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

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A RECENT report[1] indicated that acetic acid reacted with trisisopropylthioborane 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 available[4] 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. Repetition of Lalancette's work[1] (but using trisethylthioborane) yielded 24% of thioester (based on thioborane).

TABLE*

Acid	Time (hr.)	Solvent	% Yield†
$Me[CH_2]_4 \cdot CO_2H$	2	PhH	81
$Me_2CH \cdot CO_2H$	8	Et_2O	74
$Me_3C \cdot CO_2H$	168	Et_2O	75
$PhCO_2H$	6	PhH	72
$PhCO_2H$	7	Glyme	78
p-$MeO \cdot C_6H_4 \cdot CO_2H$ ..	6	,,	78

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

Due to the extreme lability of the B–S bond[5] the multiple reaction sequence proceeds in two well-defined stages.

$$6R^1CO_2H + 6B(SR^2)_3 \rightarrow 6R^2SH + 6R^1CO\cdot O\cdot B(SR^2)_2 \quad \text{(1a)}$$

$$6R^1CO\cdot O\cdot B(SR^2)_2 \twoheadrightarrow (R^1CO\cdot O)_2B\cdot O\cdot B(O\cdot COR^1)_2 + (R^1CO)_2O + 4B(SR^2)_3 \quad \text{(1b)}$$

$$\begin{tikzcd} (R^1CO\cdot O)_2B\cdot O\cdot B(O\cdot COR^1)_2 \arrow[r, two heads] & R^1COSR^2 & \text{(2a)} \\ (R^1CO)_2O \arrow[ur, two heads] & & \text{(2b)} \end{tikzcd}$$

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 triacyloxyboranes[6] it is not certain that they are intermediates in these processes.

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