Base-Promoted Reactions of Epoxides. V. 1-Alkylcycloalkene Oxides[1]

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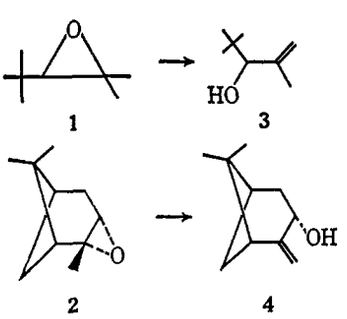
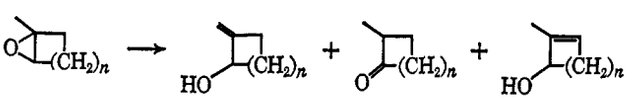
The lithium diethylamide isomerizations of the C_6–C_8 1-methylcycloalkene oxides result initially in formation of the corresponding 2-methylenecycloalkanols. Under the appropriate conditions this reaction provides a convenient preparative source of these alcohols. However, these materials are subject to an interesting further isomerization which leads to 2-methylcycloalkanones and 2-methyl-2-cycloalkenols under more severe reaction conditions. 1-*t*-Butylcyclooctene oxide gives the two possible allylic alcohols derived from β elimination (1- and 2-*t*-butyl-2-cyclooctenol) upon similar base isomerization. None of the products encountered in this study requires an α-elimination mechanism to account for its formation.

In earlier papers of this series,[1-3] the reactions of a variety of cyclic and acyclic epoxides caused by strongly basic, nonnucleophilic reagents were examined. Two major competing reaction pathways were suggested, the relative efficiencies of which depend on the specific molecule in question. In systems where a favorable *trans*, coplanar, transition-state geometry can be readily attained, β elimination to give allylic alcohols is preferred. When such is not the case, the products are thought to evolve from α elimination at an epoxide ring carbon and carbenoid insertion into a neighboring carbon–hydrogen bond.

The lithium diethylamide treatment of β-diisobutylene oxide (1) and α-pinene oxide (2) resulted in a remarkably clean conversion to the respective allyl alcohols **3** and **4**.[2] Exclusive β elimination into the substituent methyl groups was rationalized as a consequence of the unique ability of the methyl group to provide a relatively unhindered version of the necessary β-elimination geometry. In the present work the 1-methylcycloalkene oxides of ring-size five through eight have been examined in order to ascertain the suitability of base rearrangement as a synthetic route to the corresponding exocyclic methylene alcohols.



After considerable exploratory work, experimental conditions were devised which effected the predominant conversion of the six-, seven-, and eight-ring epoxides to the desired isomeric methylene alcohols in good yields. Thus, treatment of 1-methylcyclohexene oxide (**5**) with lithium diethylamide in refluxing ether for 1 day gave 2-methylenecyclohexanol (**6**) as 79% of the distilled product along with a minor amount (11%) of 2-methylcyclohexanone (**7**). Similar conditions transformed 1-methylcycloheptene oxide (**8**) to 1-methylenecycloheptanol (**9**). However, reaction in refluxing benzene generated a more complex mixture which contained 2-methylcycloheptanone (**10**) and 2-methyl-2-cycloheptenol (**11**) in addition to **9**. 1-Methylcyclooctene oxide (**12**) was isomerized to 2-methylenecyclooctanol (**13**) containing 6% of 2-methylcyclooctanone (**14**) when reacted with diethylamide in ether at room temperature for 5 hr. Again, more severe reaction conditions resulted in a mixture of **13**, **14**, and 2-methyl-2-cyclooctenol (**15**). Finally, it should be mentioned that 1-methylcyclopentene oxide (**16**) gave no 2-methylenecyclopentenol (**17**) under even the mildest conditions examined; 2-methylcyclopentanone (**18**) and 2-methyl-2-cyclopentenol (**19**) were the important products. Therefore, insofar as preparative utility is concerned, it appears that the diethylamide rearrangement of 1-methylcycloalkene oxides provides a viable and general synthetic route to the corresponding 2-methylenecycloalkanols, so long as careful attention is devoted to experimental detail.[4]



