

THE REACTION OF LITHIUM TRIALKYLALKYNYLBORATES WITH OXIRANES
 PRODUCING *r*-HYDROXYKETONES AND TRISUBSTITUTED OLEFINS
 OF DEFINITE CONFIGURATION

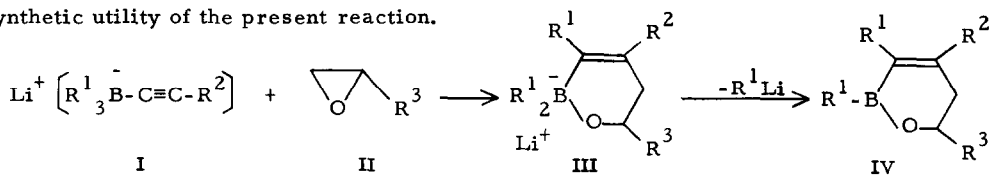
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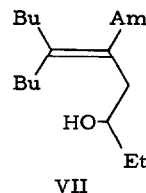
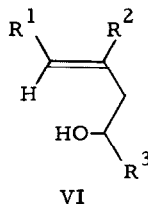
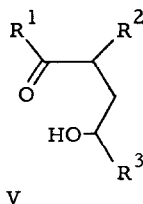
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In continuation of the studies on synthetic applications of trialkyl-1-alkynylborates (I),^{1,2} the present paper discloses a novel reaction of I with oxiranes II affording non-isolable intermediates III, from which we have obtained *r*-hydroxyketones V, trisubstituted olefins VI, and a tetrasubstituted olefin VII upon the appropriate work-up in three different ways.

To a solution of 1-heptyne (0.48 g, 5.0 mmol) in THF (5.0 ml) at 0° under nitrogen atmosphere, butyllithium (5.0 mmol in 5.0 ml of hexane) was added and stirring was continued at room temperature for 30 min. Tributylborane (0.91 g, 5.0 mmol) was added to the solution and the reaction mixture was stirred at room temperature for 1 hr. To the mixture ethyloxirane (0.54 g, 7.5 mmol) was added at room temperature and the whole was heated at reflux for 10 hr. We believe the reaction mixture thus obtained is a solution of non-isolable cyclic borate IIIa, but the presence of reactive borinate IVa, which was isolated upon glc of the reaction mixture, can not be excluded rigorously.^{3,4} The reaction of I with oxirane itself was performed by bubbling it in the solution of the ate complex at room temperature. Following observations on working up the reaction mixture warranted the synthetic utility of the present reaction.



Ia, IIa, IIIa, IVa: R¹=Bu, R²=Am, R³=Et



r-Hydroxyketones V. The above-described reaction mixtures containing III gave V⁵ upon usual oxidative work-up with alkaline H₂O₂ as listed in Table 1. The yields are based on I initially added.

TABLE 1. *r*-Hydroxyketones V^a

R ¹	R ²	R ³	Yield (%)	bp °(mm)	$\nu_{\text{C=O}}$ (cm ⁻¹) (neat)	MS m/e (rel. %) ^b Parent Peak
n-Bu	Am	Et	53	112-115 (5)	1703	314 (0.5)
i-Pr	Am	Et	72	162-163 (26)	1713	300 (0.5)
i-Pr	Ph	Et	59	136-140 (4)	1710	306 (0.2)
i-Pr	Am	Ph	65	150-152 (5)	1708	348 (0.4)
i-Pr	Am	Me	72	102-104 (6)	1709	286 (0.5)
i-Pr	Am	H	82	127-131 (5)	1710	272 (0.2)
n-Bu	Am	H	74	142-145 (5)	1710	286 (0.3)

^a *r*-Hydroxyketones V listed in this table are new compounds.⁷

^b Ms were taken with the trimethylsilyl ethers of the respective V.

The C-O cleavage of II thus occurred regioselectively at the unsubstituted carbon to afford the corresponding single isomer of V. Cyclohexene oxide as a sym. disubstituted oxirane gave only 19% yield of 2-(1-amy1-2-oxohexyl)cyclohexan-1-ol,⁷ bp 111-114° (3mm), ir (neat) 3450, 1706 cm⁻¹, ms m/e (rel. intensity %) 340 (M⁺, 1), 170 (100), 73 (97) (Ms was taken with the trimethylsilyl ether). The low yield may be ascribed to the steric hindrance at the reaction site.⁸ In this way, C-1 of the substrate acetylene is transformed into an acyl group containing the R¹ of the borane and C-2 joins the oxirane II to form the *r*-hydroxyketone V.

Trisubstituted olefins VI with rigorous stereochemistry. The above-described reaction

mixtures containing III were treated with AcOH (2.1 g, 30 mmol) under reflux for 5 hr and treated with 6N NaOH (10 ml). Extraction (hexane), drying (Na_2SO_4), and distillation in vacuo gave VI as listed in Table 2. Structures of VI were consistent with the spectra.

When R^2 was phenyl, a mixture of (Z) and (E) isomers (52:48) was obtained. This is attributed to the configurational change in the course of C-B bond protonolysis. With this exception in mind, the sequence is a novel addition to the stereoselective syntheses of trisubstituted olefins and schematically involves alkylation at C-1 and 2-hydroxyalkylation at C-2 of the acetylenes, both occurring 100% selectively in a trans fashion.

TABLE 2. Trisubstituted Olefins VI.^a

R ¹	R ²	R ³	Yield (%)	bp °(mm)	MS m/e (rel. intensity %)	
					Base Peak	Parent Peak
n-Bu	Am	Et	75	117-120 (5)	55	226 (1)
i-Pr	Ph	Et	51 ^b	112-114 (4)	43	218 (2)
i-Pr	Am	Me	70	81 - 83 (6)	83	198 (4)
i-Pr	Am	H	80	90 - 91 (6)	31	184 (3)
n-Bu	Am	H	74	102-105 (4)	31	198 (4)

^a Trisubstituted olefins VI listed in this table are new compounds.⁷

^b This is a mixture of (Z) and (E) isomers. See Text.

A tetrasubstituted olefin VII. Treatment of the above-described reaction mixture containing IIIa with 6N NaOH (3.0 ml) and then with iodine (1.27 g, 5.0 mmol),¹⁰ followed by extraction (hexane) and chromatography on silica-gel column, gave 5-amyl-6-butyl-5-decen-3-ol⁷ (VII, 0.48 g, 34%), bp 134-136° (4 mm), ms of trimethylsilyl ether m/e (rel. intensity %) 354 (M^+ , 0.3), 131 (100), 73(34). The reaction schematically consists of gem-dialkylation at C-1 and 2-hydroxyalkylation at C-2 of 1-heptyne.

A straight-chain γ -hydroxyketone VIII. Trimethylsilylacetylene¹¹ (0.98 g, 10 mmol) dissolved in THF (10 ml) was treated with butyllithium (10 mmol in 20 ml of hexane) at 0° under nitrogen atmosphere. After stirring was continued at room temperature for 20 min, trihexylborane (10 mmol in 5 ml of THF) was added to the solution at 0° and the mixture was stirred for 1 hr at room temperature. Methyloxirane (1.16 g, 20 mmol) was added and the mixture was heated at reflux for 20 hr. Oxidative work-up gave undecan-2-ol-5-one⁷ (VIII,

