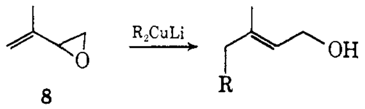
Diphenylcopper lithium[17] in ether–benzene, 5:1, and **1** gave a mixture of **2**[11b,c] (85%, R = C_6H_5) and **3**[11b] (15%, R = C_6H_5) in an overall yield of 85%. Oxidation of **2** (R = C_6H_5) with Collins' reagent to aldehyde **6** (R = C_6H_5) and nmr analysis proved the stereoselectivity of the addition again for the trans alcohol **2** over the cis, 90:10. In this instance, the ratio could be determined not only from the aldehyde signal (cis, 10.3 ppm, d, J = 8 Hz; trans, 9.58 ppm, d, J = 8 Hz) but also from the benzylic methylene (cis, 3.97 ppm, d, J = 7 Hz; trans, 3.65 ppm, d, J = 7 Hz). This result is again in marked contrast to the reaction of **1** with the corresponding Grignard reagent, phenylmagnesium bromide[5] (see Table I).

A useful extension of this reaction provides a direct method for addition of an isoprenyl unit in a highly stereoselective manner to form the allylic alcohol terminus of many naturally occurring acylic terpenes (see Scheme II). To this end, chloroacetaldehyde was treated with isopropenylmagnesium bromide in tetrahydrofuran to give the relatively unstable 4-chloro-2-methyl-1-buten-3-ol[11b] (**7**; 3,5-dinitrobenzoate,[11b,c] mp 65–66°). Methanolic potassium carbonate action on **7** gave the desired 3,4-epoxy-2-methyl-1-butene (**8**) [ν_{max}^{film} 3065, 1650, 890 cm^{-1} ($H_2C{=}C$); nmr ($CDCl_3$) 1.63 (3 H, d, J = 1 Hz, $CH_3C{=}C$), 2.78 (2 H, m, $-CH_2O-$), 3.38 (1 H, m, $=CCHO-$), and 5.03 and 5.17 ppm (2 H, $H_2C{=}C$). *Anal.* Calcd for C_5H_8O: C, 71.39; H, 9.59. Found: C, 71.28; H, 9.51] purified by preparative vpc (15-ft 10% UCON 75-H-90,000; column temperature, 100°). Addition of **8** (1 equiv) to an ether solution of 5 equiv of lithium dimethyl cuprate (0.33 M in $(CH_3)_2CuLi$) at −10° under argon led immediately to allylic alcohol **9**[11b] (R = CH_3),[18] again stereoselectively for the trans alcohol product (ratio 92:8). These allylic alcohols were identified (ir, nmr, and vpc) with authentic samples obtained by lithium aluminum hydride reduction of the ester isomers **10**[19] prepared from 2-butanone and sodium triethylphosphonoacetate.

Scheme II



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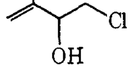
9



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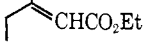

10

Thus, when organocopper reagents are utilized for addition to unsaturated epoxide systems, 1,4 addition predominates in a reaction stereoselective for the trans allylic alcohol.

Acknowledgments. Acknowledgment is made to Mr. Loren Dunham of Zoecon Corporation for advice and assistance in the preparative vpc separations, and to Dr. E. E. van Tamelen at Stanford University for providing facilities to complete this work.

Richard J. Anderson
274 College Avenue
Palo Alto, California 94306
Received April 22, 1970

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[17] Formed by addition of phenyllithium (Alfa Inorganics, Inc., ether–benzene (30:70) solution) to a suspension of CuI in ether.

[18] A third unidentified product was present in the amount of 4%; overall yield, 97% (determined by vpc using 1-octanol as standard).

[19] Sample was graciously provided by Dr. J. B. Siddall of Zoecon Corporation.

