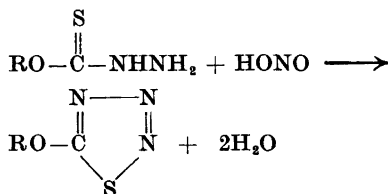


5-Alkoxy-1,2,3,4-thiatriazoles

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5-Alkoxy-1,2,3,4-thiatriazoles have so far been unknown. We have, however, prepared compounds of this type by the reaction between alkoxythiocarbonylhydrazines ("xanthogenhydrazides"), and nitrous acid:



No reaction took place between xanthates and sodium azide.

These thiatriazoles are very unstable and decompose, sometimes explosively, even at room temperature. Only the ethoxy compound described below was analysed. It is a crystalline compound melting at 44.5–45°C, but undergoes decomposition at room temperature with formation of sulfur and evolution of nitrogen. An ethereal (20 %) solution of this thiatriazole evolved the calculated amount of nitrogen in the course of 16 h and from the solution 98 % of the calculated amount of sulfur could be isolated. Even when kept in an ice box the compound decomposed slowly. Without essential change of appearance it was transformed into a mixture of sulfur and triethyl isocyanurate. A closer examination of the primary decomposition products forms the object of the following communication.²

The propyl derivative was obtained as crystals melting just below room temperature, the isopropyl, butyl, isobutyl and *sec*-butyl derivatives were only obtained as oils. The methyl derivative was obtained

as crystals at 0°C but decomposed explosively at room temperature.

Finally it should be mentioned that we tried without success to prepare 5-hydroxy-1,2,3,4-thiatriazole from carbonyl sulfide and sodium azide or from hydrazinemonothiocarboxylic acid and nitrous acid.

Experimental. Ethoxythiocarbonylhydrazine¹ (22.1 g) was dissolved in 0.05 N hydrochloric acid (480 ml). In the course of 30 min a solution of sodium nitrite (12.7 g) in water (150 ml) was added with stirring to the well cooled solution of the hydrazine, the temperature being kept between –2 and +3°C. The addition of sodium nitrite should be stopped as soon as a test with potassium iodide-starch paper shows positive HNO₂ reaction. The 5-ethoxy-1,2,3,4-thiatriazole separated during the reaction. The suspension was extracted four times with 125 ml ether each time. The combined ether solutions were kept at 0°C and dried with Na₂SO₄ and then rapidly evaporated *in vacuo*. The residue was dissolved in anhydrous ether and cooled in a "dry ice"-acetone mixture. The solid was isolated in small portions by centrifugation, dried by evacuation of the centrifuge glass for a few min at 20°C and placed in an ice box. Yield 23.1 g = 96 %.

The product is colourless when pure, but is sometimes obtained with a pinkish colour which may be removed by repeated crystallisations from ether. M.p. 44.5–45°C, deflagration taking place a little above the melting point. (Found: C 27.30; H 4.03; S 24.50. Calc. for C₃H₅N₃OS: C 27.48; H 3.82; S 24.43). It proved impossible to obtain correct nitrogen values by Dumas analysis because the compound decomposed with evolution of nitrogen on mixing with copper(II) oxide; only about 18 % N instead of the calculated 32.06 % was found. When the copper(II) oxide was cooled at –80°C before mixing with the thiatriazole much better, but still too low values (near 30 %) were found.

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