complex"[8] such as **6**. While **6** probably oversimplifies the total structure,[9] it represents the essential structural features. Based on the proposed intermediacy of **6**, a rational reaction pathway can be envisioned. With both alkenyl moieties attached to the same silver atom, electron transfer from the anion to the cation, possibly producing an intermediate **7**, should lead to a concerted breaking of the C–Ag bonds and forming of the C–C bond. Stretching of the C–Ag bonds in the sense of a homolytic cleavage must cause an overlap of the carbon orbitals resulting in bond formation.

Experimental Section[10]

2,3-Dibromocyclohexene (**1**).—6,6-Dibromobicyclo[3.1.0.]-hexane[3,5] (105 g, 0.44 mol) was added dropwise over 0.5 hr to a flask maintained at 155° to effect rearrangement to **1**. Distillation afforded 95 g (90%) of **1**, bp 70° (1.7 mm), n^{25}D 1.5761 (lit.[3] n^{25}D 1.5764).

2,2′-Dibromo-3,3′-bicyclohexenyl (**2**).—2,3-Dibromocyclohexene (95 g, 0.41 mol) was added rapidly to a suspension of 5.9 g (0.24 g-atom) of magnesium in 120 ml of refluxing ether. Refluxing was continued for 1 hr, water was added, and the ether layer was separated and dried (Na_2SO_4). Distillation afforded 35 g (57%) of **2**, bp 135° (0.4 mm), n^{25}D 1.5780. Glc analysis (silicone nitrile XF-1150, 180°) indicated that the product was a 1:1 mixture of the *meso* and *dl* isomers. The ir and nmr spectra were superpositions of the spectra of the individual isomers reported below. The mass spectrum showed peaks at *m/e* 322, 320, and 318 in a 1:2:1 ratio (molecular ions of a dibromide).

Anal. Calcd for $C_{12}H_{16}Br_2$: C, 45.03; H, 5.04; Br, 49.92. Found: C, 44.87; H, 4.89; Br, 50.08.

The 1:1 mixture of *meso*- and *dl*-**2** was found to crystallize from methanol to give lead fractions enriched in the less soluble *dl* isomer. Repeated fractional crystallization eventually produced pure samples of each isomer as shown by glc analysis. From *ca.* 30 g of the 1:1 mixture, 3–4 g of each pure isomer was obtained (prior to recycling).

meso-**2**: mp 54–55°; ir (CCl_4) 3035, 1635, and fingerprint bands (not in *dl*) at 1240, 1200, 1040, 1020, 965 (broad), 950, 915, 860 cm^{-1}; nmr (CCl_4) δ 1.75 (∼8 H, m), 2.0 (∼4 H, m), 2.84 (2 H, m), 6.13 (2 H, m).

dl-**2**: mp 67.5–69.5°; ir (CCl_4) 3035, 1640, and fingerprint bands (not in meso) at 1250, 1210, 1108, 1030, 980, 940, 922, 870 cm^{-1}; nmr (CCl_4) δ 1.72 (∼8 H, m), 2.0 (∼4 H, m), 3.02 (2 H, m), 6.15 (2 H, m).

cis-**Tricyclo[6.4.0.0^{2,7}]dodeca-2,12-diene** (*cis*-**5**).—A solution of 12 ml of 1.6 *M n*-butyllithium in hexane and 1.51 g (4.7 mmol) of *meso*-**2** in 45 ml of ether was stirred for 4 hr at room temperature. Analysis of an aliquot (the method is presented below) indicated a 65% yield of 2,2′-dilithio-3,3′-bicyclohexenyl (**3**). The dilithium reagent **3** was added to a suspension of 4.76 g (20 mmol) of anhydrous silver iodide in 40 ml of ether (to which 0.8 ml of 1.6 *M n*-butyllithium had been added to remove any traces of water) cooled to −78°. After being stirred for 25 min at −78°, the mixture was allowed to warm to room temperature. After 16 hr, the reaction mixture was filtered under nitrogen through Celite and the filtrate, diluted to 100 ml, was stored under nitrogen at −10°. In some instances, the reaction mixture was hydrolyzed and the ether layer was washed with water and dried (K_2CO_3) before storing. The yield of **5** was not changed.

