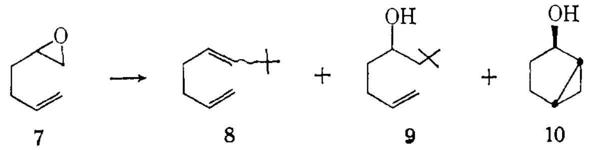
of an external olefin have been uniformly unsuccessful. However, more satisfactory results are achieved when the reacting partners are incorporated into the same molecule. Thus, *t*-butyllithium transformed 5,6-epoxy-1-hexene (**7**) into a 54% yield of a mixture of *cis*- and *trans*-7,7-dimethyl-1,5-octadienes (**8**), 7,7-dimethyl-1-octen-4-ol (**9**), and *trans*-2-bicyclo[3.1.0]hexanol[9] (**10**) in a ratio of 63:30:17.



The formation of **10** appears to require an α-elimination mechanism as described above, except that the final step of the sequence is carbenoid addition to the neighboring double bond. The bicyclic alcohol is formed stereospecifically in this case; none of the epimeric alcohol is observed. Compound **9** is the expected nucleophilic addition product, while the mixture of olefins is thought to derive from carbenoid decomposition of **7** also.[10] No appreciable amounts of β-elimination products were found.

These studies illustrate that the scope of epoxide decomposition by α-elimination mechanisms is more general than heretofore realized and that the use of alkyllithium reagents as bases enhances reaction by this pathway, presumably by favoring the metalation reaction. Current knowledge concerning the details of α-elimination processes of organometallic species[11] suggests that *free* divalent carbon intermediates are probably not involved, but rather that insertion and addition are occurring simultaneously with bond breaking to the leaving groups. Further work will be required to establish this point and to probe the interesting stereochemical aspects of these reactions.[12]

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(9) We thank Professor Paul Gassman for kindly providing comparison infrared spectra of the epimeric 2-bicyclo[3.1.0]hexanols: P. G. Gassman and F. V. Zalar, *J. Am. Chem. Soc.*, **88**, 2252 (1966).

(10) J. K. Crandall and L.-H. C. Lin, *ibid.*, **89**, 4527 (1967).

(11) For a recent discussion of this area see G. Köbrich, *Angew. Chem. Intern. Ed. Engl.*, **6**, 41 (1967).

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J. K. Crandall, Luan-Ho C. Lin
Contribution No. 1413, Department of Chemistry
Indiana University, Bloomington, Indiana 47401

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Base-Promoted Reactions of Epoxides. IV. Formation of Substituted Olefins from the Reaction of Epoxides with Organolithium Reagents[1]

Sir:

The reaction of epoxides with organometallic reagents constitutes a well-known synthetic method for the preparation of alkyl-substituted alcohols.[2] In the course of our studies on base-induced epoxide rearrangements,[3] we have examined the action of alkyllithiums on a variety of typical epoxides. The present communication records an unexpected reaction of an entirely different nature which occurs as a relatively general consequence of the interaction between these two reactants. This unique transformation results in the overall conversion of the epoxide to the corresponding olefin *with concomitant substitution of the alkyl group of the alkyllithium at one of the olefinic carbons.*[1] Equation 1 illustrates the general reaction which should have some synthetic potential. Simple nucleophilic addition of the organometallic and base isomerization[3] are competing modes of epoxide utilization of variable efficiency. However, these side reactions are surprisingly ineffective in most of the examples which we have investigated.

(1)

In a typical experiment, 1 equiv of *t*-butylethylene oxide (**1**) was treated with 3 equiv of commercial *t*-butyllithium at reflux temperature in pentane for 24 hr to give a 64% *isolated* yield of *trans*-di-*t*-butylethylene[4] (**2**) along with only 6% of 2,2,5,5-tetramethyl-3-hexanol[5] (**3**), the nucleophilic addition product. This particular reaction constitutes an especially expedient synthesis for small amounts of the hindered olefin product. *sec*-Butyllithium and *n*-butyllithium gave comparable results with epoxide **1** (67 and 39% yields, respectively, of the corresponding olefins). 1,2-Epoxybutane and 1,2-epoxycyclopentane also gave acceptable preparative yields of the appropriate olefins when treated with *n*-butyllithium (37 and 41%) and *t*-butyllithium (57 and 49%). However, only a small amount of 3-hexene was detected from ethyllithium and 1,2-epoxybutane. Epoxides which are thought to form rearrangement products by carbenoid pathways[3] with basic reagents (*e.g.*, cycloheptene, cyclooctene, and bicyclo[2.2.1]heptene oxides) gave small amounts of the substituted olefin with *t*-butyllithium but none with the *n*-butyl derivative. The usual base isomerizations were the major reactions with these epoxides. The several hindered and trisubstituted epoxides which were examined did not give the olefin-forming reaction.

