

$M(\text{CO})_5(\text{diene})$ species should, however, lead to intramolecular CO scrambling.¹⁰ The observed stereospecificity of CO exchange in addition to the fact that under no conditions was the monoolefin pentacarbonyl species ever observed strongly suggests this alternative mechanism to be unlikely.

As indicated earlier this study has also afforded an assignment of the $\nu(\text{CO})$ vibrations in $(\text{NBD})\text{M}(\text{CO})_4$ complexes. Table I contains the calculated CO force constants obtained with the aid of ^{13}C frequency data. The observation of the B_1 band occurring at higher frequency than the B_2 band in these complexes is in agreement with the assignment proposed in a recent Raman study by Butler and Barna.¹¹

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(10) (a) D. J. Darensbourg, M. Y. Darensbourg, and R. J. Dennenberg, *J. Amer. Chem. Soc.*, **93**, 2807 (1971); (b) W. J. Knebel, R. J. Angelici, O. A. Gansow, and D. J. Darensbourg, *J. Organometal. Chem.*, **66**, C11 (1974).

(11) I. S. Butler and G. G. Barna, *J. Raman Spectrosc.*, **1**, 141 (1973).

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Organoaluminum Reagents of Type $\text{R}^1\text{R}^2\text{NAlEt}_2$ Which Allow Regiospecific Isomerization of Epoxides to Allylic Alcohols

Sir:

The reaction of epoxides with strong base constitutes a well known synthetic method for the preparation of allylic alcohols.¹ The best current method for this transformation discovered by Cope,² and thoroughly developed by Crandall³ and Rickborn,⁴ involves isomerization with lithium diethylamide. Because of our needs to carry out such transformation under very mild conditions,⁵ we developed a new method based upon diethylaluminum dialkylamide.⁶ The method takes advantage of the affinity of aluminum metal for oxygen.⁷

(1) A. Rosowsky, "Heterocyclic Compounds with Three- and Four-Membered Rings," A. Weissberger, Ed., Interscience, New York, N. Y., 1964, pp 1-523; recently Sharpless and Lauer reported a unique method for the above transformation using organoselenium reagent: K. B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, **95**, 2697 (1973).

(2) (a) A. C. Cope, H. H. Lee, and H. E. Petree, *J. Amer. Chem. Soc.*, **80**, 2849 (1958); (b) A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *ibid.*, **82**, 6370 (1960); (c) A. C. Cope and J. K. Heeren, *ibid.*, **87**, 3125 (1965); (d) A. C. Cope, M. Brown, and H. H. Lee, *ibid.*, **80**, 2855 (1958).

(3) (a) J. K. Crandall, *J. Org. Chem.*, **29**, 2830 (1964); (b) J. K. Crandall and L. Chang, *ibid.*, **32**, 435, 532 (1967); (c) J. K. Crandall and L. C. Lin, *J. Amer. Chem. Soc.*, **89**, 4526, 4527 (1967).

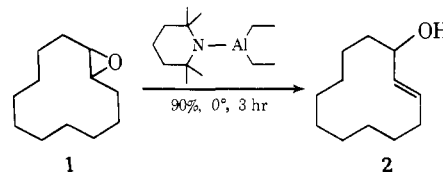
(4) (a) B. Rickborn and R. P. Thummel, *J. Org. Chem.*, **34**, 3583 (1969); (b) R. P. Thummel and B. Rickborn, *J. Amer. Chem. Soc.*, **92**, 2064 (1970); (c) R. P. Thummel and B. Rickborn, *J. Org. Chem.*, **36**, 1365 (1971); (d) C. L. Kissel and B. Rickborn, *ibid.*, **37**, 2060 (1972).

(5) S. Tanaka, H. Yamamoto, H. Nozaki, K. B. Sharpless, R. C. Michaelson, and J. D. Cutting, *J. Amer. Chem. Soc.*, in press.

(6) (a) J. K. Gilbert and J. D. Smith, *J. Chem. Soc. A*, 233 (1968); (b) R. Köster and P. Binger, *Advan. Inorg. Chem. Radiochem.*, **7**, 263 (1965); (c) see also, T. Mole and E. A. Jeffery, "Organoaluminum Compounds," Elsevier, Amsterdam, 1972.

