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REACTIONS OF 4-NITROSO-1,2,4-TRIAZINE WITH DERIVATIVES OF HYDRAZINE

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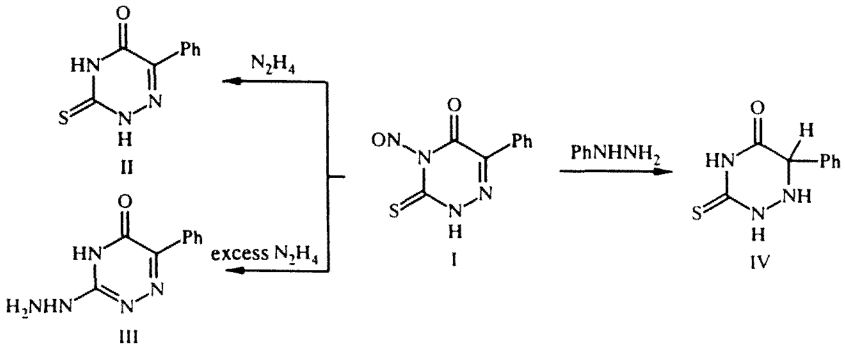
The action of hydrazine on 4-nitroso-6-phenyl-1,2,4-triazine-3(2H)-thione-5-one results in the cleavage of the nitroso group. The action of phenylhydrazine results in the reduction of the double bond in the triazine ring together with the cleavage of the nitroso group. The spectral characteristics of the compounds are considered, and the reaction mechanism is proposed.

For derivatives of 1,2,4-triazine, the 4-substituted derivatives are particularly characterized by pesticidal and pharmacological activity [1]. It was previously shown [2] that 4-arylazotriazines are obtained when 4-nitroso-6-phenyl-1,2,4-triazine-3(2H)-thione-5-one (I) is boiled in glacial acetic acid with primary aromatic amines. The present work investigates the reaction of compound (I) [3] with hydrazine and phenylhydrazine.

The boiling of compound (I) with a small excess of 84% hydrazine hydrate in isopropyl alcohol led to the isolation of 6-phenyl-1,2,4-triazine-3(2H)-thione-5(4H)-one (II), and the threefold excess of hydrazine hydrate led to 3-hydrazino-6-phenyl-1,2,4-triazin-5(4H)-one (III). The boiling of compound (I) with excess phenylhydrazine in isopropyl alcohol leads to the formation of 1,6-dihydro-6-phenyl-1,2,4-triazine-3(2H)-thione-5(4H)-one (IV). The characteristics and properties of the compounds (II) and (III) corresponded with those described in [4, 5].



Compound (IV), of white color, is insoluble in water, and soluble in polar organic solvents. The IR spectrum of compound (IV) lacks the absorption band at 1500 cm^{-1}, characteristic of the stretching vibrations of the N–N=O group of compound (I). The stretching vibrations of the carbonyl and thioxo groups are shifted up to 1685 and 1195 cm^{-1} by comparison with the compound (I) (1620 and 1185 cm^{-1} correspondingly). The PMR spectra of compound (IV) contain two doublets at 3.04 and 6.11 ppm, assigned to protons at the positions 6 and 1 of the triazine ring correspondingly, and the singlets of the protons at the $N_{(2)}$ and $N_{(4)}$ atoms occur at 12.81 and 13.43 ppm. The mass spectrum of compound (IV) is characterized by the peak of the molecular ion 207.2 (M^+, 5.4).

Certain interest is presented by the analysis of reasons for the differing course of the reaction of the 4-nitrosotriazine with hydrazine and phenylhydrazine. If the reaction mechanism includes the formation of the "triazinazo compound" with the subsequent cleavage by the base, then the difference from the Kishner—Wolff reaction consists as well in the formation of the