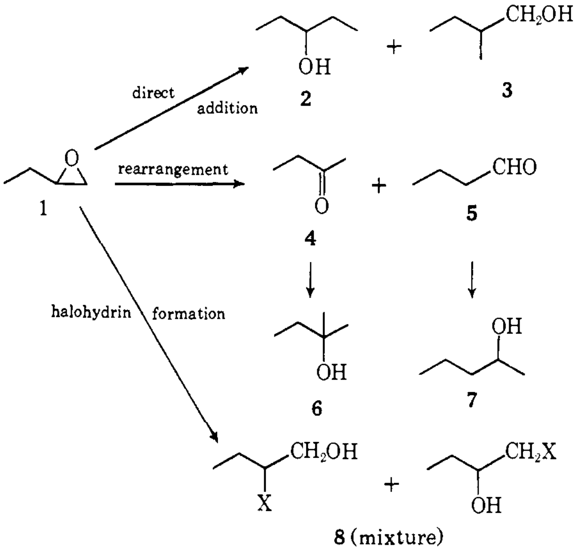
A Comparison of the Reactions of Methylmagnesium, Methyllithium, and Methylcopper Reagents with 1,2-Epoxybutane and 3,4-Epoxy-1-butene

Sir:

We have recently described the nucleophilic ring-opening reactions of oxiranes by organocopper reagents.[1] The synthetic potential of these reactions has encouraged us to make a detailed comparative analysis of the reactions of a simple and a vinyl oxirane with a variety of metallomethyl reagents. The principal substrates chosen for this study were 1,2-epoxybutane and 3,4-epoxy-1-butene.

Organometallic reagents are unique in that they may act as nucleophiles (or bases) or as Lewis acids. In the reactions with oxiranes this ambivalent character can lead to three competing mechanistic pathways, particularly in the case of the Grignard reagents.[2] Possible products resulting from the reactions of metallomethyl reagents with 1,2-epoxybutane (**1**) are shown in Scheme I.

Scheme I



The product distributions from the reactions of 1,2-epoxybutane with some metallomethyl reagents are summarized in Table I.[3] An inspection of the results shows that dimethylmagnesium, methyllithium, and lithium dimethylcuprate[4] are far superior to the Grignard reagents with respect to yield of nucleophilic ring-opening product. Lithium dimethylcuprate ap-

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

[2] R. E. Parker and N. S. Isaacs, *Chem. Rev.*, 59, 779 (1959).

[3] Product distribution was observed to be quite sensitive to temperature and mode of addition; see A. Rosowsky in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part One, A. Weissberger, Ed., Interscience, New York, N. Y. 1964, Chapter 1, p 396.

[4] (a) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, 31, 3128 (1966); (b) H. Gilman, R. G. Jones, and L. A. Woods, *ibid.*, 17, 1630 (1952).

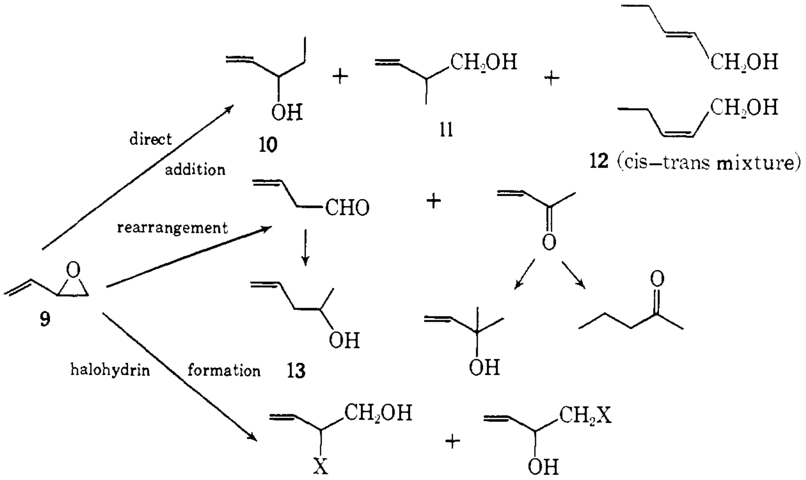
Table I. Reactions of Metallomethyl Reagents with 1,2-Epoxybutane in Diethyl Ether[a]