3[a]	5	6	7	...
4[a]	8	9	10	11
5[a]	12	13	14	15
2[a]	16	17	18	19

[a] n

The obvious conclusion derived from the reactions run under more severe conditions is that the initially formed 2-methylenecycloalkanols are subject to further reaction in strongly basic media which leads to the 2-methylcycloalkanones and 2-methyl-2-cycloalkenols. Experimental confirmation of this deduction was secured by showing that the methylene alcohols **9** and **13** did, in fact, undergo the proposed conversions. Similar processes appear likely for the five- and six-ring analogs. The absence of 2-methylenecyclopentanol (**17**) in the product from **16** is notable, but the formation of 2-methyl-2-cyclopentenol as the sole allylic alcohol rather convincingly implicates the methylene compound as the precursor of the endocyclic allylic alcohol, since simple β elimination internal to the carbocycle would be expected to yield the 5-methyl derivative in addition to **19**.

The secondary isomerizations of the methylene alcohols appear to be best rationalized in terms of reversible allylic metallation of the corresponding lithium alkoxide and attendant double bond migration during the lifetime of the resulting allyllithium species or in the

(1) Part IV: J. K. Crandall and L. C. Lin, *J. Amer. Chem. Soc.*, **89**, 4527 (1967).

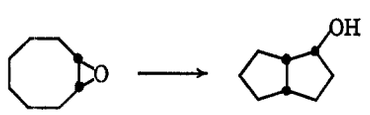
(2) J. K. Crandall and L. Chang, *J. Org. Chem.*, **32**, 435, 532 (1967).

(3) J. K. Crandall and L. C. Lin *J. Amer. Chem. Soc.*, **89**, 4526 (1967).

(4) Professor E. Warnhoff has kindly informed us that *trans*-caryophyllene oxide is converted into the corresponding exocyclic methylene compound in good yield.

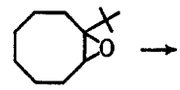
process of its protonation.[5] Bond migration into the ring away from the alkoxide function leads to the lithium alkoxide of the endocyclic allylic alcohols (or related organolithium intermediates), while isomerization toward the alkoxide group eventually generates the lithium enolates of the methylcycloalkanones. The first transformation is a relatively routine one, but the isomerization leading to ketones is not, to our knowledge, a recognized mode of allylic alcohol rearrangement under strongly basic conditions. Support for the proposed mechanism for interconversion of the two allylic alcohols is found in the demonstration that partial isomerization of **11** and **15** to the exocyclic isomers **9** and **13** does occur. It is probably significant that ketones **10** and **14** were not found in these experiments since this surprising result was checked several times. The last observation is consistent with the results of our earlier work.[2,6] For example, 2-cycloheptenol has been rigorously shown not to yield cycloheptanone under isomerization conditions.[2] 2-Cycloheptenol is, however, converted into 1,3-cycloheptadiene upon such treatment, and a similar process probably accounts for the small amount of olefinic materials found in several of the above isomerizations (see Experimental Section). Thus, it would appear that there is a special feature of the exocyclic methylene alcohols, probably geometric in origin, which renders their behavior exceptional with respect to more usual allylic alcohols. Rational proposals accounting for the unusual features of ketone formation can be contrived, but detailed discussion seems best delayed until additional experimental information is available.

In an attempt to promote transannular reactions of the type observed with the unsubstituted seven- and eight-membered cycloalkene oxides (for example, **20** → **21**),[2,7] 1-methylcycloheptene oxide was treated with *t*-butyllithium, a reagent which has been found to enhance metallation at the epoxide ring. However, the major products were again ketone **10** and alcohol **9**, along with a new material identified as 1-*t*-butyl-2-methylcycloheptanol.