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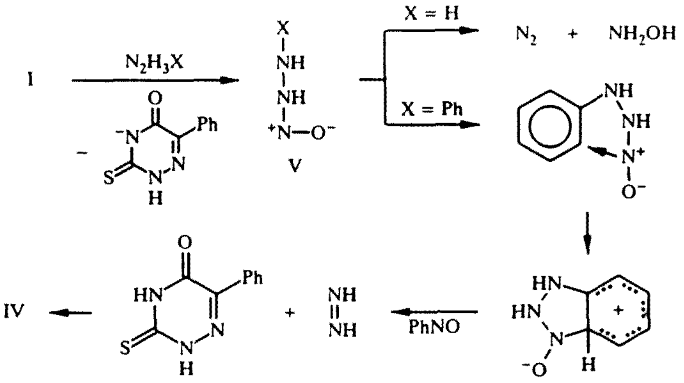
hydroxylamine derivative (or nitrene) besides nitrogen in the mixture of reaction products. It is possible that the reaction of compound (I) with hydrazine proceeds by such a mechanism. The similarity in the structure of the reagents — hydrazine and phenylhydrazine — allows the presence of one, if only, common intermediate to be assumed, and the reduction of the triazine ring does not follow the mechanism according to Kishner—Wolff. It is known that the ring position 5 in 1,2,4-triazines is the most electron-deficient and sensitive to attack by reducing agents [1]. In the given case, it is not affected; this allows the indirect conclusion that there is some selectivity of the reducing agent. Such an agent, selectively reducing double bonds in the ring and not affecting the carbonyl group, could be the diimide (NH=NH) under the experimental conditions adopted [6]. There should also be a reason for the increased formation of the diimide in the case of the application of phenylhydrazine. In our opinion, the scheme presented below can satisfy all these requirements.



The fate of the intermediate (V) probably depends on the nature of the substituent. In the case of the phenyl substituent, rearrangement occurs with the release of the diimide and the formation of nitrosobenzene in the end. If the substituent does not have a stabilizing influence (H, Alk), then the decomposition of the intermediate (V) occurs with the release of nitrogen. The reaction of the resulting diimide with the double bond in the triazine ring proceeds by analogy with the description in [6] via the nonpolar transition state with the release of nitrogen.

EXPERIMENTAL

The IR spectra were taken on the UR-10 instrument using tablets of KBr. The PMR spectra were taken on the Tesla BS-4878 instrument with the working frequency 80 MHz in DMSO-D_6, and HMDS as the internal standard. The mass spectrum was taken on the MS-1302 mass spectrometer; the energy of the ionizing electrons was 70 eV. The purity of the products was monitored by the method of TLC on plates of Silufol UV-254 in the 8:4:1 system of benzene—chloroform—acetone.

1,6-Dihydro-6-phenyl-1,2,4-triazine-3(2H)-thione-5(4H)-one (IV). The mixture of 0.04 mole of 4-nitroso-6-phenyl-1,2,4-triazine-3(2H)-thione-5-one and 0.041 mole of phenylhydrazine in 50 ml of isopropyl alcohol is boiled for 4-4.5 h. The mixture is left overnight. The precipitated residue is filtered off and dried in air. Purification is performed by recrystallization from isopropyl alcohol. The yield is 48%. The mp is 262-263°C (decomp.). The IR spectrum (ν) is as follows: 1685 cm^{-1} (C=O), 1195 cm^{-1} (C=S), 1100 cm^{-1}, 1030 cm^{-1}, and 995 cm^{-1} (triazine, ring). The PMR spectrum (δ) is as follows: 7.50-7.87 ppm (5H, m), 3.04 ppm (1H, d), 6.11 ppm (1H, d), 12.81 ppm (1H, s), and 13.43 ppm (1H, s). The mass spectrum (m/z) is as follows: M^+ 207.2 (5.4), 205.0 (95.8), 119.1 (26.6), 118.1 (100.0), 104.2 (19.7), 103.1 (15.3), 91.1 (30.4), 89.1 (23.4), 77.1 (21.7), 76.1 (11.9), 59.0 (12.3), and 28.1 (1.8). Found, %: C 52.2, H 4.4, and N 20.2. $C_9H_9N_3OS$. Calculated, %: C 52.2, H 4.4, and N 20.3.

3-R-6-Phenyl-1,2,4-triazin-5(4H)-ones (II) and (III). The mixture of 0.04 mole of compound (I) and 0.045 mole of 84% hydrazine hydrate or 0.12 mole of hydrazine hydrate in 50 ml of isopropyl alcohol is boiled for 3.5-4 h. The mixture is left overnight. The residue is filtered off and dried in air. Purification is performed by recrystallization from isopropyl alcohol.

Compound (II). The yield is 68%. The mp is 258-259°C. The characteristics and properties correspond with the compound obtained according to the method of [4].

Compound (III). The yield is 64%. The mp is 222-223°C. The characteristics and properties correspond with the compound obtained according to the method of [5].

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