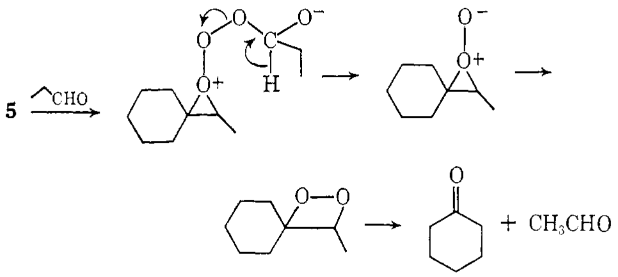
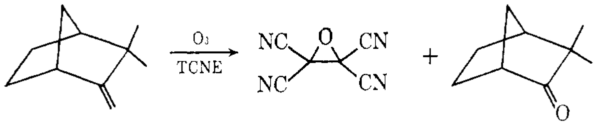
An interesting alternative to the intermediacy of the Staudinger molozonide must also be considered. It is possible that the Staudinger molozonide is not the species reduced by excess aldehyde or ketone but that reduction of the σ complex occurs, *e.g.*



The resulting perepoxide is the same intermediate considered by Kearns[8] for singlet oxygen–olefin reactions. Rearrangement of the perepoxide to the corresponding dioxetane followed by scission to the carbonyl compounds would account for the results reported here.

It is noteworthy that a reaction which, at least phenomenologically, corresponds to the observations reported here has been described by Criegee.[13] Criegee observed that the ozonolysis of several olefins in the presence of tetracyanoethylene resulted in high yields of tetracyanoethylene oxide and the carbonyl compounds derived from cleavage of the olefin.[13] In view of the present findings it would appear likely that tetracyanoethylene is also intercepting and reducing a primary ozonide.



The new information and interpretation offered here require a critical reexamination of the literature dealing with the ozonolysis reaction. The new data very likely offer the key to correlation and explanation of the great number of seemingly unrelated ozonolysis reactions.

Acknowledgment. We thank the National Air Pollution Control Administration for support of this work through Grant No. AP 00505.

(13) R. Criegee and P. Gunther, *Chem. Ber.*, **96**, 1564 (1963).

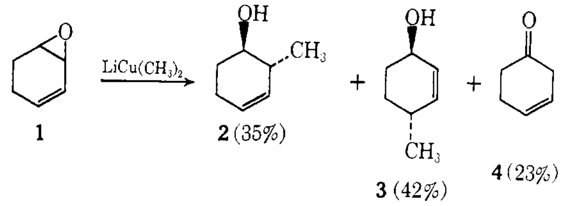
Paul R. Story,* John A. Alford
Wesley C. Ray, John R. Burgess
Department of Chemistry, The University of Georgia
Athens, Georgia 30601

Received March 23, 1971

Reaction of 1,3- and 1,4-Cyclohexadiene Monoepoxides with Methylorganometallic Reagents

Sir:

The title epoxides exhibit several interesting features in their reactions with common methylorganometallic reagents. For example, 1,3-cyclohexadiene monoepoxide (**1**), while not showing the high regioselectivity (preferred 1,4 addition) noted earlier with butadiene monoepoxide,[1,2] on treatment with lithium dimethylcuprate[3] gives both direct-opening product **2** and conjugate-addition product **3** with complete trans stereospecificity.[4]



The stereochemistry of **2** and **3** was established by catalytic reduction of the crude product mixture from which the unsaturated ketone **4** had been removed.[5] Analysis by vpc of the reduction product allowed the determination of upper limits on *cis*-2-methylcyclohexanol ($<1\%$) and *cis*-4-methylcyclohexanol ($<1\%$). Direct opening of **1** exclusively at the allylic rather than the homoallylic position is in agreement with earlier reports.[1,2] Anti opening to give **2** is expected on the basis of an analogous stereochemical result with cyclohexene oxide.[7] The formation of rearrangement product **4** also finds precedent in the cyclohexene oxide reaction, which gave approximately 20% cyclohexanone.[7]

The exact mechanisms of reactions involving lithium dialkylcuprates remain unknown, in spite of extensive study, particularly by House and coworkers.[8] Nucleophilic attack on **1** by the copper center to give a complex which subsequently decomposes with methylation[8] would fit the available data. Regardless of the mechanistic details, the net result is the apparent nucleophilic addition of a methyl group to **1**; as such, the conjugate addition might be appropriately considered as an S$_N$2′ process. However, the classical S$_N$2′ mechanism should lead to cis[9] rather than the observed trans product **3**.[10] Because of the limited

---

(1) R. J. Anderson, *J. Amer. Chem. Soc.*, **92**, 4978 (1970).