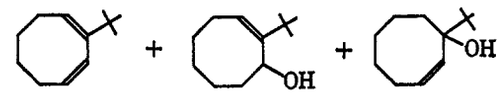


20 **21**

The last part of this study involved the preparation of 1-*t*-butylcyclooctene oxide (**22**), a molecule which is not capable of elimination into the substituent group. For this reason, we expected that this material might parallel the parent cyclooctene oxide in its reactions.[7] However, the only isomeric compounds formed upon lithium diethylamide treatment were the two possible allylic alcohols, 1-*t*-butyl-2-cyclooctenol (**23**) and 2-*t*-butyl-2-cyclooctenol (**24**). In addition, 2-*t*-butyl-1,3-cyclooctadiene (**25**) and a second unidentified olefin (probably the 1-*t*-butyl isomer) were found. The



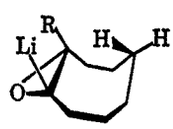
22



25 **24** **23**

same two allylic alcohols were secured as the major products with *t*-butyllithium as the basic reagent.

These results can be explained, after the fact, on the basis of the steric influence of the bulky *t*-butyl substituent. We have suggested earlier[2] that a transition-state conformation similar to **26** is necessary to rationalize the stereochemistry of alcohol **21** formed from the parent cyclooctene oxide. In the same transition-state geometry for the *t*-butyl compound (**27**), there may be enough destabilization owing to nonbonded interactions of the substituent that decomposition occurs by more favorable pathways, namely β elimination.[8] Similar effects can be anticipated for other substituents. An alternate possibility for the suppression of α elimination is simply that the *t*-butyl group inhibits metallation at the epoxide ring, a process which must precede the



26, R = H
27, R = *t*-Bu

transannular insertion reaction. In any event, it is clear that substituted medium-ring epoxides will not necessarily parallel the parent compounds in their base rearrangements.

Experimental Section

General.—All nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60 spectrometer. Data are given in ppm relative to tetramethylsilane as internal standard in carbon tetrachloride solution. Infrared spectra were recorded on Perkin-Elmer 137 and 137G spectrometers and were taken on neat samples unless indicated otherwise. Gas chromatography (glpc) was performed on a 5 ft × 0.125 in. 15% Carbowax 20M column on an Aerograph A-600 (analytical) instrument and on a 10 ft × 0.375 in. 15% Carbowax 20M column or a 20 ft × 0.375 in. 20% Carbowax 20M column on an Aerograph A-700 (preparative) instrument. Percentage composition data were estimated by peak areas and are uncorrected. All melting points were determined in capillary tubes. Microanalyses were performed by Midwestern Microlab, Inc., and Huffman Laboratories, Inc. Anhydrous magnesium sulfate was used throughout as a drying agent.

Preparation of Epoxides.—Epoxides were prepared by a modification of the procedure of Korach, *et al.*[9] To an ice-cold, mechanically stirred mixture of 1 equiv of olefin and 3 equiv of powdered, anhydrous sodium carbonate in methylene chloride was added dropwise 1.1 equiv of 40% peracetic acid which had been treated with a small amount of sodium acetate. The mixture was stirred at room temperature until the methylene chloride solution gave a negative test with moist starch–iodide paper. The solid salts were removed by suction filtration and washed well with additional methylene chloride. The solvent was re-

(5) A general discussion of allylic carbanions is found in D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 176–210.

(6) Unpublished results of L. C. Lin and A. C. Clark. Interestingly, cycloheptene and cyclooctene oxides are converted by lithium diethylamide *in tetrahydrofuran* into mixtures of the allylic alcohols *and their double bond isomers* to the exclusion of bicyclic products.[2]

(7) A. C. Cope, H. H. Lee, and H. E. Petree, *J. Amer. Chem. Soc.*, **80**, 2849 (1958).

(8) The β elimination may proceed with a *cis*, coplanar geometry: M. Svoboda, J. Zavada, and J. Sicher, *Collect. Czech. Chem. Commun.*, **32**, 2104 (1967); J. Sicher and J. Zavada, *ibid.*, **32**, 2122 (1967).

