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REACTIONS OF TRIALKYLALKYNYLBORATES WITH 2-ALKYL-1,3-DIOXALAN-2-YLIUM FLUOROSULPHONATES. VERSATILE DIRECT ROUTES TO Z-$\alpha\beta$-UNSATURATED KETONES, SPECIFICALLY PROTECTED 1,3-DIKETONES AND OTHER KETONIC SPECIES.

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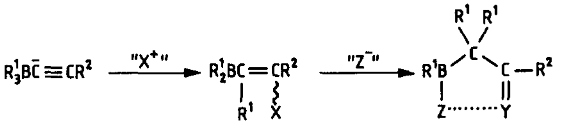
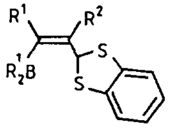
The reactions of 2-alkyl-1,3-dioxolan-2-ylium fluorosulphonates with trialkylalkynylborates proceed at the β-position of the alkynylborates and may be controlled to give either one or two migrations from boron to carbon. The one migration is stereospecific and the products on hydrolysis yield Z-$\alpha\beta$-unsaturated ketones, whilst oxidation gives specifically mono-protected 1,3-diketones. If the reactions are allowed to proceed for a longer time, then a second migration from boron to carbon occurs to yield intermediates that give other $\alpha\beta$-unsaturated ketones on oxidation.

Triorganylalkynylborates, $R^1_3\bar{B}C{:}CR^2Li^+$, 1, are versatile intermediates[1] due to their ability to react at their β-position with electrophiles with concomitant migration of an organyl group from boron to the α-position of the alkynyl group. This one migration (eq.1) may be followed by a further migration induced by nucleophilic attack on boron. The nucleophile may be external or it may be associated with the initial electrophile (e.g. in acylation) as shown in equation 1. To potentiate these reactions to obtain one or two migrations at will remains a prime objective in this field.



(1)

However, direct functionalisation of the alkyne group has presented problems. Reactions with acetyl chloride[2] and titanium tetrachloride activated orthoesters[3] leads to two migrations of groups from boron to carbon without the possibility of isolation of the important one migrated intermediates. We recently introduced the reactions of 1 with benzodithiolium tetrafluoroborate which proceeds with one migration to yield protected 3-oxoaldehydes and $\alpha\beta$-unsaturated aldehydes by oxidation and hydrolysis of intermediates 2 and 3.[4] Overall yields are good and the ratio of 2 : 3 varies from 83:17 to 100:0, the reaction being highly stereoselective.



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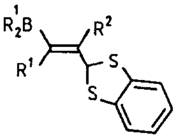
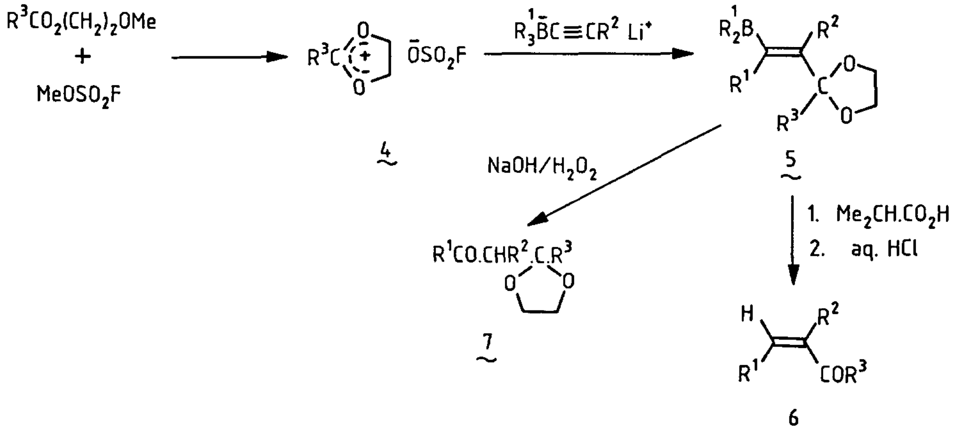


3

More recently an elegant stereospecific carboxylation of 1 to give $\alpha\beta$-unsaturated acids has been described.[5]

If salts 1 could be induced to react with dioxolanium salts with one migration rather than with benzodithiolium salts there could be real advantages. In particular, specific oxidation of the intermediates and removal of the protecting groups when required would be considerably easier. A method has recently been developed[6,7] for the general synthesis of 2-alkyl-1,3-dioxolan-2-ylium fluorosulphonates. The use of these salts to induce one migration reactions in 1, seemed possible as to us it appeared that the Lewis acid required was responsible for the second migration observed in the orthoester condensation. In addition, salts 4 are considerably more generally available than orthoesters.

In the event the reactions shown in Scheme 1 were carried out with results as detailed in Table 1.



