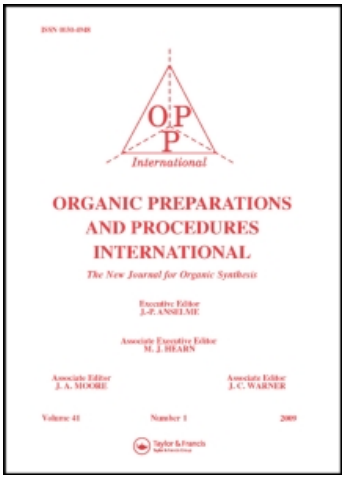

Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A CONVENIENT PREPARATION OF THIOFORMAMIDE. SYNTHESIS OF THIAZOLE-4-CARBOXYLIC ACID

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To cite this Article Rohály, J. , Novák, L. and Szántay, Cs.(1999) 'A CONVENIENT PREPARATION OF THIOFORMAMIDE. SYNTHESIS OF THIAZOLE-4-CARBOXYLIC ACID', Organic Preparations and Procedures International, 31: 6, 693 — 694
To link to this Article: DOI: 10.1080/00304949909355351
URL: http://dx.doi.org/10.1080/00304949909355351

A CONVENIENT PREPARATION OF THIOFORMAMIDE. SYNTHESIS OF THIAZOLE-4-CARBOXYLIC ACID

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(10/19/99)

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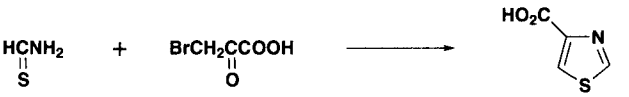
Thiazole-4-carboxylic acid (**3**), an important precursor of the fungicide *thiabendazol*,[1] is prepared from the reaction of thioformamide (**1**) and bromopyruvic acid (**2**).[2]



1 **2** **3**

Several routes are known for the preparation of thioformamide, *e. g.* a) by interaction of formamide with P_2S_5,[3] b) by reaction of ethyl thioformate with gaseous ammonia,[4] and c) by interaction[4] of hydrogen cyanide and hydrogen sulfide in the presence of triethylamine.[5] All of these methods are either inconvenient to carry out or require a high degree of care and caution.

We anticipated that with the use of sodium cyanide and sodium sulfide in the presence of acid and ammonia or triethylamine instead of the dangerous hydrogen cyanide and hydrogen sulfide, we could obtain the desired thioformamide, suitable for the preparation of thiazole-4 carboxylic acid. We have now realized this preparation. While the yield is moderate (55%), the product is obtained without the need for further purification under very convenient conditions.

EXPERIMENTAL SECTION

CAUTION! This reaction should be performed in an efficient hood.

Thiazole-4-carboxylic Acid.- Sodium cyanide (5.0 g , 0.1 mol) and sodium sulfide nonahydrate (48 g, 0.2 mol) were stirred for 30 min. in methanol (60 mL) containing NH_3 (5.5 g, 0.323 mol). The stirred mixture was cooled to 0° and sulfuric acid (96%, 25.5 g, 14 mL, 0.25 mol) was added dropwise over 10 min. The mixture was allowed to warm to ambient temperature and stirred further for 22 hrs. The light yellow suspension was stirred with ether (200 mL) (or alternatively with *tert*-butyl methyl ether), filtered and the solid washed with 2x50 mL ether. The combined ethereal extract was washed with

saturated NaCl (50 mL), dried ($MgSO_4$) and evaporated. The orange residue (thioformamide, 1.2 g, 20%) solidified upon cooling, mp 26°.

To a solution of the crude thioformamide (1.9 g, 0.031 mol) obtained above in monoglyme (15 mL), was added with stirring a solution of bromopyruvic acid (2.7 g, 0.016 mol) in monoglyme (5.5 mL) at such a rate that the temperature remained under 28° (15-20 min.). The mixture was further stirred for 3 hrs, the yellow precipitate was collected and dried to give thiazole-4-carboxylic acid HBr (1.8 g, 53%), m.p. 244-246°. The salt was treated with ammonium hydroxide (1.5 mL) to afford 0.72 g (74%) of thiazole-4-carboxylic acid, mp. 196-197°, lit.[6] mp. 195-197°, identical in all respects with an authentic sample.[6]

REFERENCES

1. H. D. Brown, A. R. Matzuk, I. R. Ilves, L. H. Peterson, S. A. Harris, L. H. Sarrett, J. R. Egerton, J. J. Yarsits, W. C. Campbell and A. C. Cuckley, *J. Am. Chem. Soc.*, **83**, 1764 (1961).

2. L. Yuying and T. Sigi, *Chinese Patent*, CN 1.042.150 (1990.05.16); *Chem. Abstr.*, **114**, 122366s (1991).

3. T. E. Londergan, N. L. Hause and W. R. Schmitz, *J. Am. Chem. Soc.*,**75**, 4456 (1953).

4. A. R. Todd, F. Bergel, F. Karimullah and F. Keller , *J. Chem. Soc.*, 361 (**1937**).

5. R. Tull and L. M. Weinstock, *Angew. Chem.*, **81**, 291 (1969); *Int. Engl. Ed.*, **8**, 278 (1969).

6. H. Erlenmeyer and C. J. Morel, *Helv. Chim. Acta*, **25**, 1075 (1942).

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REDUCTIVE OXIDATION OF CARBOXYLIC ACIDS TO ALDEHYDES WITH SODIUM BOROHYDRIDE AND PYRIDINIUM CHLOROCHROMATE

Submitted by (09/15/99)

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Carboxylic acids are readily reduced to aldehydes by stepwise treatment with sodium borohydride and dimethyl sulfate.[1] This method involves the reaction of carboxylic acids with sodium borohydride to form acyloxyborohydride (**1**), followed by the treatment of **1** with dimethyl sulfate to