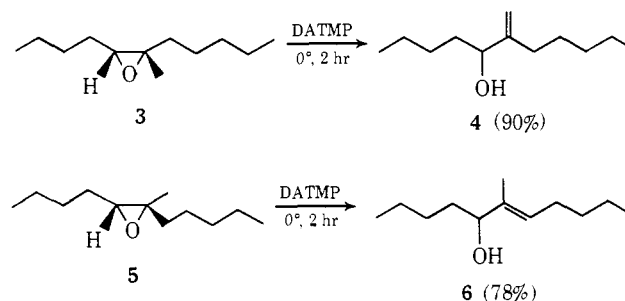
(7) For example, E. J. Corey and D. J. Beamer, *J. Amer. Chem. Soc.*, **95**, 5829 (1973).

Diethylaluminum 2,2,6,6-tetramethylpiperidide (DATMP) can be prepared *in situ*⁸ from diethylaluminum chloride and lithium 2,2,6,6-tetramethylpiperidide (LiTMP)⁹ (molar ratio 1:1) in benzene at 0° for 30 min. Reaction of DATMP (4 equiv) with (*E*)-cyclododecene oxide (**1**) in benzene was completed at 0° (external cooling) for 3 hr. The addition of 1 *N* hydrochloric acid, washing with water, and concentration *in vacuo* afforded (*E*)-2-cyclododecen-1-ol (**2**) in 90% yield after purification by plc (silica gel, $R_f = 0.23$ with 3:1 hexane-ether).¹⁰ The examples cited in Table I illustrate the synthesis of allylic alcohols using the indicated reactants and reaction conditions.



DATMP has proved to be most satisfactory for the isomerization, while some variation in the reagent was studied in detail. The yield of alcohol **2** with DATMP (4 equiv) used as the base in its production from the oxido **1** at 0° for 1 hr¹¹ is compared with the same data for several other $\text{R}^1\text{R}^2\text{NAlEt}_2$ species: diethylamide, <5%; dicyclohexylamide, 36%; diisopropylamide, 45%; TMP, 80%. It should be noted that LiTMP itself was an unsatisfactory reagent for this transformation under the same reaction conditions (<5% of **2** and >70% of the starting oxido **1** was recovered).

Regioselectivity was reported in the reaction of unsymmetrical epoxides with lithium diethylamide, leading to allylic alcohols.⁴ The preference for elimination is primary > secondary > tertiary in these systems and this has been attributed to a combination of steric effects and preferred geometry.^{4,12} It seemed logical to expect that the bulk of the extremely large TMP group might play an even more significant role in determining the course of reaction and a useful regiospecific route to allylic alcohols might thereby become available. Thus, the reaction of DATMP in benzene at 0° with *Z* epoxide **3**⁵ for 2 hr produced the disubstituted allylic alcohol **4** in 90% yield after work-up in the usual way. A dramatic alteration in the product distribution occurs when the same reaction with DATMP is conducted with *E* epoxide **5**⁵ (0° for 2 hr); although alcohol **4** was



(8) T. Hirabayashi, H. Imaeda, K. Itoh, S. Sakai, and Y. Ishii, *J. Organometal. Chem.*, **19**, 299 (1969).


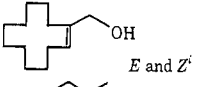
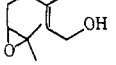
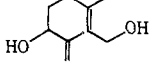
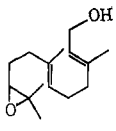
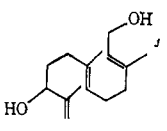
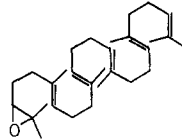
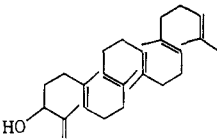
(9) R. A. Olofson and C. M. Dougherty, *J. Amer. Chem. Soc.*, **95**, 583 (1973).

(10) The crude reaction mixtures are almost free of by-products, so that for most further applications purification is not necessary.

(11) The reaction was terminated at this point for comparison.

(12) B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **95**, 5311 (1973); B. M. Trost and S. Kurozumi, *Tetrahedron Lett.*, 1929 (1974); see also ref 2c.