Scheme 1

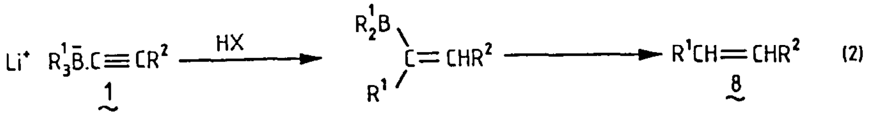
Table 1.

Synthesis of trisubstituted $\alpha\beta$-unsaturated ketones 6.

Exp^t	R^1	R^2	R^3	Yields[a]		
				6	8	10
1.	Hexyl	Hexyl	Propyl	60	10	8
2.	Hexyl	Hexyl	Methyl	57	14	10
3.	Hexyl	Phenyl	Methyl	50	13	16
4.	Butyl	Phenyl	Propyl	70[b]	7[b]	18[b]

[a] Yields are of isolated, characterised products. [b] G.c. yield. Isolated product characterised from a separate, unoptimised experiment.

Various points are of importance. Firstly our reactions were standardly carried out for 3h. at -78°C, but a later experiment showed that two migration product **10** (Expt.4) increased from 18% in 30 min. to 40% in 3h. Hence all reactions designed to yield one migration product would benefit from very short reaction times, an unexpected result as it was not thought that lithium fluorosulphonate at low temperature could bring about the migration shown in Scheme 2. Secondly, we did not try to isolate the dioxolanes corresponding to **5**, but in experiments 1 and 4 the initial products were mainly the dioxolanes, suggesting this is possible, if required. Thirdly the methylation[8] and protonation[9] of alkynylborates is very rapid and efficient (eq.2) and despite careful washing of salts **4**, there was always sufficient protic acid present to give some, readily separated, protonation product **8**.



(2)

The main point of interest is that the reactions are highly stereoselective. In the cases of experiments **1**, **2** and **3** only the *Z*-αβ-unsaturated ketones **6** (structures from ^{1}H n.m.r. experiments)[10,11] could be detected and isolated. With experiment **4**, *ca* 3% of the *E*-isomer was obtained, this being useful in establishing n.m.r. data for structure determination. Thus the process leads almost exclusively to the *Z*-isomers, in complete contrast to the reactions with benzodithiolium tetrafluoroborate, and in line with simple alkylation reactions.[8] The stereospecificity of the process is one of its most valuable features.

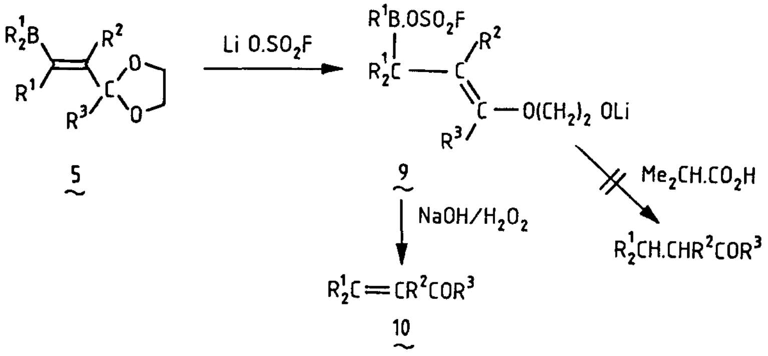
Oxidation of intermediates **5** with alkaline hydrogen peroxide gave the specifically protected 1,3-diketone derivatives **7** as detailed in Table 2.

Table 2.
Synthesis of β-oxo-1,3-dioxolanes, **7**

R^1	R^2	R^3	% yield[a]
Hexyl	Hexyl	Methyl	50
Hexyl	Phenyl	Methyl	49
Butyl	Phenyl	Propyl	46

[a] Yields are of isolated, purified, characterised product.

The same reactions that gave one migration products were allowed to stand for *ca* 16 h. at room temperature to give intermediate **9**, Scheme 2. Attempts to hydrolyse **9** were unsuccessful in each case, but subsequent oxidation gave αβ-unsaturated ketones **10** as detailed in Table 3. Thus simply by varying the reaction time it is possible to accomplish one migration (Scheme 1) or two migrations (Scheme 2) of organyl groups from boron to carbon in this system.



Scheme 2

A direct oxidation (without attempted hydrolysis) of **9** (Table 3. Exp.3) gave a better g.c. yield of product.

The overall yields are modest but are based on initial alkyne and include two migrations, an oxidation, and a dehydration. The ketones **10** are similar products to those previously obtained by Suzuki[3] and Utimoto[2].

Table 3

Synthesis of tetrasubstituted αβ-unsaturated ketones **10**.

Exp.	R^1	R^2	R^3	% yield of 10[a]
1.	Hexyl	Phenyl	Methyl	40
2.	Butyl	Phenyl	Methyl	45(60)[b]
3.	Hexyl	Hexyl	Methyl	48
4.	Hexyl	Hexyl	Prop	43

a) Yields are of isolated, purified products. b) The yield in parenthesis is a g.c. yield without hydrolysis prior to oxidation.

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