(9) M. Korach, D. R. Nielsen, and W. H. Rideout, *J. Amer. Chem. Soc.*, **82**, 4328 (1960).

moved from the filtrate by distillation through a Vigreux column, and the residue was purified by distillation through a spinning band column. The following epoxides were prepared by this method: 1-methylcyclopentene oxide (**16**),[10] yield 61%, bp 108–110°, infrared bands at 10.8, 12.0 μ, epoxide ring proton in the nmr spectrum at δ 3.07, methyl at 1.39; 1-methylcycloheptene oxide (**8**), yield 65%, bp 70–75° (50 mm), ir 11.0, 12.2 μ, nmr, a one-proton triplet at δ 2.68 (epoxide ring proton, J = 9 cps), methyl singlet at 1.22 and the other ten protons at 2.0–1.2 (*Anal.* Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.26; H, 11.22); 1-methylcyclooctene oxide (**12**),[11] yield 63%; bp 97–100° (33 mm), ir 10.9, 12.0 μ; and 1-*t*-butylcyclooctene oxide (**22**), yield 45%, bp 72–76° (6 mm), ir 10.7, 11.9 μ, nmr, a one-proton multiplet at δ 2.75 (epoxide ring-proton), *t*-butyl singlet at 0.96 and the other twelve protons between 2.5 and 1.3 (*Anal.* Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.06; H, 12.06).

1-Methylcyclohexene Oxide (5).—Epoxidation of 1-methylcyclohexene with peracetic acid led to 2-methylcyclohexanone; however, epoxidation with *m*-chloroperbenzoic acid gave the desired epoxide. To an ice-cold, mechanically stirred solution of 20 g of 1-methylcyclohexene in 200 ml of methylene chloride was added 44 g of 85% *m*-chloroperbenzoic acid in portions. The mixture was stirred at room temperature until the methylene chloride solution gave a negative test with starch–iodide paper (3 days). The solid salts were removed by suction filtration and washed well with additional methylene chloride. The methylene chloride solution was washed with saturated sodium carbonate solution and water and dried. The solvent was removed by distillation through a Vigreux column, and the residue was distilled through a spinning band column to give 17.9 g (80%) of pure 1-methylcyclohexene oxide, bp 85–88° (30 mm).[12] This material shows bands at 7.28, 11.0, and 11.9 μ, and its nmr spectrum displays a one-proton triplet at δ 2.78 (epoxide ring proton, J = 2 cps), and the other 11 protons are at 2.0–0.9 with a methyl singlet at 1.23.

Typical Procedure for Rearrangement of Epoxides by Lithium Diethylamide.—To an ice-cold solution of 2.5 equiv of diethylamine in anhydrous ether was added 2.5 equiv of commercial 15% butyllithium in hexane under a nitrogen atmosphere. After 10 min a solution of 1 equiv of the appropriate epoxide in anhydrous ether was added; the mixture was heated to reflux for the specified period. The reaction mixture was cooled and poured into water; the organic layer separated. The aqueous layer was extracted with ether, and the combined organic layers were washed with 1 *N* hydrochloric acid, saturated sodium bicarbonate solution, and water. After drying, the solvent was removed by distillation through a column, and the residue was purified by distillation. If the product was a mixture, further purification was effected by preparative glpc. Product identification was by comparison of spectral data with those of authentic samples obtained from commercial sources or by literature methods unless indicated otherwise.

Rearrangement of 1-Methylcyclopentene Oxide (16).—The reaction was carried out with 4.9 g of **16** in 300 ml of ether in the usual fashion for 5 hr. Distillation of the product gave 3.62 g (74%) of a pale liquid of wide boiling range. In addition to several trace products it contained 10% of 2-methylcyclopentanone and 82% of 2-methyl-2-cyclopentenol[13] which were identified by spectral data. 2-Methylcyclopentanone shows infrared absorption at 5.75 and 7.3 μ. Its nmr spectrum shows a methyl doublet (J = 6 cps) at δ 1.03 and a broad band at 2.03 for the other seven protons. 2-Methyl-2-cyclopentenol has infrared bands at 3.0, 3.3, and 7.3 μ. Its nmr spectrum displays a one-proton multiplet at δ 5.48 (C=C*H*), a two-proton multiplet at 4.3 (C*H*O*H*), a methyl singlet at 1.7, and the other four protons at 2.4–1.8.

