice.

3,7-Dinitrophenothiazine. Sodium nitrate (5 g, 0.072 mol) was added to a mixture of phenothiazine (5 g, 0.017 moles) in chloroform (20 cm^3) and acetic acid (5 cm^3), the mixture was stirred for 1 h after which more acetic acid was added (5 cm^3), and the mixture was stirred for a further 15 min. The course of the reaction was monitored by chromatography on Silufol UV-254 strips with 4:1 petroleum ether–ethyl acetate as eluant and development with UV light. At the end of the reaction, the brown precipitate was filtered off, washed with glacial acetic acid, ethanol, water, and ethanol. The compound was crystallized from aniline. Yield 60%, mp 286-287°C.

3,7-Bis(hydroxyamino)phenothiazine (VII). 3,7-Phenothiazine (4.5 g, 0.015 moles) was added to a solution of ammonium chloride (1.1 g, 0.02 moles) in water (50 cm^3), and then powdered zinc (3 g) was added in small portions with stirring and water cooling. Further zinc (6 g) was added with continuous stirring. The temperature of the reaction mixture was maintained between 10 and 15°C. After 2 h the precipitate was filtered off and the filtrate was brought to pH 7 with acetic acid.

The solution was used without further purification.

3,7-Bis(1-phenyl-3-hydroxytriazenyl)phenothiazine (I). A solution of phenyldiazonium chloride containing sodium acetate was added slowly with stirring to an acetic acid solution of compound VII at 0-5°C. The precipitate which formed slowly was filtered off, dried and recrystallized from aqueous ethanol to give light yellow crystals, yield 32%, mp 95°C. IR spectrum: 3200 (ν_{NH}), 1600 (ν_{NH}), 1200, 1248 cm^{-1} ($\nu_{N-N=N-OH}$). Found, %: C 61.38, H 4.07, N 20.85. Calc. for $C_{24}H_{19}N_7O_2S$, %: C 61.41, H 4.07, N 20.85.

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