with tetraalkylthiodiamines,[16] while primary amines evolve hydrogen sulfide (isolated as the alkylammonium polysulfide[17]). The other product from the primary amine must also be a thiodiamine. Steps 2–4 were examined independently of steps 5 and 6 by adding a sulfide scavenger to suppress the sulfide-catalyzed reaction (5). The resulting products (in the presence of lead oxide) were benzylidenimine polysulfides.[10] The stoichiometry given in (7) accounts for over 90% of the

$$(b + 3)S + 2C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH{=}NS_bN{=}CHC_6H_5 + 3H_2S \quad (7)$$

benzylamine under these conditions.[11] Benzylidenimine tetrasulfide exposed to benzylamine in the presence of lead oxide survived for at least 24 hr at room temperature with little change except for equilibration of the sulfur chain length (*i.e.*, tetrasulfide gave a mixture of sulfur and di-, tri-, and tetrasulfides). Small amounts of unsymmetrical mixed amine–imine polysulfides, $C_6H_5CH{=}NS_xNHCH_2C_6H_5$, were also formed under these conditions.

In the *absence* of lead oxide benzylidenimine tetrasulfide was quite reactive toward benzylamine, forming ammonia, N-benzylidenebenzylamine, and benzylammonium polysulfides (eq 8).[11]

$$3C_6H_5CH{=}NS_4N{=}CHC_6H_5 + 20C_6H_5CH_2NH_2 \longrightarrow 11NH_3 + 11C_6H_5CH{=}NCH_2C_6H_5 + 2(C_6H_5CH_2NH_3^+)_2S_6^{2-} \quad (8)$$

Exchange of one amine for another (eq 5) has been previously observed in thiodiamines[18] and is expected to occur here in the presence of the excess benzylamine. The observed unsymmetrical material isolated in the presence of lead oxide is most likely an intermediate in this reaction. Benzylidenimine is quite reactive toward nucleophiles[20] and has been previously[21] proposed to react with benzylamine to give N-benzylidenebenzylamine and ammonia (eq 6). The other product in (5), a thiodiamine, decomposes according to (4) to regenerate more benzylidenimine polysulfide. The probable intermediacy of thiodiamines in the scheme was substantiated by examining the decomposition of an authentic sample of benzylamine disulfide (prepared from sulfur monochloride and benzylamine). Although fairly stable in the absence of base (eventually undergoing autocatalytic decomposition), the sample underwent rapid decomposition in the presence of small amounts of base at room temperature. The product of these decompositions was N-benzylidenebenzylamine and ammonia (about 80% of theory) along with smaller amounts of benzylidenimine tetrasulfide and benzylammonium polysulfides. As required by (2–6) the ammonia : benzylidenebenzylamine ratio as well as the benzylidenimine tetrasulfide : benzylammonium polysulfide ratio were both near 1:1. When the autocatalyzed decomposition was monitored by nmr, benzylamine and benzylidenimine tetrasulfide (about 4:1 molar ratios) were observed to increase to a maximum concentration in the early stages of the decomposition and later to decrease in amount as the concentration of N-benzylidenebenzylamine increased. A direct decomposition of the thiodiamine to sulfur, ammonia, and N-benzylidenebenzylamine was therefore eliminated.

Additional evidence for a benzylidenimine polysulfide–thiodiamine "cycle" was obtained by allowing *p*-methoxybenzylidenimine tetrasulfide to react with unsubstituted benzylamine. As required by (2–6), all of the amine obtained by hydrolysis of the N-benzylidenebenzylamine formed was unsubstituted; all of the *p*-methoxy substituent was present in the aldehyde. Not all of the aldehyde formed was substituted, however; the ratio of anisaldehyde to benzaldehyde was 1.3:1 (required by (2–6), 1.2:1).

The ease with which these reactions occur—a few hours or less at room temperature—suggests that they may well play a role in the various sulfur–primary amine reactions[2–6] involving organic substrates.

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(15) T. G. Levi, *Gazz. Chim. Ital.*, **60**, 975 (1930).

(16) H. Jenne and M. Becke-Goehring, *Chem. Ber.*, **91**, 1950 (1958); T. G. Levi, *Gazz. Chim. Ital.*, **61**, 286 (1931); P. Longi, R. Montagna, and R. Mazzocchi, *Chim. Ind.* (Milan), 47, 480 (1965).

