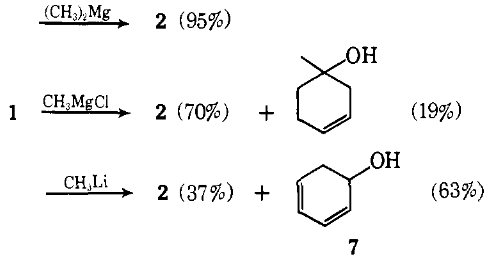
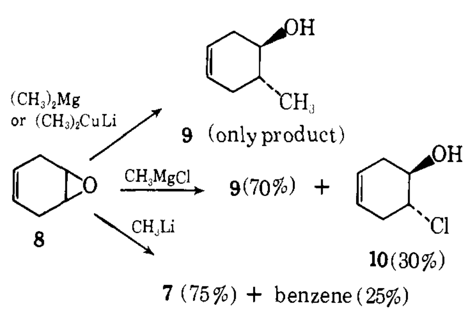
number of stereochemical results for purported $\mathrm{S_N2'}$ processes, the general stereochemical outcome of such reactions may require further study.

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



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.



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 $\lambda_{\max}$ 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$_3$MgX 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$_2$CO$_3$, 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.

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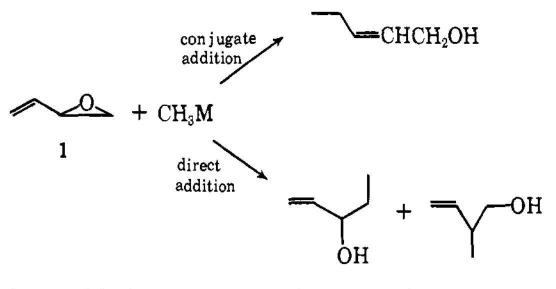
Additions of Organometallic Reagents to 3,4-Epoxycyclohexene

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

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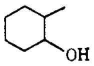
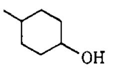
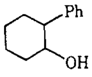
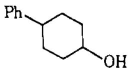
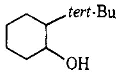
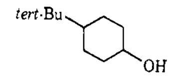
(1) R. W. Herr and C. R. Johnson, *J. Amer. Chem. Soc.*, **92**, 4979 (1970).

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

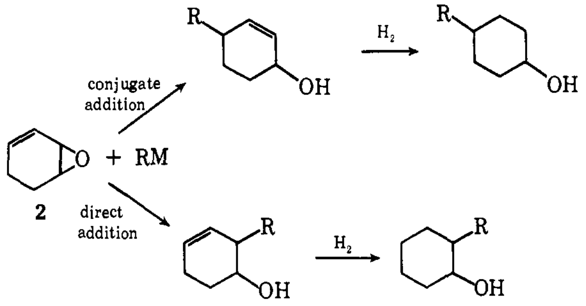
Table I. Addition Products Obtained from the Reaction of Organometallic Reagents with 3,4-Epoxycyclohexene (**2**) in Diethyl Ether[a,b]

Reagent	Temp, °C	Molarity		Reaction time, hr	Yield,[c] %	Composition[d] (after hydrogenation), %					
		R-M	**2**			1,2 addition			1,4 addition		
						Cis		Trans	Cis		Trans
$(CH_3)_2CuLi$[e]	0	0.10	0.05	0.5	91			46			54
CH_3Li (5 mol % CuI)	0	0.20	0.05	0.5	43[f]			75	3		22
CH_3Li[g]	35	0.20	0.05	15	25			100			
Ph_2CuLi	0	0.25	0.05	0.5	87			69			31
PhLi	25	0.25	0.05	15	63			70	2		28
$(tert\text{-}Bu)_2CuLi$	−40	0.25	0.05	4	72	23		12[h]	8		57

[a] A solution of **2** was added to the organometallic reagent under an argon atmosphere. [b] The crude reaction product was hydrogenated and separated into its components by preparative vpc; structural assignments were made by spectral comparison with authentic samples. [c] Determined by quantitative vpc analysis. [d] Determined by capillary vpc. [e] In this reaction 3-cyclohexenone (0–6%) was the only detectable by-product. [f] Based on incomplete reaction. [g] Major product as indicated by vpc was benzene, which presumably arises from 2,4-cyclohexadienol; however, no attempt was made to isolate and characterize this compound; see ref 11. [h] We thank Dr. W. L. Dilling of Dow Chemical Co., Midland, Mich., for samples of the cis and trans isomers.

