

A New Route to 2,3-Dihydro-1,4-benzoxathiine and 2,3-Dihydro-1,4-benzodithiine

James Y. Satoh,* Amos M. Haruta, Christopher T. Yokoyama, Yasuo Yamada, and Masakatsu Hirose

Department of Chemistry, St. Paul's (Rikkyo) University, Nishi-Ikebukuro, Toshima-ku, Tokyo 171, Japan

The ethylene monothioacetals and dithioacetals of alkylcyclohexanones react with copper(II) bromide to give 2,3-dihydro-1,4-benzoxathiine and 2,3-dihydro-1,4-benzodithiine derivatives, respectively.

1,4-Benzoxathiines have been synthesized from 2-mercapto-phenol¹ or allyl phenyl ether,² and 1,4-benzodithiines from 1,2-mercaptobenzene³ or 1,4,2-benzodithiazine,⁴ but the direct syntheses of these derivatives from acetals (**1a—h**) have not been reported. We now report that the cyclohexanone ethylene monothioacetals (**1a—e**) and dithioacetals (**1f—h**) react with copper(II) bromide to give the 2,3-dihydro-1,4-benzoxathiines (**2a—e**) and 2,3-dihydro-1,4-benzodithiines (**2f—h**), respectively.

The following procedure is typical: compound (**1a**) was heated at 110 °C with copper(II) bromide (5 mol. equiv.) in diglyme for 1 h. Ether extraction, column chromatography on silica gel, and then distillation gave the 8-methyl compound (**2a**), together with a very small amount of the 5-methyl derivative. The structure of both products was determined by reduction to phenetole derivatives with Raney nickel.

In the reactions of the alkyl substituted monothioacetals (**1a—e**) with copper(II) bromide, bond cleavage occurred smoothly between carbon and sulphur rather than between carbon and oxygen, and the sulphur-migration products (**2a—e**) were formed. In the case of the dithioacetals (**1f—h**),

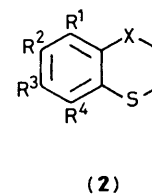
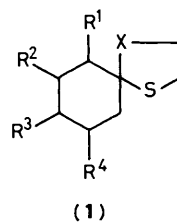


Table 1. Reaction of cyclohexanone mono- and di-thioacetals (**1**) to give benzoxathiines and benzodithiines (**2**).

Starting acetal	Substituents					Product (2) ^a	
	X	R ¹	R ²	R ³	R ⁴	% Yield	B. p., t/°C (p/mmHg)
(1a)	O	Me	H	H	H	51 ^b	106—108 (3.5)
(1b)	O	H	H	Me	H	44 ^b	113—115 (3.5)
(1c)	O	Me	H	H	Me	35	107—108 (3.0)
(1d)	O	H	Me	H	Me	68	110—112 (2.5)
(1e)	O	Pr ⁱ	H	H	Me	45 ^b	101—103 (2.0)
(1f)	S	Me	H	H	H	66	109—111 (1.0)
(1g)	S	Me	H	H	Me	78	124—126 (3.0)
(1h)	S	Pr ⁱ	H	H	Me	47	127—129 (3.5)

^a Satisfactory elemental analyses and spectroscopic data were obtained for all compounds; isolated yields are given. ^b Oxygen-migration products were obtained in minor quantities.

the reaction was carried out in dioxane under refluxing conditions.

The present reaction, utilizing readily available starting materials, thus affords an improved one-pot method for synthesising these heterocyclic compounds with alkyl groups in the desired positions.

Received, 23rd July 1985; Com. 1079

References

- 1 D. Greenwood and H. A. Stevenson, *J. Chem. Soc.*, 1953, 1514.
 - 2 M. Muhlstadt, N. Stransky, A. Seifert, E. Kleinpeter, and H. Meinhold, *J. Prakt. Chem.*, 1978, **320**, 113.
 - 3 W. E. Parham, T. M. Roder, and W. R. Hasek, *J. Am. Chem. Soc.*, 1953, **75**, 1647.
 - 4 J. Nakayama, H. Fukushima, R. Hashimoto, and M. Hoshino, *J. Chem. Soc., Chem. Commun.*, 1982, 612.
-