Reaction of Thioboronite. A Convenient Method for the Preparation of β-Hydroxyalkanethioates

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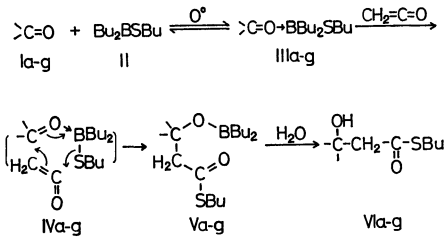
As a part of our study on the reactions of thioboronites, a new and convenient method for the preparation of β-hydroxyalkanethioates by the reaction of carbonyl compounds with ketene was established.

It was reported that nitriles react with thioboronites to form co-ordination complexes, which react with isocyanates or diphenyl ketene to give the corresponding acetamidine or acetaldimine derivatives in fairly good yields.[1,2]

Based on these facts, the analogous reaction of thioboronite with carbonyl compounds and ketene were examined. As an example, equimolar amounts of *n*-butyl di-*n*-butyl thioboronite (1.09 g, 5.1 mmol) and benzaldehyde (0.54 g, 5.1 mmol) in 15 m*l* dry ether were treated with ketene[3] at 0°C for 2 hr. After removal of ether, the oily substance was treated with H_2O–MeOH–H_2O_2 at room temperature. The solution was allowed to stand overnight and MeOH was removed *in vacuo*. The resulting mixture was extracted with ether and the ether layer was washed with 5% solution of sodium bicarbonate and dried over anhydrous sodium sulfate. Ether was evaporated to afford 1.09 g (90%) of *S*-*n*-butyl β-hydroxyhydrocinnamethioate (VIb).

A possible reaction path is outlined in Scheme 1. Initially, an intermediate (III), co-ordination complex, might be formed from carbonyl compound (I) and thioboronite (II). Ketene will react with the complex to form V through the cyclic transition state (IV). Formation of V was confirmed by the infrared spectrum and hydrolysis to β-hydroxyalkanethioate (VI).



Scheme 1

Paetzold and Kosma reported that α,β-unsaturated carboxylic acid chlorides are obtained by a similar reaction of boron chloride with ketene and carbonyl compounds except in the case of benzophenone.[4]

TABLE 1. YIELDS AND PROPERTIES OF β-HYDROXYALKANETHIOATES[a]

	Ia—g	Product	Bp °C (mmHg)	Isolated Yield, %
Ia	$CH_3(CH_2)_2CHO$	VIa	97—98 (4.5)	84
Ib	C_6H_5CHO	VIb	145—146 (4.5)	90
Ic	$C_6H_5CH{=}CHCHO$	VIc	163 (0.18)	90
Id	$(CH_3)_2CO$	VId	82—84 (3.0)	98
Ie		VIe	112—113 (1.5)	91
If	$C_6H_5(C_2H_5)CO$	VIf	139 (3.0)	91
Ig	$(C_6H_5)_2CO$	VIg	b)	94

a) In ether at 0°C for 2 hr.
b) Mp 75.5—76.5°C

The present β-hydroxyalkanethioate synthesis using thioboronite affords the corresponding β-hydroxyalkanethioates in excellent yields from aliphatic, aromatic, and α,β-unsaturated aldehydes and aliphatic, cyclic, and aromatic ketones (including benzophenone, see Table 1). In addition, this reaction has another synthetic utility, since β-hydroxyalkanethioate can be used as an active synthetic intermediate. As an example, the thiol ester can be reduced to aldehyde by unactivated Raney nickel, which indicates the different characteristics of the compound from β-hydroxyalkanoate obtained by Reformatsky reaction.[5]

1) T. Mukaiyama, K. Inomata, and S. Yamamoto, *Tetrahedron Lett.*, **1971**, 1097.
2) T. Mukaiyama, S. Yamamoto, and K. Inomata, This Bulletin, **44**, in press (1971).
3) Prepared by thermal cracking of acetone.
4) P. I. Paetzold and S. Kosma, *Chem. Ber.*, **103**, 2003 (1970).
5) R. L. Shriner, "Organic Reactions," Vol. 1, Wiley, New York, N. Y., (1942), p. 1.