(17) M. G. Voronkov and A. Ya Legzdyn, *Zh. Org. Khim.*, **3**, 465 (1967).

(18) Either aniline with N-methylaniline disulfide or N-methylaniline with aniline disulfide results in rapid disproportionation to aniline, N-methylaniline, aniline disulfide, N-methylaniline disulfide, and the mixed aniline–N-methylaniline disulfide.[19]

(19) J. Barrick and F. P. Olsen, unpublished observations.

(20) T. L. Tolbert and B. Houston, *J. Org. Chem.*, **28**, 695 (1963).

(21) M. Pesez and J. Bartos, *Bull. Soc. Chim. Fr.*, 1122 (1963).

Reactions of Organocopper Reagents with Oxiranes

Sir:

The nucleophilic ring opening of oxiranes by organometallic reagents is a useful synthetic method which has been limited in scope due to competing reactions arising from either the Lewis acidity or the basicity of the organometallic reagent.[1] We have found that lithium dimethylcuprate[2] and lithium diphenylcuprate[3] appear to be excellent reagents for the nucleophilic ring opening of oxiranes under mild conditions. Such reagents show promise of largely circumventing the side reactions encountered with other organometallic reagents.

Lithium dimethylcuprate reacts with propylene oxide and 1,2-epoxybutane to give the expected secondary alcohols as predominant products.

The reactions of cyclohexene oxide with some organocopper and organolithium reagents are summarized in Table I. These results indicate that lithium dialkylcuprates are more reactive toward oxiranes than the corresponding alkyllithiums and possibly are superior to the alkyllithiums with respect to yields of nucleophilic addition product. On the other hand, polymeric methylcopper[4] and methylcopper complexed with trimethyl phosphite[4] or tri-*n*-butylphosphine[2a] gave

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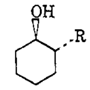
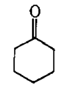
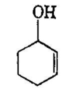
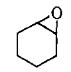
(1) A. Rosowsky in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part I, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, pp 386–417.

(2) (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).

(3) (a) 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); (b) P. Rona, L. Tokes, J. Tremble, and P. Crabbe, *Chem. Commun.*, 43 (1969).

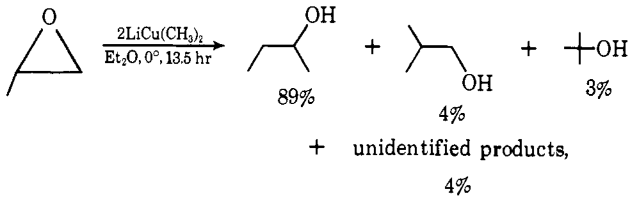
(4) H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **33**, 949 (1968).

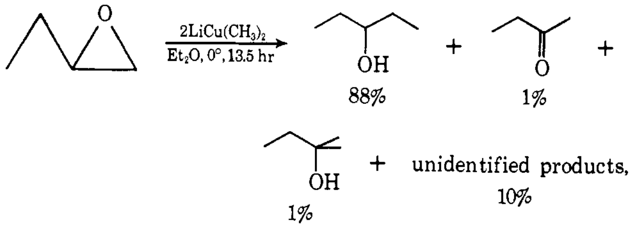
Table I. Reactions of Organocopper and Organolithium Reagents with Cyclohexene Oxide

					Product distribution, %			
R-M	Equiv	Temp, °C	Solvent	T, hr				
$LiCu(CH_3)_2$	2	0	Et_2O	5	54	19		27
$LiCu(CH_3)_2$	2	0	THF	14	11	8		81
$LiCu(CH_3)_2$	2	25	Et_2O	5	70	22		8
$LiCu(CH_3)_2$	5	25	Et_2O	14	76	24		
CH_3Li	2	0	Et_2O	5	1		3	97
CH_3Li[a]	1	36	Et_2O		55-60		5-6	33-37
$LiCu(Ph)_2$	2	0	Et_2O	5	81	1		18
PhLi	2	0	Et_2O	5	4	1	6	90

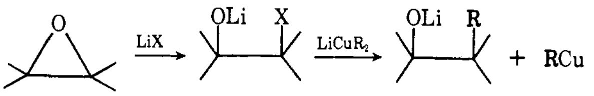
[a] J. K. Heeren, T. C. Flood, and R. H. Cunningham, *J. Organometal. Chem.*, 9, 18 (1967).

