

The Reaction of Trisalkylthioboranes with Carboxylic Acids; a New Thioester Synthesis

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A RECENT report¹ indicated that acetic acid reacted with tris(isopropyl)thioborane to yield tetra-acetyl diborate in unstated yield. No mention was made of any production of *S*-isopropyl thioacetate, an omission that was surprising in view of work currently proceeding on the mechanism of the reaction between boron amines and carboxylic acids to yield amides.^{2,3}

Accordingly, approximately molar equivalent portions of various carboxylic acids were treated with trisethylthioborane in a refluxing solvent; in each case a high yield of the corresponding thioester was isolated (Table).

As *ca.* 10% of unchanged acid was always recovered, the actual yield on the acid converted was correspondingly higher. The work-up procedure is simple (wash with aqueous sodium hydrogen carbonate, then water) and the thioboranes are readily available⁴ and easier to handle than the thiols.

Acetic acid behaved normally in this reaction to yield 77% of the thioester after 2 hr. reflux in benzene. Repe-

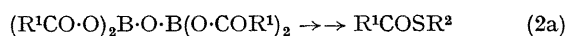
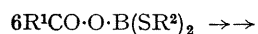
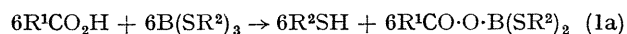
TABLE*

Acid	Time (hr.)	Solvent	% Yield†
Me[CH ₂] ₄ ·CO ₂ H	2	PhH	81
Me ₂ CH·CO ₂ H ..	8	Et ₂ O	74
Me ₃ C·CO ₂ H ..	168	Et ₂ O	75
PhCO ₂ H ..	6	PhH	72
PhCO ₂ H ..	7	Glyme	78
<i>p</i> -MeO·C ₆ H ₄ ·CO ₂ H ..	6	„	78

* All products completely characterised; † yield of isolated, distilled thioester.

tition of Lalancette's work¹ (but using trisethylthioborane) yielded 24% of thioester (based on thioborane).

Due to the extreme lability of the B-S bond⁵ the multiple reaction sequence proceeds in two well-defined stages.



At lower temperatures (*i.e.* room temperature) the reaction may be stopped at stage (1b), all acids tried proceeding rapidly to this stage. This represents a gentle and efficient method for activating a carboxylic acid.

At higher temperatures the two anhydride species are separately attacked to yield thioester. The main attacking

species is not the ethyl thiol liberated, since, if acetic acid and thioborane are mixed in the ratio of 3 : 1 (no thioborane regenerated) the attack on the mixed anhydride is inhibited. After 24 hr. reflux in benzene, most of the tetra-acetyl diborate was intact, whereas reaction is complete in 2 hr. when molar equivalents of the two reactants are used. As the previous workers used twelve-fold excess of acetic acid,¹ this observation explains their isolation of some tetra-acetyl diborate. The nature of the attacking species is under investigation.

Due to the speed of the reactions in stage (1) the actual steps leading to the anhydrides are not known. Despite the attested instability of triacyloxyboranes⁶ it is not certain that they are intermediates in these processes.

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² P. Nelson and A. Pelter, *J. Chem. Soc.*, 1965, 5142.

³ T. Levitt and A. Pelter, *Nature*, 1966, **211**, 5046.

⁴ J. Goubeau and H. W. Wittmeier, *Z. anorg. Chem.*, 1952, **270**, 16.

⁵ R. H. Cragg and M. F. Lappert, *Organometallic Chem. Rev.*, 1966, **1**, 43.

⁶ W. Gerrard, "The Organic Chemistry of Boron," Academic Press, New York, 1961, p. 51.