Table I^a

Epoxide ^b	Product ^b	Reagent ^c (equiv)	Reaction time, hr, and temp, °C ^d	Yield ^e %
Cyclopentene oxide	2-Cyclopenten-1-ol	DATMP (4)	2, 0	0 ^f
Cyclohexene oxide	2-Cyclohexen-1-ol	DATMP (4)	3, 0	0 ^f
Cycloheptene oxide	2-Cyclohepten-1-ol	DADIP ^g (4)	12, 25	0 ^h
(<i>E</i>)-Cyclododecene oxide	(<i>E</i>)-2-Cyclododecen-1-ol	DATMP (4)	3, 0	0 ^f
(Z)-Cyclododecene oxide	(E)-2-Cyclododecen-1-ol	DATMP (4)	1, 0	80
			3, 0	20
	 <i>E</i> and <i>Z</i> ⁱ	DATMP (4)	2, 0	85
		DATMP (4)	0.5, 0	88
	 ^j	DATMP (5)	0.5, 0	90
		DATMP (4)	2, 0	84

^a Most of these reactions were carried out on a 1 mmol scale. ^b All compounds have been adequately characterized by analytical and spectral data. ^c 2,2,6,6-Tetramethylpiperidine was obtained from Aldrich Chemical Co., Inc., and converted to LiTMP using *n*-butyllithium (hexane solution) at 0° for 10 min. ^d Cooling bath temperature. ^e Yields are for isolated pure products. ^f Starting epoxide was recovered. ^g Diethylaluminum diisopropylamide. ^h Several by-products were noted in this reaction. ⁱ *E/Z* = 3:1 by nmr assay. ^j This compound was converted to C₁₇-*Cecropia* juvenile hormone; S. Tanaka, H. Yamamoto, and H. Nozaki, unpublished results.

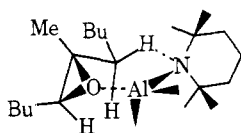
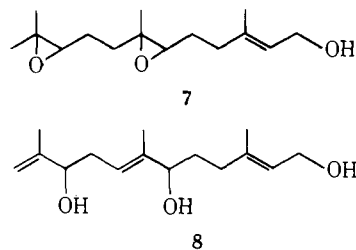


Figure 1. Possible intermediary complex of the DATMP-epoxide reaction.

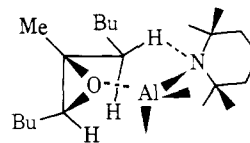
formed in small amounts (12%), the predominant product was the trisubstituted *E* allylic alcohol **6** (78%). The stereochemistry of **6** is clearly indicated by the analysis of the nmr spectrum (in CCl₄) and further confirmed by an independent synthesis of the same alcohol by the β -oxido ylide.¹³

A considerable number of experimental findings are in accord with predictions based on the above results. One interesting example is the reaction of diepoxide **7**, a useful synthetic intermediate for C₁₈-*Cecropia* juvenile hormone,^{5,14} furnishing the triol **8**¹⁵ in 41% yield.¹⁶ Thus, taken together with the results of Table I, DATMP reacts much more rapidly with *E* epoxide than with the *Z* isomer to yield *E* allylic alcohol (see (*E*)-cyclododecene oxide and *Z* isomer in Table I).

The high regiospecificity could be in keeping with a cyclic syn-elimination mechanism where the ring open-



ing has substantial stereoelectronic requirements.¹² The favored direction of elimination is accounted for by the preferred abstraction of the hydrogen which enables a greater orbital overlap in the cyclic transition state.^{2c,4a,12} Figure 1 shows a view of the DATMP-epoxide complex (from the epoxide **5**) in what appears to be the energetically favorable molecular conformation. This is introduced with rigid stereochemical control by the indicated nonbonding interactions.¹⁷



Work is currently in progress on the extension of this reaction to other systems and application to the synthesis of several natural products.

(17) Alternative chair-like conformation of the transitory six-membered ring turned out infeasible upon model inspections.

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(13) E. J. Corey and H. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 226, 3523 (1970).

(14) (a) R. J. Anderson, C. A. Henrick, and J. B. Siddall, *J. Amer. Chem. Soc.*, **92**, 735 (1970); (b) E. E. van Tamelen and J. P. McCormick, *ibid.*, **92**, 737 (1970).

(15) Stereochemistry of the central double bond (*E*) is anticipated on the stereochemical outcomes of other examples, since nmr analysis is not effective enough in this case.

(16) The low yield of the reaction was attributed to the thermal lability of the triol **8**.