Glc analysis (Carbowax 20M, 120–170°, using *n*-tridecane as in internal standard) established that *cis*-**5** was formed in 70% yield based on the dilithium reagent (46% from **3**). A small amount of 3,3′-bicyclohexenyl (2%) was found along with small amounts of several higher molecular weight materials which were not identified. Several repetitions of the reaction gave essentially the same overall yield of *cis*-**5**.

Pure *cis*-**5** was obtained by preparative glc (Carbowax 20M, 150° and silicone SE 30, 90°) with the collected material being stored at liquid nitrogen temperatures prior to spectral and analytical measurements: ir (CCl_4) 3020, 2930, 2880, 2860, 2830, 1670, 1645 (w), 1450, 1435, 1335, 1250, 1205, 1135, 1065, 935, 875 cm^{-1}; nmr (CCl_4) δ 0.8–1.9 (complex m, 8 H), 2.1 (broad m, ∼4 H, $C\mathbf{H}_2CH{=}C$), 2.72 (broad m, 2 H, $CH{=}CC\mathbf{H}$), 5.40 (m, 2 H, $C\mathbf{H}{=}C$); mass spectrum *m/e* (relative intensity) 39 (28), 65 (21), 67 (21), 77 (32), 79 (44), 81 (22), 91 (91), 104 (37), 105 (30), 115 (25), 117 (90), 118 (27), 119 (31), 131 (59), 132 (37), 145 (65), 160 (100, M$^+$); uv (hexane) λ_{max} 256 [log ϵ 4.15 (5)], sh 246 and 265 nm.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.07. Found: C, 89.60; H, 10.20.

Attempts to obtain pure samples of *cis*-**5** by distillation led to extensive polymerization with formation of a nonvolatile white solid. The pure liquid diene (from glc) was found to polymerize readily under helium at room temperature. It is extremely reactive toward oxygen; initial attempts to obtain a mass spectrum led to a peak at *m/e* 192 (*cis*-**5** + O_2) and only a weak molecular ion peak at *m/e* 160.

Analysis of the dilithium reagent can be accomplished by quenching an aliquot with water and determining the yield of 3,3′-bicyclohexenyl by glc (Carbowax 20M, 120–170°) using *n*-tridecane as an internal standard. The amount of 3,3′-bicyclohexenyl formed in preparing the dilithium reagent, typically 2–3%, can be determined by quenching an aliquot with 1,2-dibromoethane followed by glc analysis. A small amount of methyllithium should be added to the dibromoethane immediately before use to ensure complete removal of traces of water or HBr. Very small amounts of **5** were formed during the preparation of **3**; the maximum yields were in the range of 2–3%. This material presumably is derived from coupling of the 2-lithio-2′-bromo intermediate which is a precursor to **3**.

trans-**Tricyclo[6.4.0.0^{2,7}]dodeca-2,12-diene** (*trans*-**5**).—Using the same molar ratios of reactants employed in the preparation of *cis*-**5**, *dl*-**2** was converted into *trans*-**5** in overall yields of 41–45%. The product was identified by glc and infrared comparison with an authentic sample.[5]

The 1:1 mixture of *meso*- and *dl*-**2** similarly gave a 1:1 mixture of *cis*- and *trans*-**5** in essentially the same yields. On several glc columns employing different liquid phases (both polar and nonpolar), *cis*-**5** was found to have a retention time *ca.* 10–20% longer than that of *trans*-**5**.

Registry No.—*meso*-**2**, 28229-12-1; *dl*-**2**, 28229-13-2; *cis*-**5**, 28229-14-3; *trans*-**5**, 28229-15-4.

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[8] G. Wittig, *Quart. Rev., Chem. Soc.*, **20**, 191 (1966).

[9] The Ag$^+$ would probably be coordinated to the solvent and possibly halide ions and/or the ate complex **6** may be a part of a larger aggregate.

[10] Spectral measurements were determined with the following instruments: ir, Perkin-Elmer Model 237; nmr, Varian T-60; uv, Cary Model 14; mass spectra, Hitachi Perkin-Elmer RMU-6. Melting points are corrected and boiling points are not. All reactions were conducted under a nitrogen atmosphere.