Chart I

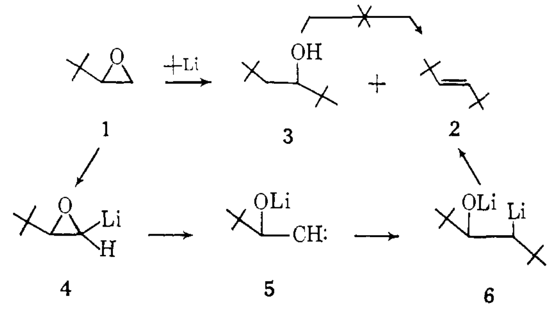

Chart I shows a proposed mechanistic sequence for the over-all reaction indicated in eq 1 using compound **1** as an example. Intermediacy of the nucleophilic

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(1) Part III: J. K. Crandall and L.-H. C. Lin, *J. Am. Chem. Soc.*, **89**, 4526 (1967).

(2) For a review, see A. Rosowsky in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part 1, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 1–523.

(3) J. K. Crandall and L.-H. Chang, *J. Org. Chem.*, **32**, 435, 532 (1967).

(4) W. H. Puterbaugh and M. S. Newman, *J. Am. Chem. Soc.*, **81**, 1611 (1959).

(5) Compound **3** was prepared by lithium aluminum hydride reduction of the corresponding acetate.[4]

addition products has been ruled out by the observation that the lithium salt of **3** is unchanged by *t*-butyllithium, either by itself or in the presence of a functioning epoxide reaction. The fact that olefin formation is not as important for those epoxides which undergo facile carbenoid reactions is suggestive that a related carbenoid mechanism is also operative for eq 1. Thus, metalation at an epoxide ring carbon produces the organolithium intermediate **4**. This species can undergo α elimination and carbenoid insertion into the carbon–lithium bond of a second *t*-butyllithium molecule to give **6**. This unusual chemical entity is proposed to *spontaneously eliminate the elements of lithium oxide*, thereby generating the olefinic bond of **2**. This description is an oversimplification, since it is well known that alkyllithiums exist as monomer aggregates in hydrocarbon solvents and that these units are modified by coordination with Lewis bases such as ethers (epoxides) and alkoxides.[6] However, it is not profitable to pursue this complicating factor for the present except to note that the carbenoid insertion into the carbon–lithium bond is therefore essentially an intramolecular event. Current knowledge[7] suggests that the α-elimination–insertion process is concerted and probably by-passes the free carbene stage.

The mechanistic sequence shown above is well precedented and relatively unexceptional, save for the last step involving loss of lithium oxide. The driving force for this elimination from **6** is thought to derive from the exceptionally high heat of formation of the metal oxide (142 kcal/mole).[8] We believe that the loss of stable metal oxides (Li, Al, B, etc.) may well prove to be a general reaction for species such as **6**, which have a metal and a metal alkoxide bonded to vicinal carbon atoms. The gross details of certain lithium aluminum hydride reductions of metal salts of β-dicarbonyl compounds to yield allylic alcohols[9] and the reactions of geminally dimetalated alkanes with carbonyl compounds to produce olefins[10] can be envisioned as proceeding *via* intermediates related to **6**. The dehydration of primary amides to nitriles is a further example of the elimination of lithium oxide to give a multiple bond.[11] We are currently engaged in looking for additional instances of such reactions[12] and in probing the stereochemical details of metal oxide eliminations, which show a strong preference for the formation of *trans* olefins in the epoxide reactions described above.[13]

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(6) T. L. Brown, *Advan. Organometal. Chem.*, **3**, 365 (1965).

(7) For a recent discussion of this point, see G. Köbrich, *Angew. Chem. Intern. Ed. Engl.*, **6**, 41 (1967).

(8) "Handbook of Chemistry and Physics," 46th ed, The Chemical Rubber Co., Cleveland, Ohio, 1965, p D24.

(9) J. A. Marshall, N. H. Andersen, and A. R. Hochstetler, *J. Org. Chem.*, **32**, 113 (1967).

(10) G. Zweifel and R. B. Steele, *Tetrahedron Letters*, 6021 (1966); G. Cainelli, G. D. Bello, and G. Zubiani, *ibid.*, 4315 (1966); G. Cainelli, F. Bertini, P. Grasselli, and G. Zubiani, *ibid.*, 1581 (1967).

