acid **15** (R = H), mp 273–276°; treatment with diazomethane gave the ester **15** (R = CH$_3$), mp 167–168°; oxidation with Jones reagent[4] afforded the keto ester **14,** mp 120–122.5°. The substance **14** was converted, by a known method,[5] into the unsaturated keto ester **13** (R = CH$_3$), mp 136.5–138°. Treatment with ethylene glycol and *p*-toluenesulfonic acid gave the ketal ester **12** (R = CH$_3$), mp 200–200.5°, $[\alpha]^{21}_{589}$ −80° and $[\alpha]^{21}_{320}$ −352° (dioxane) by ORD.

Acknowledgment. We wish to express our thanks to the U. S. Public Health Service and the National Science Foundation for supporting this study. We also acknowledge with pleasure the efforts of E. R. Habicht, Jr., and E. T. Jones, who helped to develop the procedures for preparing the tetracyclic material **9**, and of J. W. Scott, who performed some of the transformations involving the naturally derived intermediates. Finally we wish to thank Professor H. S. Mosher for helpful suggestions regarding the resolution experiments.

(4) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(5) R. M. Evans, J. C. Hamlet, J. S. Hunt, P. G. Jones, A. G. Long, J. F. Oughton, L. Stephensen, T. Walker, and B. M. Wilson, *ibid.*, 4356 (1956).

(6) The preparation of the tricyclic ketone 8 was first performed by W. S. J. and H. W. W. at the University of Wisconsin; H. W. Whitlock, Jr., Ph.D. dissertation, University of Wisconsin, 1960.

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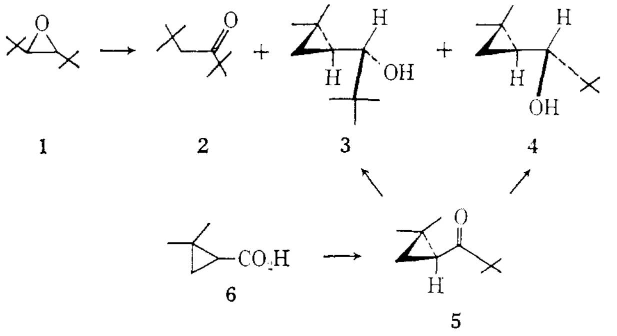
Base-Promoted Reactions of Epoxides. III. Carbenoid Decomposition in Acyclic Derivatives

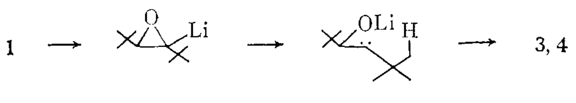
Sir:

Several medium-ring epoxides have been shown to give bicyclic alcohols in transannular reactions induced by strong, nonnucleophilic bases.[1] The rearrangement of cyclooctene oxide shown below is an example of this process. This transformation was demonstrated by Cope and co-workers[2] to proceed by an α elimination–carbenoid insertion mechanism. We have recently examined a number of additional epoxides under similar reaction conditions and have provided several more examples of this type of behavior.[3] However, all of the known instances of carbenoid insertion resulting from base treatment of epoxides have involved a transannular C–H bond in a medium ring,[4] and it was consequently of interest to determine if such reactions are unique to this class of compounds. We are now able to describe two cases of typical carbenoid behavior in noncarbocyclic molecules.

trans-Di-*t*-butylethylene oxide[6] (**1**) was selected for examination since competing β elimination[7] is not possible for this species. Treatment of **1** with commercial *t*-butyllithium in hydrocarbon solvent generated three products in the ratio of 28:56:16. The first material was readily recognized as *t*-butyl neopentyl ketone (**2**). The two remaining compounds were deduced to be alcohols from their infrared spectra and are assigned as the diastereomeric cyclopropylcarbinols **3** and **4**. The nmr spectra of the two compounds are very similar; **3** displays a one-proton doublet at δ 2.74 (C*H*OH, *J* = 9 cps), a one-proton absorption at 1.4 (O*H*), three-proton singlets at 1.17 and 1.07 (C*H*$_3$), a nine-proton singlet at 0.92 (*t*-Bu), and a three-proton complex absorption below 0.8 (cyclopropyl protons), while similar absorption for **4** at δ 2.76 (*J* = 9 cps), 1.05, 1.03, 0.91, and below 0.8 is given a parallel interpretation (the OH proton was obscured in this spectrum). Confirmation of these structures was obtained by the lithium aluminum hydride reduction of cyclopropyl ketone **5** which was in turn prepared by the reaction of *t*-butyllithium with the known acid **6**.[8] The observation of a 91:9 ratio of **3**:**4** in the reduction allows for differentiation between the diastereomeric alcohols on the assumption that steric features determine the course of hydride attack.



The formation of **2** is doubtless similar to several other base rearrangements of epoxides to ketones.[3] Conceivably either an α- or β-elimination mechanism may be operative here, but experimental distinction is lacking. The formation of the diastereomeric cyclopropyl alcohols is rationalized by the sequence of metalation, α elimination, and carbene insertion into a C–H bond of the adjacent *t*-butyl substituent, and this process is depicted below. It is of interest to note that, in contrast to the medium-ring epoxide rearrangements, the insertion products are formed *nonstereospecifically*. The mechanistic implications of this observation will be discussed in the full paper describing this work.



The second example of a carbenoid reaction involves the characteristic addition to an olefinic bond. Attempts to trap a reactive intermediate from various base-induced epoxide decompositions in the presence

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(1) A. C. Cope, H. H. Lee, and H. E. Petree, *J. Am. Chem. Soc.*, **80**, 2849 (1958); A. C. Cope, M. Brown, and H. H. Lee, *ibid.*, **80**, 2855 (1958).

(2) A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *ibid.*, **82**, 6370 (1960).

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

(4) The rearrangement of norbornene oxide to nortricyclanol[5] is an exception, but this carbon skeleton is also particularly prone to transannular reactions.

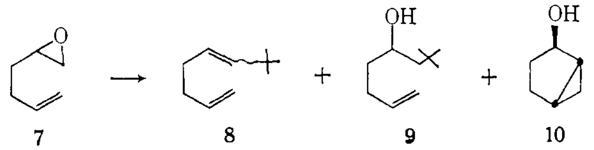
(5) J. K. Crandall, *J. Org. Chem.*, **29**, 2830 (1964).

(6) All new compounds have spectroscopic and microanalytical data in full agreement with the proposed structures. Known materials have been identified by comparison with authentic samples.

(7) A. C. Cope and J. K. Heeren, *J. Am. Chem. Soc.*, **87**, 3125 (1965).

(8) E. R. Nelson, M. Maienthal, L. A. Lane, and A. A. Benderly, *ibid.*, **79**, 3467 (1957).

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).

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

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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 over-all 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

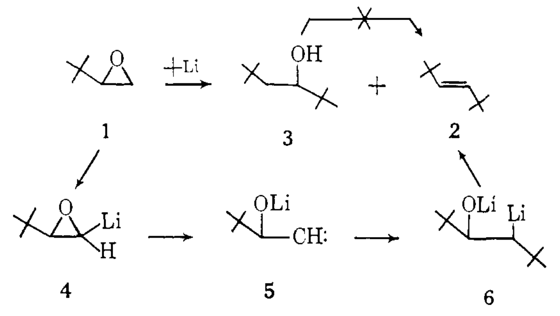

Chart I shows a proposed mechanistic sequence for the over-all reaction indicated in eq 1 using compound **1** as an example. Intermediacy of the nucleophilic

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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]