A Convenient Synthesis of Alkyl-1,3,5-hexatrienes by Reaction of Dienyl Halides with 1,5-Diazabicyclo[4.3.0]non-5-ene[1]

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Most reported preparations of substituted 1,3,5-hexatrienes either yield mixtures or require several steps. The most common impurities from either acid-catalyzed or high temperature preparations are substituted 1,3-cyclohexadienes resulting from electrocyclic ring closure[2] and aromatics from dehydrogenation of the cyclic dienes.[3] Trienes free of these impurities may be obtained *via* a modified Hofmann elimination

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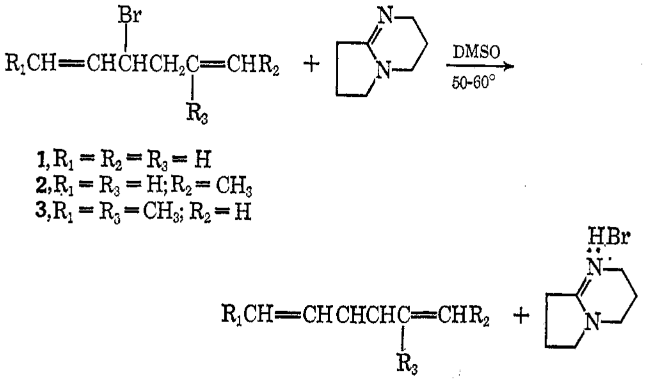
[1] Supported in part by a National Science Foundation Student Science Training Program Grant, GW-5221.

[2] C. W. Spangler and N. Johnson, *J. Org. Chem.*, **34**, 1444 (1969).

[3] C. W. Spangler, *ibid.*, **31**, 346 (1966).

sequence which we have described previously.[4,5] We would now like to report a new preparation of acyclic trienes of high purity (99%) in yields comparable to the Hofmann sequence.

1,5-Diazabicyclo[4.3.0]non-5-ene (DBN)[6] has recently been shown to be a highly versatile dehydrohalogenation reagent reactive under much milder conditions than with most other basic reagents.[7,8] In fact, dehydrohalogenation can be realized between 25 and 80° in dimethyl sulfoxide (DMSO). Volatile products can then be distilled directly from the reaction media.



1, $R_1 = R_2 = R_3 = H$

2, $R_1 = R_3 = H; R_2 = CH_3$

3, $R_1 = R_3 = CH_3; R_2 = H$

The observed ease of reaction and isolation is in marked contrast to other common means of dehydrohalogenation. For example, 1,3,5-hexatriene can be obtained from 3-bromo-1,5-hexadiene in 30% yield with DBN–DMSO, while potassium *tert*-butoxide–DMSO yields only polymeric material under identical conditions.

Both the Hofmann and DBN syntheses of pure trienes utilize common dienyl bromide intermediates, obtained from appropriately substituted hexadienols by treatment with phosphorus tribromide, without further purification.[9] However, it then becomes necessary in the Hofmann sequence to prepare an appropriate quaternary ammonium salt by treatment of the bromide with a tertiary amine such as *N*,*N*-dimethylbenzylamine. In most reported examples, in particular those from primary or secondary allylic bromides, this "salt" is precipitated as an impure glass whose further purification, prior to decomposition in base, is quite difficult.[4,5] Direct dehydrohalogenation with DBN, however, eliminates these difficulties.

As examples of the synthetic utility of the DBN–DMSO procedure, the following trienes were prepared: 1,3,5-hexatriene (**1**), 1,3,5-heptatriene (**2**), and 2-methyl-1,3,5-heptatriene (**3**). The results are shown in Table I and compared to reported Hofmann results. An interesting result is the difference in the trans/cis ratio for the two procedures. For **1** and **2**, this difference (approximately a factor of two) indicates that the DBN reaction probably is of the Saytzeff type. However, other workers have reported that base-catalyzed isomerizations producing substituted trienes show a marked preference for trans orientation.[10] Similarly, Bartsch[11] has recently shown that base-induced eliminations in DMSO under conditions of negligible product isomerization show unusually high trans/cis ratios. However, these correlations cannot explain the presence of *cis*-2-methyl-1,3,5-heptatriene in the DBN–DMSO product and its absence in the Hofmann product. The reason for this difference remains obscure.

TABLE I

Triene	% yield[a]		*trans*-Triene/*cis*-triene[b]	
	DBN–DMSO	Hofmann	DBN–DMSO	Hofmann
1	30	59[c]	5.0	2.3[c]
2	39	35[d]	2.7	1.3[d]
3	26	10	5.6	[e]

[a] Overall yield based on substituted hexadienol. [b] Isomer ratio of incipient double bond. [c] See ref 13. [d] See ref 5. [e] Only the trans,trans isomer was obtained.