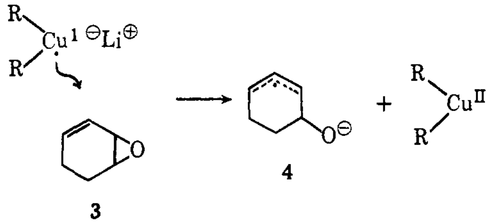
system allows determination of the direction of attack of the organometallic with respect to the epoxide oxygen (Scheme II). The results of the reaction of **2** with organolithium and organocuprate compounds are summarized in Table I. Product distributions were determined after hydrogenation of the crude mixture of cyclohexenols. The results show that with the exception of methyllithium the conjugate and direct addition reactions are competitive processes. The copper reagents reacted more rapidly and under milder conditions to give better yields of addition products than their organolithium counterparts. The marked rate enhancement and stereochemical effect that small amounts of copper(I) iodide have on the reaction of methyllithium with **2** suggests the possibility of regioselective control by simply varying the amount of copper(I) in the reaction. The methyl and phenyl reagents displayed high trans stereoselectivity in both the 1,2 and 1,4 additions. In contrast lithium di-*tert*-butylcuprate showed decreased stereoselectivity in conjugate addition and actually favored the cis product in 1,2 addition. Reaction of lithium di-*tert*-butylcuprate with cyclohexene oxide (**3**) yielded only *trans*-2-*tert*-butylcyclohexanol. Exclusive trans ring opening of **3** with cuprates[3] and the 100% inversion of cyclohexyl tosylates with cuprates[4] implicate an S_N2 process for these reactions.

Scheme II



However, the low stereoselectivity of the reaction of lithium di-*tert*-butylcuprate with **2** can be rationalized by a mechanism, first suggested by House and Fischer[5] for conjugate addition to cyclohexenones, involving an intermediate radical anion (**4**) such as depicted in Scheme III. Subsequent coupling of **4** with the metastable copper(II) species[6] would yield the observed products. A Lewis acid catalyzed S_N1 mechanism involving an "allylic carbonium ion," though less attractive, is also tenable.

Scheme III



The high stereoselectivity observed with the other reagents in this report may reflect concerted nucleophilic processes. In regard to the 1,4 additions, the entering nucleophile generally[7] bears a cis relationship to the leaving group in an S_N2' reaction.[8] However, as pointed out recently by Bordwell,[9] the entire class of S_N2' reactions may be enjoying a mythical existence.

At present, any definitive explanation of the product stereochemistry is tenuous in view of the association

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

(4) Unpublished observations of G. A. Dutra, Department of Chemistry, Wayne State University, Detroit, Mich.

(5) H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **33,** 949 (1968).

(6) Dialkylcopper(II) has recently been suggested as a possible intermediate in the reaction of copper(II) chloride with 2 equiv of Grignard reagent: K. Wada, M. Tamura, and J. Kochi, *J. Amer. Chem. Soc.*, **92,** 6656 (1970).

(7) An example of a trans S_N2' reaction involving the acylolysis of a steroidal α-bromo ketone has recently been reported: J. Y. Satoh and T. T. Takahashi, *Chem. Commun.*, 1714 (1970).

(8) G. Stork and W. N. White, *J. Amer. Chem. Soc.*, **78,** 4609 (1956).

(9) F. G. Bordwell, *Accounts Chem. Res.*, **3,** 281 (1970), and references cited therein.

of these reagents in solution[10] and the as of yet uncertain role that copper(I) itself plays in the reaction.[11]

(10) (a) H. L. Lewis and T. L. Brown, *J. Amer. Chem. Soc.*, **92**, 4664 (1970); (b) T. L. Brown, *Accounts Chem. Res.*, **1**, 23 (1968).

(11) For a related study, see the accompanying communication: J. Staroscik and B. Rickborn, *J. Amer. Chem. Soc.*, **93**, 3046 (1971). We thank Professor Rickborn for discussions prior to publication.

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Electron Spin Resonance Evidence for the Existence of a Dimeric Form of the Copper(II) Chelate of Kojic Acid

Sir:

On the basis of magnetic susceptibility measurements on the manganese(II), iron(II), cobalt(II), nickel(II), and copper(II) chelates of 2-hydroxymethyl-5-hydroxy-γ-pyrone (kojic acid), Wiley, *et al.*, deduced that the most probable coordination configuration was a tetrahedral one for the chelates of nickel(II), cobalt(II), iron(II), and manganese(II).[1] In the case of the copper(II) chelate, it was not possible on the information provided by magnetic susceptibility measurements alone to draw a distinction between tetrahedral or essentially planar configurations. A more recent investigation confirmed the fact that the copper(II) chelate of kojic acid possessed a magnetic moment corresponding to one unpaired electron per copper(II) ion and that there is no evidence of the presence of exchange coupling. Furthermore, the data drawn from the electronic spectrum provided evidence for a pseudotetrahedral symmetry of the copper(II) ion.[2]