Reagent	Temp, °C	Molar concn CH_3-M	Molar concn Oxirane	Product distribution, %[b] 2	3	4	5	6	7	8	Unidentified trace products
CH_3MgI	34	1	0.33	1				12	2	77	8
CH_3MgBr	34	1	0.33	5	5			7	15	63	5
CH_3MgBr[c]	25	0.55	0.27	4	4			2	10	75	5
CH_3MgBr	0	0.63	0.26	4	3			2	3	80	8
CH_3MgCl	34	0.71	0.24	45[d]	22			1		31	1
$(CH_3)_2Mg$	34	0.35	0.17	82[d]	11	1		2			4
$CH_3Li(LiBr)$	34	1	0.33	90		1		1			8
$CH_3Li(LiBr)$	0	0.59	0.29	81		3	1	2			13
$(CH_3)_2CuLi$[e]	0	0.13	0.06	88		1		1			10

[a] A solution of the organometallic reagent was added to the epoxide; the reaction time was 12.5 hr. [b] Assignments made on the basis of ir spectra and glc retention times. [c] The epoxide was added to the organometallic. [d] A small amount of 2-pentanol (7) is present. [e] Reference 1; the reaction time was 13.5 hr.

pears to give the best yield of 3-pentanol (**2**) under the mildest conditions.[5] In the case of the methylmagnesium reagents, the presence of halide has a dramatic and devastating effect on the yield of direct addition products; the principal products in most cases are the halohydrins.

Scheme II



The conjugate addition of lithium dialkylcuprate to α,β-unsaturated carbonyl compounds,[4a,6] allylic acetates,[7] and propargylic acetates,[8] as well as their facile reaction with oxiranes,[1] raised the question of their mode of addition to vinyl oxiranes. Furthermore, in light of the incomplete and somewhat conflicting literature reports[2,9] on the reactions of organometallics with vinyl oxiranes, we decided to study the reactions of 3,4-epoxy-1-butene (**9**) with a series of metallomethyl reagents. The various anticipated reaction paths are shown in Scheme II with the experimental results summarized in Table II.[3,10]

No halohydrin formation was observed in the reactions of 3,4-epoxy-1-butene. Only the methylmagnesium reagents gave rearranged product **13**, while only methyllithium gave significant amounts of 1-penten-3-ol (**10**) resulting from addition to the least-hindered epoxide carbon. Of particular interest is the effect of halide on the amount of conjugate addition products obtained, although the mechanistic implications are at present unclear. Lithium dimethylcuprate

Table II. Reactions of Metallomethyl Reagents with 3,4-Epoxy-1-butene[a]

Reagent	Molar concn CH_3-M	Molar concn Oxirane	Product distribution, %[b] 10	11	12 (trans:cis)[c]	13
CH_3MgI	1	0.33	1	22	68 (1.9:1)	9
CH_3MgBr	1	0.33	1	36	44 (3.1:1)	19
CH_3MgCl	0.71	0.24	1	74	21 (2.6:1)	4
$(CH_3)_2Mg$	0.29	0.14	1	81	16 (4.7:1)	2
$CH_3Li(LiBr)$	1	0.33	7	38	55 (2.8:1)	
CH_3Li	1	0.33	17	63	20 (1.1:1)	
$(CH_3)_2CuLi$[d]	0.17	0.08		6	94 (3.8:1)	

[a] A solution of the organometallic reagent was added to the epoxide, followed by refluxing the mixture in ether for 24 hr. [b] The crude reaction product was separated into its components by preparative glc and assignments were made on the basis of ir and nmr spectra. [c] Stereochemical assignment based on ir spectra; trans: cis ratio determined by capillary glc (incomplete separation of the two peaks). [d] This reaction mixture was refluxed for only 0.5 hr.

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(5) In fact, lithium dimethylcuprate reacts with 1,2-epoxybutane to give 3-pentanol in good yield even at −78°. Unpublished observations of D. M. Wieland, this laboratory.