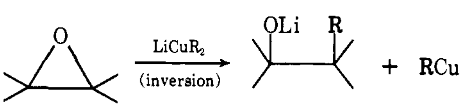
no reaction with cyclohexene oxide.[5] Lithium methylcyano(bistriethyl phosphite)copper(I)[4] reacted only slightly with cyclohexene oxide.

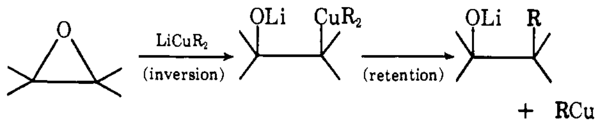




Three mechanistic pathways have been considered for the reaction of lithium dialkylcuprates with oxiranes. They are: (1) halohydrin formation followed by coupling with the "ate" complex; (2) direct nucleophilic displacement by alkyl; and (3) nucleophilic attack by copper to give a trialkylcopper intermediate,[6] followed by collapse to product.

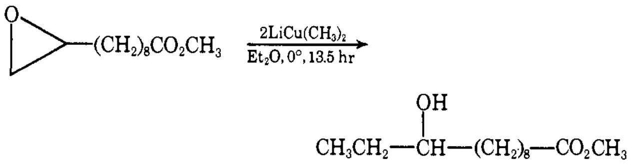
 (1)

 (2)

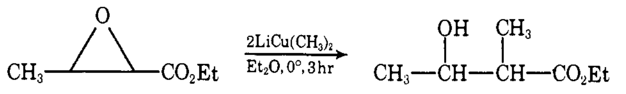
 (3)

Pathway 1 was considered unlikely because of the observation that THF retards the reaction with oxiranes (Table I) while THF is known to enhance the coupling of lithium dialkylcuprates with alkyl halides.[3a] Additional evidence against this mechanism is the observation that "halide-free" lithium dimethylcuprate[4] reacts with cyclohexene oxide to give *trans*-2-methylcyclohexanol in comparable yield to that obtained with lithium dimethylcuprate in the presence of 2 equiv of lithium halide. There is insufficient evidence available to us at this time to distinguish between paths 2 and 3.

Regardless of the mechanistic details, the mild conditions required for the reaction with oxiranes and the observation that lithium dialkylcuprates are relatively inert toward saturated carbonyl moieties[2a] suggested the possibility of selective reaction at an oxirane in the presence of an unprotected carbonyl function. Accordingly, lithium dimethylcuprate was treated with methyl 10,11-epoxyundecanoate to give methyl 10-hydroxydodecanoate in 37% yield (isolated).

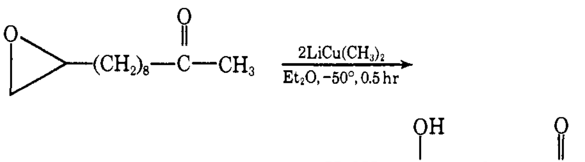


Ethyl 2,3-epoxybutyrate was treated with lithium dimethylcuprate to yield ethyl 2-methyl-3-hydroxybutyrate in 67% yield (glc). In contrast, the reaction



of methyllithium with ethyl 2,3-epoxybutyrate under identical conditions resulted in a mixture which consisted of 45% starting material, 1% ethyl 2-methyl-3-hydroxybutyrate, and 54% of unidentified products.[7]

The reaction of lithium dimethylcuprate with 10,11-epoxy-2-dodecanone yielded 11-hydroxy-2-tridecanone in 68% yield (isolated).



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(5) These results parallel those obtained with allylic acetates: R. J. Anderson, C. A. Henrick, and J. B. Siddall, *J. Amer. Chem. Soc.*, 92, 735 (1970).

(6) Such an intermediate has been proposed for the cross-coupling reaction of lithium dialkylcuprates with alkyl halides: (a) ref 3a; (b) E. J. Corey and I. Kuwajima, *J. Amer. Chem. Soc.*, 92, 395 (1970).

(7) The reaction of glycidic esters with Grignard reagents is known to give products resulting from isomerization or cleavage, followed by addition: ref 1, p 411.

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