Experimental Section[12]

DBN Dehydrohalogenation. General Procedure.—The substituted bromohexadiene (*ca.* 0.50 mol) is dissolved in 40 cc of DMSO[12b] and added to a solution of DBN (0.55 mol) in 50 cc of DMSO dropwise, with stirring, so as to maintain the reaction temperature between 50 and 60°. During the course of the reaction the medium quickly turns from colorless to a deep golden yellow. After the addition is complete, the product is distilled at reduced pressure (20–100 mm) and collected in an ice-cooled flask.

1,3,5-Hexatriene (1).—1,5-Hexadien-3-ol (0.55 mol) was allowed to react with phosphorus tribromide (0.23 mol) essentially by the method of Hwa, *et al.*,[13] yielding 75 g of crude bromodiene, a mixture of allylic isomers. The bromohexadiene (75 g, 0.475 mol) was then treated as described above in the general procedure with DBN (65 g, 0.525 mol). The product 1 was obtained as a colorless liquid (11.3 g, 30%): $n^{25}\mathrm{D}$ 1.5106; bp 78–80°; uv max 265, 255, 245 nm (ϵ 4.12, 4.97, 3.44 × 10^4); nmr τ 4.6–5.1 (m, 4 H, $CH_2{=}$), 3.35–4.0 (m, 4 H, CH=CH) [lit.[13] bp 80°; $n^{25}\mathrm{D}$ 1.5091; uv max 265, 255, 245 nm (ϵ 4.40, 5.30, 3.60 × 10^4) for trans isomer]. Glpc analysis revealed a purity of 98.9% and an isomer distribution of 83.5% trans and 16.5% cis.

1,3,5-Heptatriene (**2**).—1,5-Heptadien-4-ol (91 g, 0.76 mol) was allowed to react[5] with 90 g (0.33 mol) of phosphorus tribromide yielding 127 g of the crude bromodiene. The crude bromide was then allowed to react with DBN (96 g, 0.77 mol) as described above yielding **2** (27.6 g, 39%): bp 28–30° (20 mm); $n^{26}\mathrm{D}$ 1.5253; uv max 270, 260, 250 nm (ϵ 3.80, 4.55, 3.33 × 10^4); nmr τ 8.25 (d, 3, J = 6 Hz, $={}CCH_3$), 3.0–5.1 (m, 7 vinyl hydrogens) [lit.[5] bp 30–32° (25 mm); $n^{24}\mathrm{D}$ 1.5239; uv max 270, 260, 250 nm (ϵ 3.56, 4.45, 3.33 × 10^4)]. Glpc analysis revealed a purity of 99.2% and an isomer distribution of 73.0% trans and 27.0% cis.

2-Methyl-1,3,5-heptatriene (**3**). **A.**—*trans*-2-Methyl-1,5-heptadien-4-ol[15] (100 g, 0.79 mol) was allowed to react with phosphorus tribromide (90 g, 0.33 mol) yielding 121 g of crude bromide. Half of the bromohexadiene (60.5 g, 0.32 mol) was allowed to react with DBN (46 g, 0.37 mol) as described above yielding **3** (9.0 g, 26%): bp 68–70° (25 mm); $n^{25}\mathrm{D}$ 1.5263; uv max 272, 262, 252 nm (ϵ 3.84, 4.68, 3.48 × 10^4); nmr τ 8.0–8.3 (m, 6, $2CH_3C{=}$), 5.05 (s, 2, $CH_2{=}$), 3.6–4.6 (m, 4, CH=CH) [lit.[14]

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(4) C. W. Spangler and G. F. Woods, *J. Org. Chem.*, **28**, 2245 (1963).

(5) C. W. Spangler and G. F. Woods, *ibid.*, **30**, 2218 (1965).

(6) Aldrich Chemical Co., Inc., Milwaukee, Wis.

(7) K. Eiter, *Justus Liebigs Ann. Chem.*, **682**, 62 (1965).

(8) H. Oediger, H. Kabbe, F. Moller, and K. Eiter, *Chem. Ber.*, **99**, 2012 (1966).

(9) The present authors recognize, as have previous workers, that the crude dienyl bromides are mixtures of allylic isomers.

(10) E. A. Zuech, D. L. Crain, and R. F. Kleinschmidt, *J. Org. Chem.*, **33**, 771 (1968).

