

Michael Reactions of Lithium Trialkylalkynylborates

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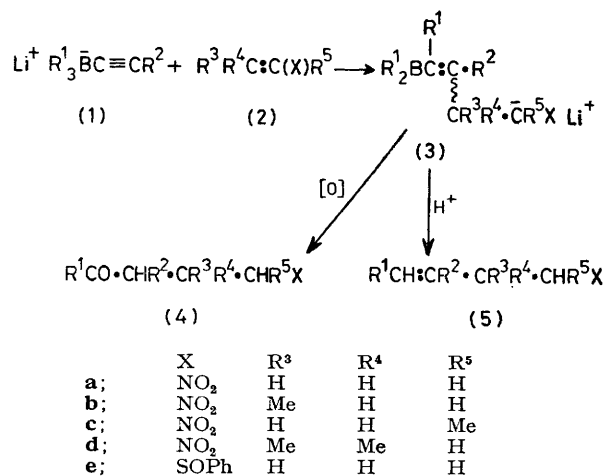
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Summary A novel Michael reaction that proceeds with migration of an alkyl group from boron to carbon is reported.

SYNTHETICALLY useful ionic reactions of organoborates normally proceed by attack of an electrophile upon the borate to produce a dipolar intermediate or transition state in which 1,2-migration from boron to carbon occurs with neutralisation of charge.¹

We now report an important extension of the chemistry of organoborates in which lithium alkynylborates (1) readily react with Michael-type acceptors (2) in a true Michael reaction in which the charge is not neutralised but displaced to an energetically more favourable position. At the same time an alkyl migration occurs (Scheme) to give intermediates (3) in a fashion unique both in organoborate chemistry and in Michael reactions.

We have oxidised the intermediates (3) to the ketones (4) and hydrolysed them to the alkenes (5). Currently we



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have concentrated on those compounds in which $X = \text{NO}_2$, the products then being capable of transformation to the corresponding carbonyl compounds³ (Table).

TABLE. Yields of products from Michael reactions of lithium alkynylborates (**1**) ($R^2 = \text{hexyl}$ throughout).

X	R ¹	R ³	R ⁴	R ⁵	Yield (%) ^a
NO ₂	Hexyl	H	H	H	80 ^{b,c}
NO ₂	Hexyl	H	Me ^d	H	93 ^c
NO ₂	Hexyl	H	Me ^d	H	82 ^e
NO ₂	Hexyl	Me	Me	H	0 ^c
NO ₂	Hexyl	H	H	Me	57 ^{b,c} +5 ^e
NO ₂	Cyclopentyl	H	Me ^d	H	75 ^c
NO ₂	Pentyl	H	Me ^d	H	75 ^c
SOPh	Hexyl	H	H	H	10 ^{e,f}

^a All yields are of isolated, characterised products with satisfactory spectral properties and elemental analyses, unless otherwise stated. ^b Alkene introduced as vapour in a stream of dry nitrogen. ^c Oxidation product. ^d *cis-trans*-Mixture of alkene used. ^e Hydrolysis product. ^f Estimated by u.v. spectroscopy.

The reaction suffers from the usual steric restrictions associated with Michael reactions³ (Table). Further when two of the alkyl groups attached to boron are replaced by a 9-borabicyclo[3.3.1]-residue, in an effort to conserve alkyl groups, the secondary bridgehead carbon atoms migrate in competition with a primary alkyl group.

The anion (**3**) does not undergo further reaction with the Michael acceptor but should be capable of further elaboration (*i.e.* alkylation, acylation). We have attempted to extend the reaction to the alkene (**2e**)⁴ but with limited success owing to a further rearrangement occurring on oxidative work-up of (**3e**)⁵ (Table).

A typical procedure is as follows. 1-Nitropropene (**2b**) (5 mmol) was added to lithium tri-*n*-hexyloctynylborate¹ (5 mmol) in dry THF (10 ml) at 0 °C and the mixture allowed to warm to 20 °C. After 20 min at this temperature oxidation or hydrolysis was carried out.

Oxidation was achieved by addition at 0 °C of 5 M aq. NaOAc (5 ml) followed by 50% H₂O₂ (5 ml). After at least 3 h at 20 °C the solution was acidified with 5 M aq. HCl (6 ml) and the crude product extracted with ether. Chromatographic purification gave the nitroketone (**4b**, R¹ = R² = *n*-hexyl) (93%). Hydrolysis was carried out by allowing the reaction mixture to stand with degassed isobutyric acid (2 ml) for 17 h at 20 °C, followed by neutralisation and oxidation (to destroy borinates and make product isolation easier) as before. The nitroalkene (**5b**, R¹ = R² = *n*-hexyl) was isolated in 82% yield following column chromatography.

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