The aqueous portion of work-up was made basic and extracted with ether to give additional 2-methyl-2-cyclopentenol. The total yield of this alcohol was 65%.

Rearrangement of 1-Methylcyclohexene Oxide (5).—Rearrangement of 5.6 g of **5** in refluxing ether for 1 day gave 3.25 g of distilled product. Analysis by glpc indicated the presence of three components in an 11:79:10 ratio. The first component was identified as 2-methylcyclohexanone.[14] The second component was identified as 2-methylenecyclohexanol[15] on the basis of its spectra: ir, 2.98, 6.08, and 11.1 μ; nmr absorption as one-proton broad singlets at δ 4.85 and 4.74 (C=C*H*$_2$), a two-proton multiplet at 3.97 (C*H*O*H*), and the other protons at 2.4–1.2. The third component is a higher molecular weight compound believed to be 2-methylenecyclohexyl 2-methyl-2-cyclohexenyl ether on the basis of its spectral properties: ir 3.28, 6.06, and 11.2 μ; nmr, a one-proton multiplet at δ 5.40 (C=C*H*), two-proton multiplets at 4.74 (C=C*H*$_2$) and 3.77 (C*H*OC*H*) and 17 additional protons at 1.9–1.4.[16]

Rearrangement of 1-Methylcycloheptene Oxide (8).—When the reaction was carried out with 1.26 g of **8** in 100 ml of ether at reflux for 1 day, there was obtained 1.30 g (102%) of a colorless oil, bp 88–90° (25 mm). Examination by glpc indicated the presence of a single compound which was identified as 2-methylenecycloheptanol on the basis of its spectral properties: ir 2.9, 3.24, 6.12, and 11.1 μ; nmr, one-proton singlets at δ 4.97 and 4.78 (C=C*H*$_2$), a one-proton multiplet at 4.16 (C*H*OH), a one-proton singlet at 3.9 (O*H*), a two-proton multiplet at 2.17 (C=CC*H*$_2$), and the remaining eight methylene protons as a broad band at 1.5.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.81; H, 11.15.

A second run on 3.8 g of **8** in 250 ml of ether gave about 9% each of two additional compounds. The first new compound was identified as 2-methylcycloheptanone[17] by its spectral data: ir, 5.88 and 7.28 μ; nmr, a broad three-proton multiplet at δ 2.4 for the protons adjacent to the carbonyl group, eight methylene protons as a broad band at 1.7, and a methyl doublet centered at 0.98 (J = 7 cps). The second new compound was assigned as 2-methyl-2-cycloheptenol again on spectral grounds: ir 3.0, 3.28, and 7.26 μ; nmr, a one-proton multiplet at δ 5.50 (C=C*H*), a two-proton multiplet at 4.10 (C*H*O*H*), and the other 11 protons as a broad band at 1.72.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.48; H, 11.19.

A run on 4.5 g of **8** in refluxing benzene for 2 days gave 3.07 g (68%) of a colorless oil which contained 2-methylcycloheptanone, 2-methylenecycloheptanol, and 2-methyl-2-cycloheptenol in a 50:35:15 ratio. There was also obtained 0.35 g (8%) of a lower boiling fraction which consisted of two isomeric olefins. The infrared spectra of both compounds have bands at 3.30 and 7.30 μ. Their nmr spectra are very similar and both show three protons at δ 5.4–5.8 and nine protons at 2.5–1.6. These compounds are believed to be 1- and 2-methyl-1,3-cycloheptadiene.