(11) R. A. Bartsch, *ibid.*, **35**, 1334 (1970).

(12) (a) Gas–liquid partition chromatography was performed with an Aerograph Model 202-1B dual column instrument equipped with a Hewlett-Packard Model 3370 electronic integrator for peak area measurement; dual 15-ft 15% TCEP on 60–80 mesh Chromosorb W columns were used for all separations. Ultraviolet spectra were obtained in isooctane with a Cary Model 14 spectrophotometer, and nmr spectra were obtaind with a Varian A60-A using TMS as an internal standard ($CDCl_3$ solvent). All spectra were consistent with the assigned structures, and satisfactory C and H analyses were obtained for all compounds. Identification of geometric isomers was accomplished by direct comparison (gc retention times and peak enhancement by admixture, and uv spectra) with known samples (see ref 2, 13, and 14) prepared in our laboratory. (b) DMSO was J. T. Baker reagent grade, used without further purification.

(13) J. C. H. Hwa, P. L. deBenneville, and H. J. Sims, *J. Amer. Chem. Soc.*, **82**, 2537 (1960).

(14) T. S. Sorensen, *Can. J. Chem.*, **42**, 2781 (1964).

(15) Chemical Samples Co., Columbus, Ohio.

n^{25}D 1.5232; uv max 274, 263.5, 253,5 nm (trans,trans isomer) (ϵ 3.56, 4.48, 3.18 × 10^4); nmr (CCl_4) identical with that above but shifted due to solvent difference]. Glpc analysis revealed a purity of 99.0% and an isomer distribution of 84.8% trans,trans and 15.2% cis,trans.

B.—Half of the above crude bromide (60.5 g, 0.32 mol) was allowed to react with *N*,*N*-dimethylbenzylamine (61 g, 0.45 mol) in 500 ml of toluene at 50–60° for 24 hr. After cooling, the toluene was decanted from the brown glassy salt which was then dissolved in *ca.* 500 ml of water. The resulting yellow solution was added dropwise to a KOH solution (70 g/1200 ml of water) undergoing distillation. The product was worked up in the usual manner[4,5] and distilled yielding **3** (3.5 g, 10%). Glpc analysis revealed a purity of 99% but essentially only one isomer, *trans,-trans*-**3** with only a trace of the *cis,trans*-**3**.

Registry No.—*trans*-**1**, 821-07-8; *cis*-**1**, 2612-46-6; **2**, 2196-23-8; *trans,trans*-**3**, 17679-94-6; *cis,trans*-**3**, 18304-16-0; DBN, 3001-72-7.

Cyclobutene Epoxides. The Stereospecific Lewis Acid Rearrangement[1]

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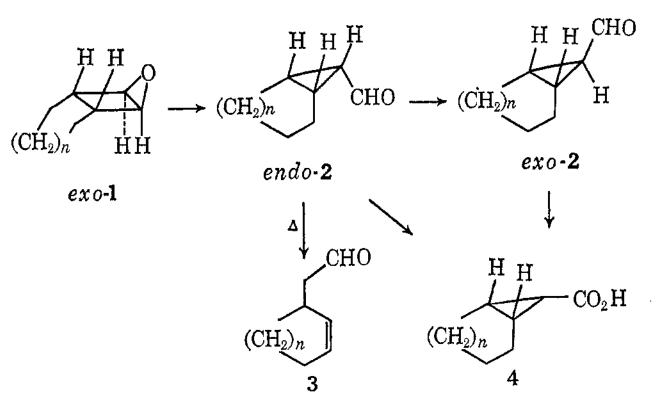
Despite numerous reports on the Lewis acid rearrangement of cyclobutene epoxides to cyclopropyl carbonyl compounds, the possible stereospecificity of the reaction (by analogy to other cycloalkene epoxides) has not been reported.[2–5]

Our investigation was prompted by the fact that the determination of the stereospecificity would enhance the synthetic utility of the reaction and by the availability of two cyclobutene epoxides suitable for such a study, bicyclo[3.2.0]hept-6-ene oxide (**1**, $n = 1$) and bicyclo[4.2.0]oct-7-ene oxide (**1**, $n = 2$).[6]

Results

The epoxides were prepared by the peracid oxidation of the corresponding cyclobutenes giving the exo isomer of **1** ($n = 1$)[7] and the exo and endo isomers of **1** ($n = 2$) which were separable by gas chromatography.[8]

