

THE REACTION OF LITHIUM TRIALKYLALKYNYLBORATES.  
 NOVEL SYNTHETIC METHOD OF  $\alpha,\beta$ -UNSATURATED KETONES

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The reaction of trialkylalkynylborates (1) with acyl chlorides was reported to give 2-oxa-3-bororenes (2) and ketones  $\text{RCOC}\equiv\text{CR}'$ .<sup>1, 2, 3</sup> Transformation and synthetic application of this kind of boron compounds, however, have not been reported. This paper describes a novel synthesis of  $\alpha,\beta$ -unsaturated ketones (4) which is based on the reinvestigation of the 2-oxa-3-bororene synthesis.

A solution of triisopropyl(1-heptynyl)borate (1a) in THF-hexane (1:1, 10 ml) was prepared from triisopropylborane (0.70 g, 5.0 mmol) and 1-heptynyllithium (10.0 ml of 0.5 M solution in THF-hexane). Acetyl chloride (0.47 g, 6 mmol) was added to the solution and the mixture was heated under reflux for 10 h. Glc of the reaction mixture indicated the formation of 2-oxa-3-bororene (2a), which was isolated by distillation, bp 120-125° (4 mm) in 65% yield. Formation of the alkynyl ketone was not detected.<sup>1</sup> Jones oxidation of 2a (0.5 M solution in acetone, at room temperature) gave the corresponding  $\alpha,\beta$ -unsaturated ketone 4a in 42% overall yield based on 1-heptyne. This is a convenient  $\alpha,\beta$ -unsaturated ketone synthesis schematically involving gem-dialkylation at C-1 and acylation at C-2 of the starting acetylene.

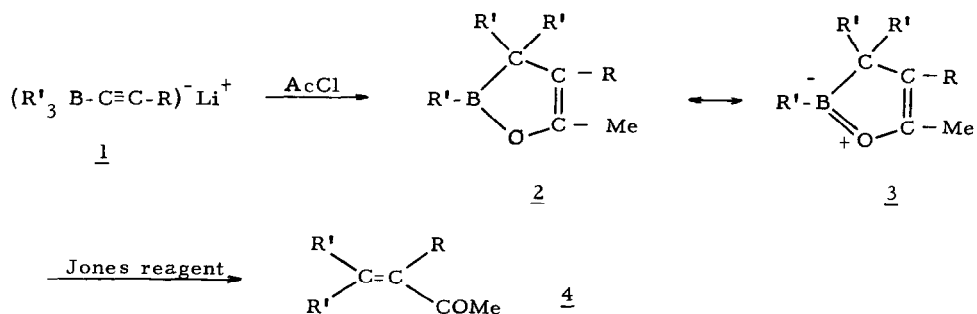


Table 1. Highly Substituted  $\alpha,\beta$ -Enones Prepared<sup>7</sup>

	R	R'	bp °C (mm)	$\nu_{\text{C=O}}$ (cm <sup>-1</sup> )	MS (m/e)		Yield (%)
					M <sup>+</sup> (%)	base peak	
<u>4a</u>	n-Am	i-Pr	106-110 (10)	1693	224 (8)	43	42
<u>4b</u>	n-Am	n-Bu	90-100 (4)	1691	252 (9)	43	36
<u>4c</u>	Ph	i-Pr	105-110 (6)	1692	230 (8)	43	36
<u>4d</u>	Ph	n-Bu	120-130 (6)	1681	258 (20)	43	30

The cyclic borinates 2 resisted usual oxidation of organoboranes using alkaline hydrogen peroxide, trimethylamine oxide, or triplet oxygen. Attempted hydrogenation of the unsaturated bond of 2 failed to proceed over Pd-C and PtO<sub>2</sub>. On the contrary, aliphatic enol borinate is easily hydrolysed and oxidized by usual oxidation reagents.<sup>4</sup> This unusual stability of cyclic enol borinates 2 is ascribed to the major contribution of the structure 3.<sup>5</sup>

## REFERENCES AND REMARKS

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5. This was evidenced by uv spectra (in EtOH): 2a,  $\lambda_{\text{max}}$  238 nm ( $\epsilon$  2800), cyclopentadiene,  $\lambda_{\text{max}}$  238 nm ( $\epsilon$  4200).<sup>6</sup>
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7. All new compounds gave correct C, H analyses.