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LETTERS TO THE EDITOR

Synthesis of 4-Amino-6-phenyl-3-thioxo-2,3-dihydro-1,2,4-triazine-5(4*H*)-one

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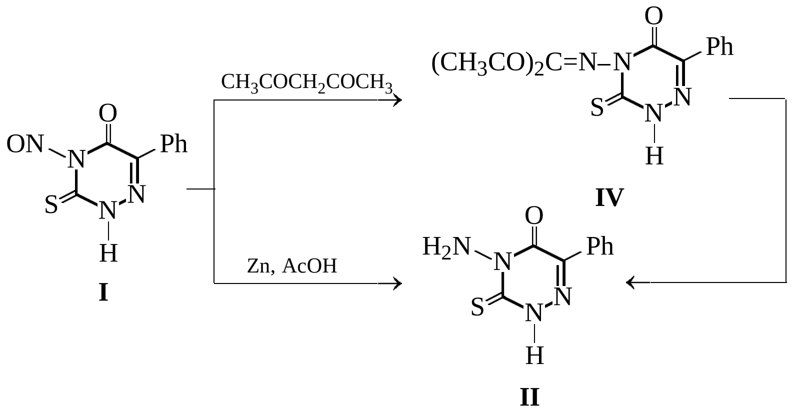
4-Amino-1,2,4-triazine derivatives have found application as pesticides. They are commonly prepared by condensation of α-ketocarboxylic acids with thiosemicarbazide in alkaline medium [1]. In the present work we studied reactions of 4-nitroso-6-phenyl-3-thioxo-2,3-dihydro-1,2,4-triazine-5(4*H*)-one (**I**), involving the nitroso group, with the aim of preparing 4-amino-6-phenyl-3-thioxo-2,3-dihydro-1,2,4-triazine-5(4*H*)-one (**II**) by previously unknown methods.

Compound **I** was prepared by direct nitrosation with sodium nitrite in hydrochloric acid medium at 0°C of 6-phenyl-3-thioxo-2,3-dihydro-1,2,4-triazine-5(4*H*)-one (**III**). The characteristics and properties of compound **I** have been described in [2].

The reaction of compound **I** with acetylacetone (like the Ehrlich–Sachs reaction of aromatic compounds) in weakly alkaline medium resulted in preparation of 4-(diacetylmethyleneamino)-6-phenyl-3-thioxo-2,3-dihydro-1,2,4-triazine-5(4*H*)-one (**IV**) [3]. Hydrolysis of compound **IV** in aqueous alcohol in the presence of acid gave 4-amino-6-phenyl-3-thioxo-2,3-dihydro-1,2,4-triazine-5(4*H*)-one (**II**). The mechanism of the hydrolysis is usual for azomethines.



4-Aminotriazines proved difficult to prepare by reduction of substituted 4-nitrosotriazines because of the attendant reduction of the triazine ring and cleavage of the nitroso group. The reductions with hydrazine hydrate or tin(II) chloride involved cleavage of the nitroso group to provide 6-phenyl-3-thioxo-2,3-dihydro-1,2,4-triazine-5(4*H*)-one (**III**). Boiling with phenyl hydrazine resulted, along with cleavage of the nitroso group, in further hydrogenation of the $C^6–N^1$ bond of the triazine ring to give 6-phenyl-3-thioxo-1,2,3,6-tetrahydro-1,2,4-triazine-5(4*H*)-one [4].

Boiling of 4-nitrosotriazine (**I**) with zinc powder in acid medium gave 4-amino-6-phenyl-3-thioxo-2,3-dihydro-1,2,4-triazine-5(4*H*)-one (**II**) whose characterstics and properties were coincident with those of a sample isolated upon hydrolysis of compound **IV** and described in [5]. The reduction of the nitroso group with zinc powder in acid medium probably occurs like the Clemmensen reaction of carbonyl compounds. Presumably, the oxygen is cleaved as water from a partly reduced intermediate bound with zinc.

4-Amino-6-phenyl-3-thioxo-2,3-dihydro-1,2,4-triazine-5(4*H*)-one (II). *a*. Compound **I**, 2.34 g, and 10 g of zinc powder were boiled in 100 ml of glacial acetic acid for 30–40 min until decoloration. The mixture was then filtered while hot, the filtrate was reduced to one third in a vacuum, and the residue was cooled and diluted with water (1:3). The precipitate was filtered, washed with water, dried in air, and recrystallized from isopropanol. Yield 1.17 g (53%), mp 231°C (tarring).

b. Compound **IV**, 3.16 g, was boiled in a 1 : 1 isopropanol–water mixture and 5 ml of conc. HCl for 12 h. The mixture was filtered while hot, the filtrate was cooled, the precipitate was filtered off, dried in air, and recrystallized from isopropanol. Yield 1.82 g (83%), mp 231°C (tarring). IR spectrum, ν, cm^{-1}: 1650 (C=O); 1190 (C=S); 3300, 3200 (NH_2). ^1H NMR spectrum, δ, ppm: 7.50–7.87 m (5H, Ph), 5.92 s (2H, NH_2), 13.43 s (1H, NH). Found, %: C 48.9; H 3.6; N 25.1. $C_9H_8N_4OS$. Calculated, %: C 49.08; H 3.66; N 25.44.

The IR spectra were recorded on a UR-10 instrument in KBr pellets. The ^1H NMR spectra were obtained on a Tesla BS-487B spectrometer at 80 MHz in DMSO-d_6, internal reference HMDS. The purity of the reaction products was checked by TLC on Silufol UV-254 plates in the system chloroform–acetone, 1 : 9.

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