(2) R. W. Herr and C. R. Johnson, *ibid.*, **92**, 4979 (1970).

(3) H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952).

(4) All new materials have been characterized by C and H analyses, spectral methods, and conversion to known materials.

(5) Cyclohexanol, generated by reduction of **4**, would have interfered with the already difficult vpc analysis of *cis*- and *trans*-2- and -4-methylcyclohexanols. Compound **4** was removed by preparative vpc and shown by infrared and nmr analysis to be free of alcohol contaminants which might have exhibited identical retention times.

The structure of **2** was established by nmr (two low-field vinyl hydrogens), through reduction to *trans*-2-methylcyclohexanol, and by demonstrating that it differed from the other two conceivable *trans*-2-methylcyclohexenols.[6]

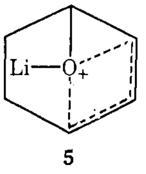
(6) B. Rickborn and R. P. Thummel, *J. Org. Chem.*, **34**, 3583 (1969). A sample of mixed (vpc separable) *cis*- and *trans*-6-methyl-2-cyclohexenols was available from this work. The alternate isomer is described in the present paper.

(7) R. W. Herr, D. M. Wieland, and C. R. Johnson, *J. Amer. Chem. Soc.*, **92**, 3813 (1970).

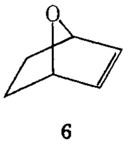
(8) (a) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966), and references therein; (b) H. O. House and W. F. Fischer, Jr., *ibid.*, **33**, 949 (1968); (c) G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969); the reaction between $(-)$-2-bromobutane and lithium diphenylcuprate was shown to occur with predominant (84–92%) inversion.

(9) G. Stork and W. N. White, *ibid.*, **78**, 4609 (1956).

(10) Rearrangement product **4** presumably arises *via* a lithium ion catalyzed carbonium ion process.[11] Products **2** and **3** might also arise from an intermediate such as **5**. To test this possibility, the isomeric



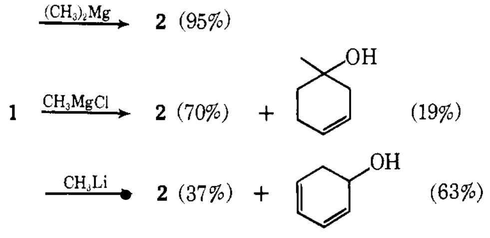
5



6

number of stereochemical results for purported S$_N$2′ processes, the general stereochemical outcome of such reactions may require further study.

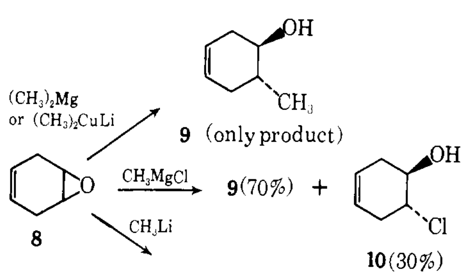
The reaction of **1** with other methylmetallic reagents was also examined. As shown below, neither the magnesium nor the lithium reagent gives any detectable conjugate addition product.[13] Methyllithium gives some of the direct opening product **2**, along with



7

benzene hydrate (**7**) which proved to be the sole alcohol product from 1,4-cyclohexadiene monepoxide (**8**).

Organomagnesium and organolithium reagents in general exhibit similar reactivity and undergo analogous reactions. However, some striking differences are observed when 1,4-cyclohexadiene monoepoxide (**8**) is treated with common methylorganometallics.



7 (75%) + benzene (25%)

Because of the acidifying effect of the double bond, **8** may undergo either base-induced isomerization or ring-opening addition. Both dimethylmagnesium and methylmagnesium chloride furnish the normal trans-opening product **9**, although the chlorohydrin **10** is a significant side product when the Grignard reagent is used. Compound **9** is the exclusive product of the reaction with lithium dimethylcuprate. Considering the relative ease of preparation and the rapid reaction of the organocopper reagent compared to dimethylmagnesium,[14] the former may in general be the reagent of choice for nucleophilic opening of epoxides (particularly base-sensitive materials).