Rearrangement of 2-Methylenecycloheptanol (9).—2-Methylenecycloheptanol (1.01 g) was treated with lithium diethylamide in the usual fashion using benzene as the solvent. Distillation of the product gave 0.57 g (57%) of a colorless oil, bp 88–97° (16 mm). Examination of this material by glpc showed the presence of 2-methylcycloheptanone, 2-methylenecycloheptanol, and 2-methyl-2-cycloheptenol in a 45:36:14 ratio.

Reaction of 2-Methyl-2-cycloheptenol (11) with Lithium Diethylamide.—The reaction was carried out with 137 mg of **11** in refluxing benzene for 53 hr. Removal of the solvent gave 114 mg of a crude product. Analysis by glpc showed the presence of 2-methylenecycloheptanol and 2-methyl-2-cycloheptenol in a 14:86 ratio in addition to a small amount of solvent.

Rearrangement of 1-Methylcyclooctene Oxide (12).—Rearrangement of 1.40 g of **12** in ether at room temperature for 1 day gave 1.32 g (94%) of distilled product which contained two compounds in a 94:6 ratio. The major product was assigned the structure 2-methylenecyclooctanol[12] (**13**) on the basis of spectral data and preparation of its phenylurethane: mp 98–99° (lit.[11] mp 98–100°); ir, 3.0, 3.28, 6.10, and 11.1 μ; nmr, one-proton multiplets at δ 5.06 and 4.87 (C=C*H*$_2$), a one-proton triplet (J = 6 cps) at 4.07 (C*H*OH), a one-proton singlet at 3.14 (O*H*), a two-proton multiplet at 2.17 (C=CC*H*$_2$), and ten additional protons at 1–2. The minor product was assigned as 2-methyl-2-cyclooctenol (**15**) on spectral grounds: ir, 3.0, 3.27, 6.0, and 7.26 μ; nmr, a one-proton triplet (J = 8 cps) at 5.38 (C=C*H*), a one-proton multiplet at 4.22 (C*H*OH), a one-proton broad band at 3.4 (O*H*), and the other 13 protons at 2.2–1.2 with a methyl singlet at 1.63.

(10) T. Wagner-Jauregg and M. Roth, *Chem. Ber.*, **93**, 3036 (1960).
(11) A. C. Cope and P. E. Burton, *J. Amer. Chem. Soc.*, **82**, 5439 (1960).
(12) R. Filler, B. R. Camara and S. M. Naqvi, *ibid.*, **81**, 658 (1959).
(13) M. C. Mitter and P. C. Dutta, *J. Indian Chem. Soc.*, **25**, 306 (1948).
(14) Sadtler Index Infrared Spectra, No. 8401.
(15) A. S. Dreiding and J. A. Hartman, *J. Amer. Chem. Soc.*, **75**, 939 (1953).
(16) 2-Cyclopentenol undergoes a similar facile ether formation upon standing in the liquid phase or in the course of preparative glpc purification.
(17) R. Jacquier and H. Christol, *Bull. Soc. Chim. Fr.*, 600 (1957).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.91; H, 11.21.

An identical 1-day run at reflux temperature gave 1.22 g (87%) of a colorless oil, bp 108–112° (15 mm). It contained 2-methylcyclooctanone,[18] 2-methylenecyclooctanol, and 2-methyl-2-cyclooctenol in a 10:43:47 ratio. 2-Methylcyclooctanone was identified by spectral data: ir, 5.90 and 7.31 μ; nmr, a three-proton multiplet at δ 2.2–2.8 for protons adjacent to the carbonyl group, ten methylene protons at 1.3–2.2, and a methyl doublet centered at 0.97 (J = 7 cps).

A 2-day run on 3.9 g of **12** in 300 ml of refluxing benzene gave 4.0 g (101%) of a pale liquid, bp 103–112° (aspirator vacuum), which contained the above three products in a 22:5:68 ratio in addition to two other trace products.

Reaction of 2-Methyl-2-cyclooctenol (15) with Lithium Diethylamide.—The reaction was carried out with 241 mg of **15** in refluxing benzene for 2 days. Removal of the solvent gave 214 mg of a crude product. Analysis by glpc indicated the presence of 89% of 2-methyl-2-cyclooctenol and 10% of 2-methylenecyclooctanol.

