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Products of the Nitration of 2-Thiazolylureas and 2-Thiazolylthioureas*

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Our recent studies have shown that 2-thiazolylthioureas are a fruitful source of chelating agents which can be used as reagents for spectrophotometric determination of metal ions. Introduction of a nitro group in the 5-position of the thiazole moiety of 1,1-dimethyl-3-(4-methyl-2-thiazolyl)thiourea caused bathochromic and hyperchromic effects on the absorption bands of the thioureas and their metal chelates. This finding prompted us to prepare the corresponding nitro compounds of the other series of 2-thiazolylureas and 2-thiazolylthioureas.

Nitration was performed by a dropwise addition of fuming nitric acid to a concentrated

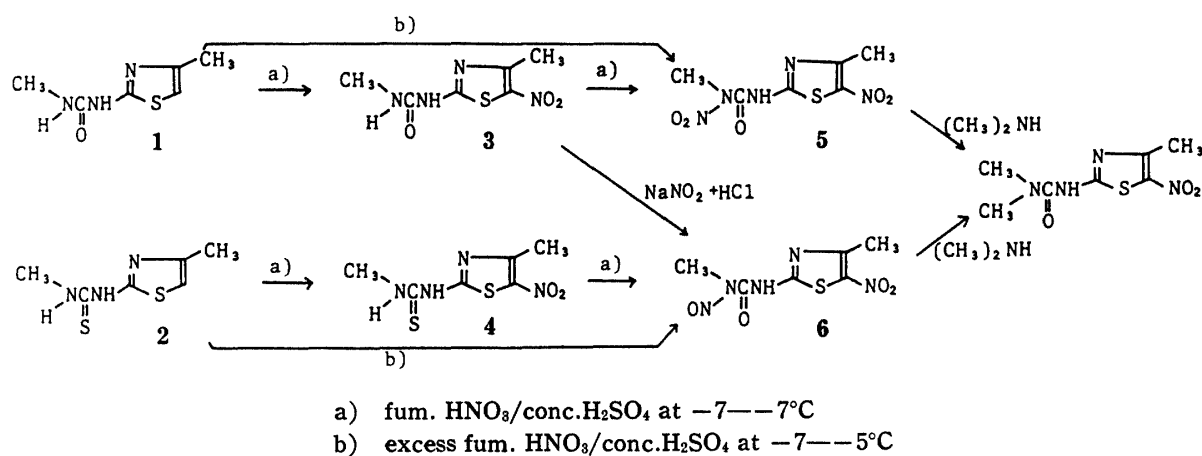


Chart 1

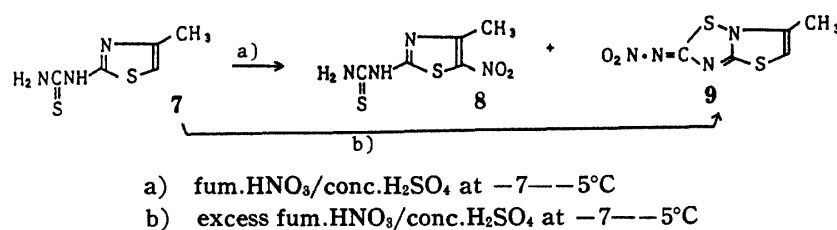


Chart 2

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sulfuric acid solution of a urea or a thiourea at low temperatures. Nitration products of 1-methyl-3-(4-methyl-2-thiazolyl)-urea (1) and -thiourea (2) were their 5-nitrothiazolyl derivatives (3 and 4, respectively). With an excess of nitric acid, 1-methyl-3-(4-methyl-5-nitro-2-thiazolyl)-1-nitrourea (5) was obtained from 1, whereas corresponding 1-nitrosourea (6) from 2. From the nitration of 3-(4-methyl-2-thiazolyl)thiourea (7), a pale yellow compound (9) was obtained with the 5-nitrothiazolyl derivative of 7 (8). Unlike other nitrated thioureas, 9 did not form a colored Cu(II) chelate and was stable to acid, alkali, and heat. It was concluded to be 6-methyl-2-nitroiminothiazolo[3,2-b][1,2,4]-thiadiazole from studies of its physicochemical properties, chemical reactions, and crystallography. Corresponding compounds were obtained from other N-(4-alkyl-2-thiazolyl)-thioureas. Chemical reactions studied are summerized in Chart 1 and 2.