

SYNTHESIS OF 4H-1,2,4,6-THIATRIAZINE 1,1-DIOXIDE:
A PRECURSOR OF 4-CYANO-1,2,6-THIADIAZINE 1,1-DIOXIDES

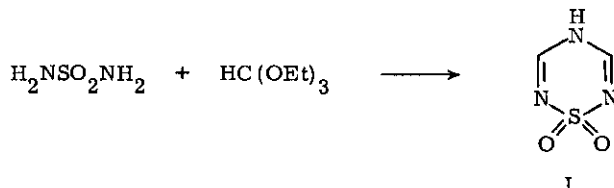
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Abstract — 4H-1,2,4,6-thiatriazine 1,1-dioxide, obtained from sulfamide and ethyl orthoformate, reacted with ethyl cyanoacetate and malononitrile to give the corresponding 4-cyano-1,2,6-thiadiazine 1,1-dioxide derivatives.

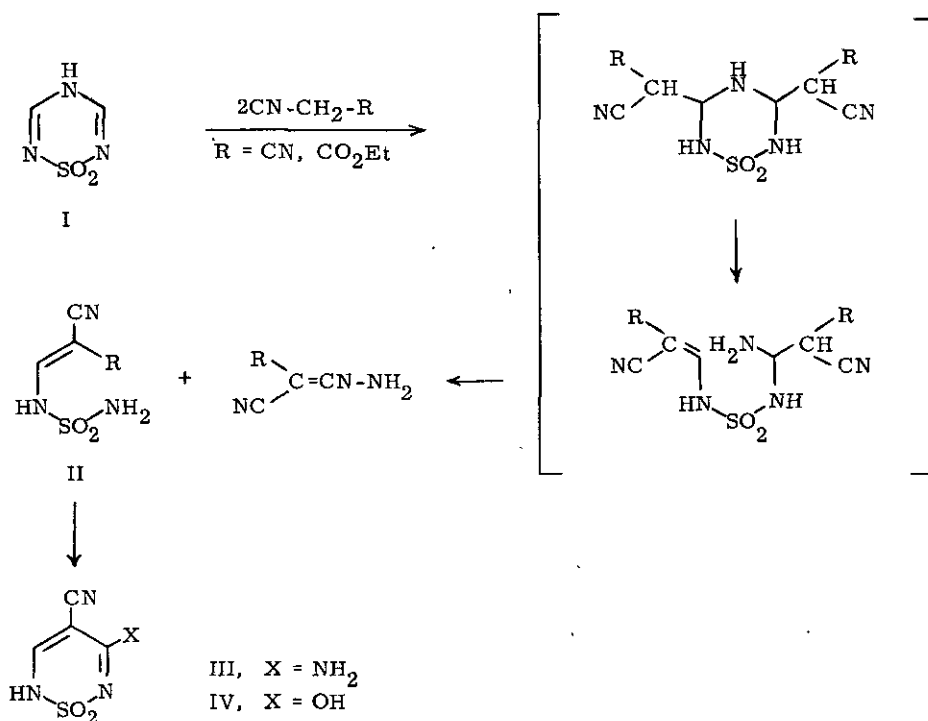
In this paper, we report the synthesis and reactions with α -methylene compounds of 4H-1,2,4,6-thiatriazine 1,1-dioxide (I). Previously, only substituted derivatives of this heterocyclic system had been described¹.

When sulfamide was treated with an excess of ethyl orthoformate in a sealed tube at 130°C for 12 h, 4H-1,2,4,6-thiatriazine 1,1-dioxide (I) was obtained (mp 270°C, 40%).



The structure of the compound was established according to its analytical and spectroscopic data². The fact that there is only one signal for the =CH- protons allows us to establish I in this tautomeric form. The mechanism of the formation of this product is not very clear but one should bear in mind that sulfamide when heated over its melting point undergoes decomposition reactions³. In an attempt to extend this reaction for the preparation of other thiatriazines, N-benzylsulfamide was treated with ethyl orthoformate, under the same conditions, but only starting material was recovered. In an experiment with N-benzylsulfamide, sulfamide and ethyl orthoformate only thiatriazine I could be isolated.

When I was treated with two equivalents of malononitrile in refluxing 2N sodium methoxide, 3-amino-4-cyano-6H-1,2,6-thiadiazine 1,1-dioxide (III) was isolated in 60% yield. This compound was identical in all respects to the product obtained in the condensation between sulfamide and ethoxymethylenemalononitrile⁴. In a similar manner, when I was treated with ethyl cyanoacetate, the sodium salt^{4,5} of 4-cyano-2H-1,2,6-thiadiazine-3(6H)-one 1,1-dioxide (IV) was isolated. The probable course of the reaction involves attack of two equivalents of the active



methylene reagent to the electron deficient positions 3 and 5 of the thiadiazine ring to give the open-chain derivative II.

The fact that compound IV and not 3-amino-4-ethoxycarbonyl-2H-1,2,6-thiadiazine 1,1-dioxide could be isolated should not be surprising since in the case of the synthesis of this same compound through the sulfamidomethylene derivative II ($\text{R} = \text{CO}_2\text{Et}$), previously described by us,⁴ the only compound obtained was also IV.

Attempts to extend this reaction to other active methylene compounds such as diethyl malonate, di-tert-butyl malonate, and malondiamide, in order to obtain other thiadiazine derivatives, were not successful.

REFERENCES AND NOTES

1. See among others, H. Walter, U.S. 2,454,261. *Chem. Abstr.* 43 P2648C (1949); H. Disselnkoetter, Ger Offen 1,946,262. *Chem. Abstr.* 74, 152740a (1971); H. Zamankhan, *Chem. Ber.*, 1976, 109, 2107; H. Gerhard, A.R. Dieter, Ger Offen DE 3,134,140. *Chem. Abstr.* 98, 198286n (1983).
2. ^1H nmr ($\text{DMSO}-d_6$) δ 8.05 (s, =CH); 11.5 (bm NH).
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