(6) (a) H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **31**, 949 (1968); (b) E. J. Corey and J. H. Katzenellenbogen, *J. Amer. Chem. Soc.*, **91**, 1851 (1969); (c) J. B. Siddall, M. Biskup, and J. H. Fried, *ibid.*, **91**, 1853 (1969).

(7) (a) P. Rona, L. Tokes, J. Tremble, and P. Crabbe, *Chem. Commun.*, 43 (1969); (b) R. J. Anderson, C. A. Henrick, and J. B. Siddall, *J. Amer. Chem. Soc.*, **92**, 735 (1970).

(8) (a) P. Rona and P. Crabbe, *ibid.*, **90**, 4733 (1968); (b) P. Rona and P. Crabbe, *ibid.*, **91**, 3289 (1969).

(9) (a) N. G. Gaylord and E. I. Becker, *Chem. Rev.*, **49**, 448 (1951); (b) H. Gurien, *Diss. Abstr.*, **16**, 1046 (1956); (c) C. B. Rose and C. W. Smith, Jr., *Chem. Commun.*, 248 (1969).

(10) Although the trans alcohol predominated in all cases for the conjugate addition product (12), the trans:cis ratio was also quite sensitive to temperature and mode of addition.

gave as the predominant product 2-penten-1-ol (**12**), demonstrating that conjugate addition is the preferred mode of reaction. The reaction was stereoselective for the trans alcohol **12**, not only for lithium dimethylcuprate but for all the other reagents as well.[11,12]

[11] Stereoselectivity for the trans olefin is also observed for the reaction of lithium dialkylcuprates with allylic acetates; see ref 7b.

[12] After the completion of the study described in this paper we learned of the complementary work by R. J. Anderson discussed in the accompanying communication (*J. Amer. Chem. Soc.*, **92**, 4978 (1970)). We thank Mr. Anderson for discussions prior to publication.

* To whom correspondence should be addressed.

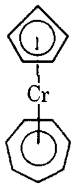
R. Wilbur Herr, Carl R. Johnson*
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

Received May 4, 1970

Formation and Structure of a New Mixed Sandwich Complex, $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3Ph_3)$

Sir:

The effective atomic number rule suggests that, among first-period transition metals, a series of mixed sandwich complexes might be expected, in which a π-cyclopentadienylmetal moiety interacts with carbocyclic ring systems of varying sizes,[1] *viz.*



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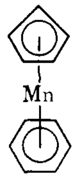

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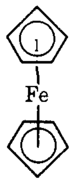

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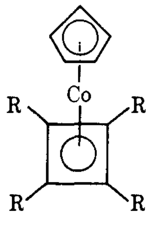
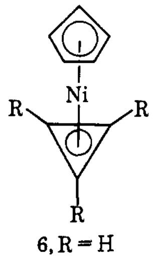


4, R = H
5, R = Ph



6, R = H
7, R = Ph

Compounds **1** through **5** are presently known,[2–7] and we now report the first authenticated[8] example in this isoelectronic series in which a nickel atom is symmetrically bonded to both five-membered and three-membered unsaturated carbocyclic rings.

π-Cyclopentadienyl-π-triphenylcyclopropenylnickel, **7**, has been obtained in 78% yield from a reaction between $[(\pi\text{-}C_3Ph_3)NiBr(py)_2]\cdot py$[9] and cyclopentadienylthallium in benzene solution at room temperature. After filtration (preferably under nitrogen) of thallium bromide and evaporation of the solvent *in vacuo*, the product was recrystallized from heptane to afford air-stable crystals, mp 137–138°. *Anal.* Calcd for $C_{26}H_{20}Ni$: C, 79.84; H, 5.15; mol wt, 390. Found: C, 79.64; H, 5.05; mol wt, 390 (mass spectrometry), 386 (osmometry in benzene). The proton nmr spectrum of the new complex in deuteriochloroform solution consists of a sharp singlet at τ 4.72, assignable to protons of the $\pi\text{-}C_5H_5$ group, and multiplet absorption due to protons of the phenyl substituents centered at τ 2.47. The mass spectrum of **7** exhibits, among others, prominent peaks at m/e 390 (molecular ion), 267 $(C_3Ph_3)^+$, and 123 $(C_5H_5Ni)^+$. The transition $390 \rightarrow 267 + 123$ is supported by a metastable peak at 182.8.

