

Alkylation of Lithium Trialkylalkynylborates with Benzo-1,3-dithiolium Fluoroborate

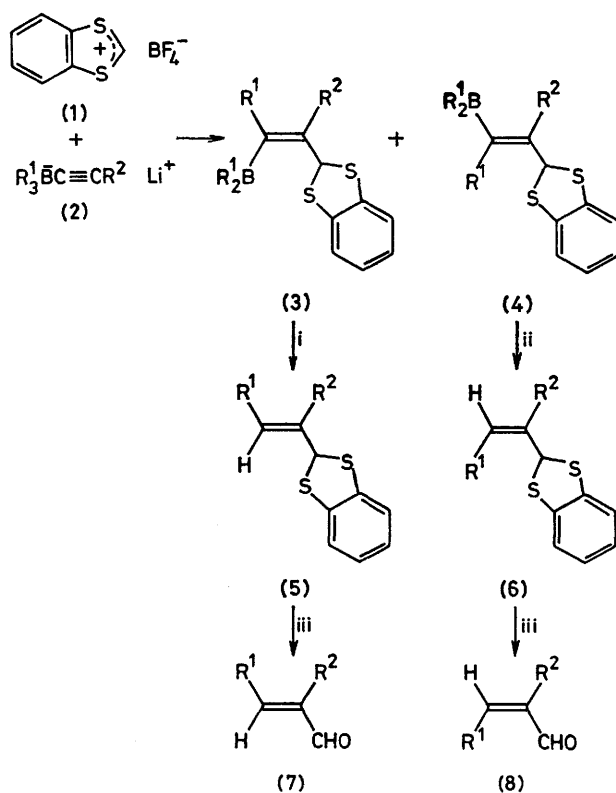
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Summary Lithium trialkylalkynylborates react in a stereoselective fashion with benzo-1,3-dithiolium fluoroborate to give vinylboranes which on oxidation yield protected 3-oxo-aldehydes and on hydrolysis give protected $\alpha\beta$ -unsaturated aldehydes; the hydrolysis is highly selective giving rise eventually to stereospecifically defined $\alpha\beta$ -unsaturated aldehydes by a novel process.

ALTHOUGH many reactions of alkynylborates are known¹ it has not proven possible to functionalise these compounds directly. We now report that they react in a facile manner with the readily available crystalline benzo-1,3-dithiolium fluoroborate² to yield intermediates (3) and (4) from which protected 3-oxo-aldehydes and $\alpha\beta$ -unsaturated aldehydes may be produced by oxidation and hydrolysis respectively.

The reaction-hydrolysis sequence is outlined in the Scheme.



SCHEME. Reagents: i, $\text{Pr}^i\text{CO}_2\text{H}$, 1 h, 25 °C; ii, $\text{Pr}^i\text{CO}_2\text{H}$, 48 h, 50 °C; iii, HgO, BF_3 .

The reaction is stereoselective, giving at least a 5:1 mixture of (3):(4), the ratio being established by total hydrolysis of the mixture and examination of the ratio of the well separated $\text{CH}(\text{SR})_2$ ^1H n.m.r. signals. That the major isomer is (3) was established by removal of the

protecting groups to give (7) and (8) and examination of the position of the ^1H n.m.r. signals of the vinyl protons. The fact that (3) is the major isomer is surprising in view of our previous findings³ on the stereochemistry of alkylation of alkynylborates and is more in line with the stereochemical results of attack by metal halides such as R_2PCl .¹

Reaction with isobutyric acid for 1 h, standard conditions for the hydrolysis of vinylboranes, readily converted compounds (3) into (5) but the boranes (4) proved remarkably stable and were recovered in pure form from the reaction mixture by column chromatography. Compounds (4) could then be separately hydrolysed at 50 °C for 48 h to give pure (6). In one case ($\text{R}^1 = \text{cyclopentyl}$, $\text{R}^2 = \text{pentyl}$) the very small amount of (4) produced could not be hydrolysed under any conditions we tried.

As the isomers (3) and (4) can be readily separated as a result of this selective hydrolysis, the whole sequence represents a novel stereospecific synthesis of $\alpha\beta$ -unsaturated aldehydes either free or in a protected form. A representative sample of results in which primary, secondary, or phenyl groups migrate and in which an alkyl or phenyl group is attached to the triple bond is given in Table 1. It is noteworthy that when a phenyl group migrates the initial alkylation is completely stereospecific to give (3; $\text{R}^1 = \text{Ph}$). When a secondary group migrates almost all the product consists of (3), with a small amount of (4) which resists hydrolysis and could not therefore be accurately analysed.

TABLE 1. Results of alkylation-hydrolysis of alkynylborates (2) with (1).

R^1	R^2	% Yield of (5) ^a	Ratio of (5):(6)
Hexyl	Pentyl	77	83:17
Cyclopentyl	"	71	? ^b
Phenyl	"	74	100:0
Hexyl	Phenyl	87	85:15

^a All yields are of isolated, purified materials. ^b Very little of (6) formed but ratio could not be analysed; see text.

Attempts to maximise the yield with respect to the migrating alkyl group by use of 9-borabicyclo[3.3.1]nonane and bis-(1,2-dimethylpropyl)alkylalkynylborates were unsuccessful as mixtures of products resulted.

If (3) and (4) could be specifically oxidised at the C-B bond then 3-oxo-aldehydes protected on the aldehyde group (9) would result [see equation (1)]. This, however, necessitates a very specific oxidation of the C-B bond in the presence of two sulphur atoms in the same molecule.

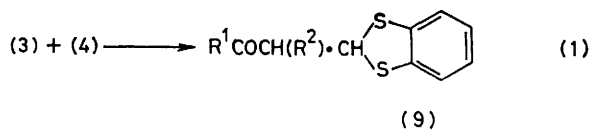


TABLE 2. Oxidation of vinylboranes (3) and (4).

R ¹	R ²	Oxidant, % yield ^a of (9)	
		Me ₃ NO (t/h at reflux)	NaOH-H ₂ O ₂ (t/h)
Hexyl	Pentyl	70(10)	66(36)
"	Phenyl	60(2)	62(3)
Pentyl	Pentyl	85(2)	90(3)
Cyclopentyl	"	42(21)	30(12) ^b

^a Yield of isolated, purified product. ^b Yield not increased by oxidation for 120 h.

We found that anhydrous trimethylamine *N*-oxide^{4,5} in tetrahydrofuran was a suitable oxidant as was strongly alkaline hydrogen peroxide.⁵ Oxygen, pyridinium dichromate, and *m*-chloroperbenzoic acid all failed to give a single product. Representative yields are given in Table 2.

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