It is especially noteworthy that none of these three organometallic reagents caused any base-induced rearrangement of **8**. In contrast, methyllithium gives exclusively the product of proton abstraction, **7** (2,4-cyclohexadienol or "benzene hydrate").[15]

Benzene hydrate is a distillable liquid, bp 36–37° (2 Torr). It exhibits λ_{max} at 256 nm (ϵ 4500), and under carefully controlled conditions will form Diels–Alder adducts with maleic anhydride or dimethyl acetylenedicarboxylate (these adducts are isomeric mixtures). As expected, compound **7** undergoes violent decomposition on contact with acid, giving benzene and water; however, samples have been successfully stored at −15° for several weeks.

When **8** is treated with lithium diethylamide in ether at 0°, benzene is formed directly and rapidly.[17] Although some benzene is also found in the methyllithium reaction,[18] it is a minor component that may be generated during the isolation procedure. The isolation of benzene hydrate suggests that alkyllithium reagents may prove useful in the syntheses of other relatively unstable unsaturated alcohols.[19]

1,4-oxide **6** was prepared[12] and subjected to the reaction conditions. It was recovered unchanged after prolonged treatment with lithium dimethylcuprate.

(11) B. Rickborn and R. M. Gerkin, *J. Amer. Chem. Soc.*, **90**, 4193 (1968); **93**, 1693 (1971).

(12) W. Nudenberg and L. W. Butz, *ibid.*, **66**, 307 (1944).

(13) It should be noted that Johnson and coworkers[7] found that the proportion of conjugate addition of CH_3MgX to butadiene monoepoxide depended on the halide ion in the order I > Br > Cl.

(14) B. G. Christensen, R. G. Strachan, N. R. Trenner, B. H. Arison, R. Hirschmann, and J. M. Chemerda, *J. Amer. Chem. Soc.*, **82**, 3995 (1960).

(15) Compound **7** is apparently not recorded in *Chemical Abstracts*. However, it has been mentioned in a review article by Vogel and Günther,[16] as the product of LAH reduction of benzene epoxide; it is described as undergoing wall-catalyzed decomposition to benzene and water on standing.

(16) E. Vogel and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967).

(17) Unpublished results with R. P. Thummel. Presumably, **7** is an intermediate in this reaction; elimination may occur *via* the small amount of free –OH form that would be generated by equilibration of the lithium salt with diethylamine.

(18) In a typical preparation, 3.0 g (0.031 mol) of **8** in 5 ml of ether was added under argon to 55 ml of 0.84 *M* methyllithium at 0–3°. The magnetically stirred mixture was allowed to warm to room temperature and gas evolution was monitored. Fifteen minutes after evolution ceased (total reaction time 3 hr), the mixture was hydrolyzed with 5 ml of 5% NaOH. The aqueous phase was separated and extracted with several small portions of ether; the combined ethereal solution was washed with NaCl-saturated water, dried over K_2CO_3, and evaporated on a steam bath. Analysis of the residue at this stage by nmr showed only **7** and benzene (and small amounts of ether). Vacuum distillation through a short Vigreux column gave 1.44 g (48%) of analytically pure **7**.

(19) For example, the "arene hydrate" 2,3-dihydrofuran-3-ol can be isolated from the reaction of 3,4-epoxytetrahydrofuran with methyllithium.

James Staroscik, Bruce Rickborn*
Department of Chemistry, University of California
Santa Barbara, California 93106

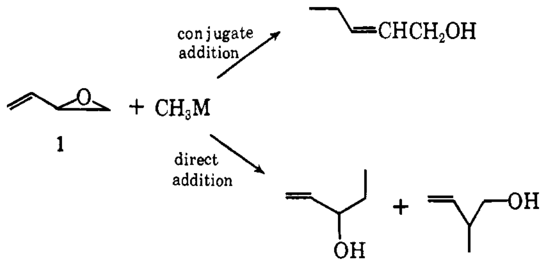
Received February 13, 1971

Additions of Organometallic Reagents to 3,4-Epoxycyclohexene

Sir:

The addition reaction of 3,4-epoxy-1-butene (**1**) with certain methylmetallo reagents has recently been observed[1] to follow two distinct pathways; *i.e.*, methyllithium gives predominantly (80%) direct addition, whereas lithium dimethylcuprate gives nearly exclusive (96%) conjugate addition (Scheme I).

Scheme I



The rigid 3,4-epoxycyclohexene[2] (**2**) is potentially more informative from a mechanistic standpoint; this

---

(1) R. W. Herr and C. R. Johnson, *J. Amer. Chem. Soc.*, **92**, 4979 (1970).

(2) J. K. Crandall, D. B. Banks, R. A. Colyer, R. J. Watkins, and J. P. Arrington, *J. Org. Chem.*, **33**, 423 (1968).