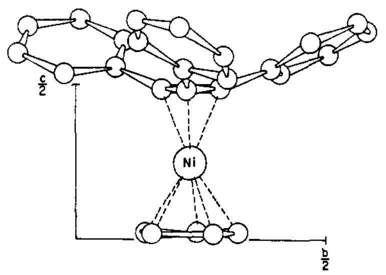


Figure 1. A molecule of $(\pi\text{-}C_5H_5)Ni(\pi\text{-}Ph_3C_3)$ as viewed along the crystallographic *a* axis.

This nickel complex, **7**, crystallizes as deep red-orange prisms in the orthorhombic space group $Pna2_1$, $a = 21.003\,(1)$, $b = 12.360\,(1)$, $c = 7.496\,(1)$ Å, $Z = 4$. Intensity data were collected on a GE XRD-5 diffractometer by the moving-crystal, moving-counter method using Cu Kα radiation. The structure was solved by the usual heavy-atom techniques and has been refined to a conventional R factor of 0.062.

The structure shows that the nickel atom is complexed in a true sandwich fashion between the parallel cyclopentadienyl and triphenylcyclopropenyl rings (Figure 1). The nickel–cyclopropenyl carbon distances are identical within experimental error and average 1.961 (3) Å, while the nickel–cyclopentadienyl carbon distances average 2.11 (1) Å. As expected, the carbon–carbon distances within the cyclopropenyl ring (average = 1.432 (5) Å) are longer than those found in the free ligand, $(C_3Ph_3)(ClO_4)$[10] (average = 1.373 (5) Å), but are essentially equal to those found in $[(\pi\text{-}C_3Ph_3)NiCl(py)_2]\cdot py$,[11] average = 1.422 (8) Å. The three phenyl rings of the triphenylcyclopropenyl group are both tilted out of the plane of the cyclopropenyl ring away from the nickel atom and rotated about their respective axes by 20 (1)° to produce a "propeller" configuration. This effect, attributable to some combination of steric and hybridization factors, has been found in other similar complexes.[11,12] The cyclopentadienyl carbon–carbon distances average 1.41 (2) Å, although this ring suffers some rotational disorder in the crystal.

Bonding in this nickel sandwich compound can probably best be visualized in terms of the following two major contributions: (1) overlap of the a_1 combination of pπ atomic orbitals (C_{3v} localized symmetry) on the

[1] F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 7281 (1969).

[2] *Cf.* M. L. H. Green, "Organometallic Compounds," Vol. II, Methuen, London, 1968, p 190.

[3] R. G. Amiet and R. Pettit, *J. Amer. Chem. Soc.*, **90**, 1059 (1968).

[4] M. Rosenblum and B. North, *ibid.*, **90**, 1060 (1968).

[5] A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Jap.*, **34**, 452 (1961).

[6] M. D. Rausch and R. A. Genetti, *J. Amer. Chem. Soc.*, **89**, 5505 (1967).

[7] Compound **6** is presently unknown, although the cyclopropenium cation has been synthesized: R. Breslow, J. T. Groves, and G. Ryan, *ibid.*, **89**, 5048 (1967).

[8] Complex **7** was briefly mentioned in an earlier publication, but no details were given [R. G. Hayter, *J. Organometal. Chem.*, **13**, P1 (1968)].

[9] E. W. Gowling, Ph.D. Thesis, Sheffield University, 1965.

[10] M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, **88**, 198 (1966).

[11] D. L. Weaver and R. M. Tuggle, *ibid.*, **91**, 6506 (1969).

[12] R. P. Dodge and V. Schomaker, *Acta Crystallogr.*, **18**, 614 (1965).