(11) E. M. Kaiser and C. R. Hauser, *J. Org. Chem.*, **31**, 3873 (1966); S. E. Ellzey, C. H. Mack, and W. J. Connick, *ibid.*, **32**, 846 (1967); L. G. Humber and M. A. Davis, *Can. J. Chem.*, **44**, 2113 (1966); M. S. Newman and T. Fukunaga, *J. Am. Chem. Soc.*, **82**, 693 (1960).

(12) Unpublished work in these laboratories by Mr. A. C. Clark has shown that *t*-butyllithium and 2-cyclopentenol cleanly produce 3-*t*-butylcyclopentene.

(13) This work was supported by a National Science Foundation research grant (GP-6610).

J. K. Crandall, Luan-Ho C. Lin
Contribution No. 1487, Department of Chemistry
Indiana University, Bloomington, Indiana 47401

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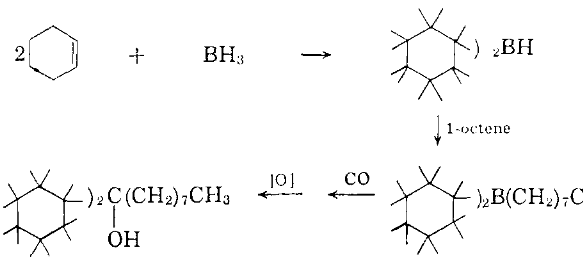
The Carbonylation of Mixed Trialkylboranes. Evidence for the Intramolecular Nature of the Transfer of Groups from Boron to Carbon in the Carbonylation Reaction. A Convenient Synthesis of Unsymmetrical Ketones, RR′CO

Sir:

The reaction of carbon monoxide with trialkylboranes[1] at atmospheric pressure[2] provides a highly convenient synthetic route to tertiary alcohols,[2a] secondary alcohols,[2b] ketones,[2b] and methylol derivatives.[2c] However, these syntheses start with R_3B, with three identical alkyl groups, and lead to tertiary alcohols, to secondary alcohols, and to ketones with identical alkyl groups. The scope of the synthesis would be greatly enhanced by its applicability to the synthesis of derivatives containing different alkyl substituents. We wish to report here the demonstration of the successful synthesis of such derivatives and the extension of this synthesis to products containing a variety of functional groups.[3]

The carbonylation of an equimolar mixture of triethylborane and tri-*n*-butylborane in the presence of ethylene glycol[2a] led to a product, after oxidation, which consisted of a mixture of triethylcarbinol and tri-*n*-butylcarbinol (1). There was no evidence for the presence of any mixed derivatives, such as diethyl-*n*-butylcarbinol or ethyl-di-*n*-butylcarbinol, which would have accompanied an intermolecular transfer of alkyl groups. Similarly, dicyclohexyl-*n*-octylborane, readily synthesized by the reaction of dicyclohexylborane and 1-octene, yielded dicyclohexyl-*n*-octylcarbinol in 82% yield, without evidence of any isomeric materials (2).

$$\begin{aligned} \mathrm{Et_3B} + \mathrm{CO} &\longrightarrow \mathrm{Et_3CBO} \xrightarrow{[O]} \mathrm{Et_3COH} \\ n\text{-}\mathrm{Bu_3B} + \mathrm{CO} &\longrightarrow n\text{-}\mathrm{Bu_3CBO} \longrightarrow n\text{-}\mathrm{Bu_3COH} \qquad (1) \end{aligned}$$



(2)

These results, indicating that the groups are transferred intramolecularly from boron to carbon, are consistent with the mechanism previously proposed.[1,2b] They are also promising for extending broadly the utility of this new synthetic route. Hydroboration[4] provides a convenient means for the synthesis of organoboranes containing either two, $R_2R'B$, or three different groups.[5] Consequently, there would appear to be no

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(1) M. E. D. Hillman, *J. Am. Chem. Soc.*, **84**, 4719 (1962); **85**, 982, 1626 (1963).

(2) (a) H. C. Brown and M. W. Rathke, *ibid.*, **89**, 2737 (1967); (b) *ibid.*, **89**, 2738 (1967); (c) M. W. Rathke and H. C. Brown, *ibid.*, **89**, 2740 (1967).

(3) H. C. Brown, G. W. Kabalka, and M. W. Rathke, *ibid.*, **89**, 4530 (1967).

(4) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(5) G. Zweifel and H. C. Brown, *J. Am. Chem. Soc.*, **85**, 2066 (1963); G. Zweifel, N. R. Ayyangar, and H. C. Brown, *ibid.*, **85**, 2072 (1963).