The copper(II) chelate of kojic acid has a very limited solubility in water, a property which commended its study in connection with analytical procedures. A search among organic solvents has, so far, not produced one in which the chelate is soluble to any useful extent and so investigations are confined to the powder form which emerges from the preparative procedure. Electron spin resonance (esr) measurements which have been carried out on frozen solutions of copper(II) chelates have provided a wealth of information which has proved useful in determining the electronic structure and bonding of the chelates, and in recent times the state of aggregation of the chelate species.[3,4] The measurements associated with providing evidence for dimer formations are equally valid for powder samples, though the information may not be as precise as that obtained in frozen solution where magnetic dilution can be more easily controlled. Accordingly, the esr spectra of the copper(II) kojate was recorded at room temperature and 77°K. The spectrum obtained at room temperature is shown by Figure 1. The low-field line is attributed to $\Delta M = 2$ transitions arising from magnetic dipolar coupling between the copper(II) ions in a dimeric form of the copper(II) chelate. As would be anticipated from this situation, the intensity of the low-field line varied very little when the signal was recorded at room temperature.

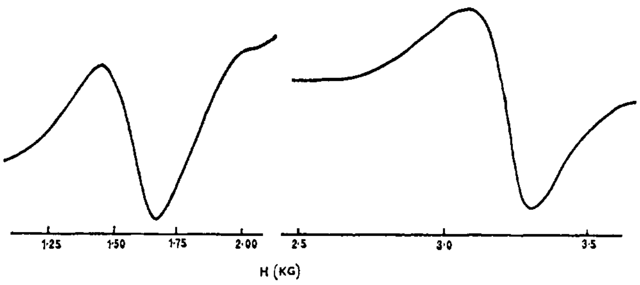

Figure 1. X-Band esr spectra at room temperature and microwave frequency 9499 mHz of copper(II) kojate.

The theory relevant to the interpretation of the results presented here has been described in detail previously, the coupling process being represented by the spin Hamiltonian[4]

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{ex} + \mathcal{H}_d$$

where $\mathcal{H}_1 = g_{\parallel}\beta H_z S_{iz} + g_{\perp}\beta(H_x S_{ix} + H_y S_{iy}) + A S_{iz} I_{iz} + B(S_{ix} I_{ix} + S_{iy} I_{iy})$. The parameters $g_{\parallel}$, $g_{\perp}$, A, and B have their customary significance. Since we assume that the two ions are in identical sites of axial symmetry and that the z direction is along the internuclear axis, we may write

$$\mathcal{H}_d = \beta^2(g_x^2 S_{1x} S_{2x} + g_y^2 S_{1y} S_{2y} - 2g_z^2 S_{1z} S_{2z})/r^3$$

where $i = 1$ or 2 and r is the distance between the magnetic point dipoles and is taken to be equivalent to the internuclear distance. In the systems described here, the major contribution to the zero-field splitting is due to $\mathcal{H}_d$ and it is assumed that high-order effects due to $\mathcal{H}_{ex}$ may be ignored. Computer simulation of the esr spectra was achieved using methods previously outlined.[4] The parameters obtained from the $\Delta M = 2$ transition of the copper(II) chelate of kojic acid are as follows: $r_{\text{Cu-Cu}} = 4.0 \pm 0.2$ Å, $g_{\parallel} = 2.37 + 0.02$, $g_{\perp} = 2.03 \pm 0.01$, $A = 180 \pm 20 \times 10^{-4}$ cm^{-1}, $B = 10 \pm 5 \times 10^{-4}$ cm^{-1}, and $\sigma = 35$ G. We do not assume that these results must necessarily mean that the symmetry of the pair of copper(II) ions is axial, but, insofar as the results can be analyzed as described, it can be inferred that the symmetry of the dimer is close to the simple axial model assumed in the theoretical approach.

It is proposed, therefore, that the structure of the copper(II) kojate dimer is similar to that of the β form of 8-hydroxyquinolinate. Palenik[5] has shown that this particular crystal form is composed of dimer-like units in which copper(II) is five-coordinate, with the out-of-plane coordinate position being occupied by the oxygen atom from a second molecule.

(1) J. W. Wiley, G. N. Tyson, and J. S. Stellar, *J. Amer. Chem. Soc.*, **64**, 963 (1942).

(2) A. Syamal, *Z. Naturforsch. B*, **25**, 166 (1970).

(3) R. H. Dunhill, J. R. Pilbrow, and T. D. Smith, *J. Chem. Phys.*, **45**, 1474 (1966).

(4) J. F. Boas, R. H. Dunhill, J. R. Pilbrow, R. C. Srivastava, and T. D. Smith, *J. Chem. Soc. A*, 94 (1969).

(5) G. J. Palenik, *Acta Crystallogr.*, **17**, 687 (1964).

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