Treatment of the exo isomers of **1** ($n = 1, 2$) with concentrated solutions of anhydrous lithium iodide in ether in a stoppered flask at *ca.* 40° for 1–24 hr produces a rearrangement to the exo and endo isomers of the ring-contracted bicyclic carboxaldehydes **2** ($n = 1, 2$) in varying amounts. Prolonged reaction time favors the formation of the exo isomer. Product mixtures were analyzed by vpc although the *endo*-carboxaldehydes **2** ($n = 1, 2$) rearrange on the vpc column to the corresponding Δ^2-cycloalkenyl acetaldehydes **3** ($n = 1, 2$) under the conditions employed.[9] The *exo*-carboxaldehydes **2** ($n = 1, 2$) were separated and collected by preparative vpc. Silver oxide oxidation under nonisomerizing conditions gives the known *exo*-carboxylic acids **4** ($n = 1, 2$).[10,11]



Our results suggested an initial isomerization of the *exo*-epoxides (**1**) to the bicyclic *endo*-carboxaldehydes (**2**) followed by a slower but competitive epimerization of *endo*-**2** to *exo*-**2**. This was verified by utilizing proton nmr spectroscopy to follow the rearrangement. Lithium iodide was added to an nmr sample of *exo*-**1** ($n = 2$) in $CDCl_3$ at room temperature. After 1 hr, the epoxide proton absorption had decreased and an aldehydic signal at 9.6 ppm had appeared in the spectrum (see Table I). After 4 hr, with 20% of **1** still unreacted, a new aldehyde signal at 9.1 ppm began to appear in the spectrum. After 16 hr, we obtained a ratio of 1:1 for the signals at 9.6 and 9.1 ppm assigned to the endo and exo isomers of **2** ($n = 2$), respectively. These two products can account for all of the absorptions observed in the spectrum[12] which is in perfect agreement with those of the known compounds.[9]

TABLE I

REARRANGEMENT OF *exo*-**1** ($n = 1, 2$) WITH LITHIUM IODIDE IN $CDCl_3$[a]

Time, hr	% of compound[b]					
	exo-**1**		*endo*-**2**		*exo*-**2**	
	$n = 2$	$n = 1$	$n = 2$	$n = 1$	$n = 2$	$n = 1$
0	100		0		0	
1	65		35		0	
2	40		60		0	
3	25		75		0	
4	20		80		Trace	
16	0	90	50	10	50	
23	0	85	30	15	70	
43	0	80	10	20	90	
64	0	70	0	25	100	5

[a] These data were obtained using 55 mg of *exo*-**1** ($n = 1, 2$) and 60 mg of lithium iodide in 0.4 ml of $CDCl_3$. [b] Based on integration of epoxide proton *vs.* aldehydic proton absorptions.

A similar experiment utilizing *exo*-**1** ($n = 1$) produced a slower conversion of epoxide to carboxaldehyde (Table I). Molar amounts of lithium iodide are not essential but lesser amounts reduce the rates of the reactions.

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(1) Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, ORGN 137.

(2) J. L. Ripoll and J. M. Conia, *Tetrahedron Lett.*, 979 (1965).

(3) J. L. Ripoll and J. M. Conia, *Bull. Soc. Chim. Fr.*, 2755 (1965).

(4) W. R. Moore and C. H. Beede, Abstracts, 144th National Meeting of the American Chemical Society, Los Angles, Calif, 1963, 11M.

(5) An extensive review of epoxide chemistry can be found: A. Rosowsky, "Heterocyclic Compounds with Three- and Four-Membered Rings," part 1, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, pp 1–523.

(6) D. L. Garin, *J. Org. Chem.*, **34**, 2355 (1969).

(7) L. A. Paquette, A. A. Youssef, and M. L. Wise, *J. Amer. Chem. Soc.*, **89**, 5246 (1967).

(8) A. C. Cope and R. W. Gleason, *ibid.*, **84**, 1928 (1962).

(9) D. L. Garin, *J. Org. Chem.*, **35**, 2830 (1970).

(10) J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Amer. Chem. Soc.*, **85**, 582 (1963).

(11) J. A. Berson and E. S. Hand, *ibid.*, **86**, 1978 (1964).

(12) The solid lithium iodide contained ether whose proton absorptions served as an internal standard for integrations.