Reaction of 2-Methylenecyclooctanol (13) with Lithium Diethylamide.—The reaction on 126 mg of **13** in 20 ml of refluxing benzene for 1 day gave 115 mg of a crude product after removal of the solvent which contained 16% of 2-methylcyclooctanone, 18% of 2-methylenecyclooctanol, and 66% of 2-methyl-2-cyclooctenol.

Rearrangement of 1-*t*-Butylcyclooctene Oxide (22).—The rearrangement was carried out with 1.82 g of **22** in 100 ml of refluxing benzene for 3 days. Distillation of the product gave 1.63 g of a pale oil, bp 89–95° (7 mm). Examination of this material by glpc indicated the presence of four compounds in a 15:4:34:47 ratio. The first compound was assigned as 2-*t*-butyl-1,3-cyclooctadiene by spectral data: ir, 3.3, 7.2 and 7.4 μ; nmr, a two-proton multiplet at δ 5.87 (C*H*=C*H*), a one-proton triplet (J = 8 cps) at 5.48 (CH_2CH=C), four-proton multiplets at 2.02 (C=CCH_2) and 1.37 (CH_2), and a nine-proton singlet at 1.04 for the *t*-butyl group; uv (cyclohexane), λ_{max} 218 mμ (ε 5300).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.64; H, 12.27.

The second compound was also an olefin as indicated by its infrared spectrum and is probably 1-*t*-butyl-1,3-cyclooctadiene.

The third compound was assigned the structure 1-*t*-butyl-2-cyclooctenol on the basis of its spectral data: ir, 2.8, 7.2, and 7.38 μ; nmr, a two-proton multiplet at δ 5.57 (C*H*=C*H*), a nine-proton singlet at 0.94 [C(CH_3)$_3$], and an additional 11 protons at 1.2–2.4.

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.21; H, 12.09.

The last compound was identified as 2-*t*-butyl-2-cyclooctenol again on the basis of spectral data: ir, 3.0, 3.3, 7.2, and 7.35 μ; nmr, a one-proton triplet (J = 9 cps) at δ 5.46 (C=C*H*), a nine-proton singlet at 1.1 [C(CH_3)$_3$], and 11 additional protons at 1.2–2.8.

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.12; H, 12.08.

General Procedure for the Reaction of Alkyllithium Reagents with Epoxides.—To a solution of 3 equiv of commercial alkyllithium in hydrocarbon solvent was added 1 equiv of an epoxide in solvent under a nitrogen atmosphere. The mixture was heated to reflux temperature for 1 day. After cooling the reaction mixture was poured into water, and the layers were separated. The aqueous layer was extracted twice with ether, and the organic layers were washed with 1 *N* hydrochloric acid, saturated sodium bicarbonate solution, water, and dried. The solvent was removed by distillation through a Vigreux column and the residue was distilled. Separation of components was effected by preparative glpc. Product identification was by comparison of spectral data with authentic samples obtained from commercial sources or by literature methods, unless otherwise stated.

Reaction of 1-Methylcycloheptene Oxide (8) with *t*-Butyllithium.—The reaction was carried out with 1.26 g of **8** in pentane for 2 days. Distillation gave 0.92 g (84%) of a colorless liquid, bp 82–90° (20 mm). Three major products were present in a 9:62:11 ratio in addition to several trace products. The first two compounds were identified as 2-methylcycloheptanone and 2-methylenecycloheptanol. The third compound was assigned the structure 1-*t*-butyl-2-methylcycloheptanol by comparison of retention times and infrared spectra with an authentic sample obtained by treating 2-methylcycloheptanone with *t*-butyllithium. It has infrared bands at 2.8, 7.24, and 7.31 μ, and the nmr spectrum shows a one-proton multiplet at δ 2.2 (C*H*), an 11-proton multiplet between 1.9 and 1 (CH_2, O*H*), and a methyl doublet centered at 1.0 with one peak buried under the *t*-butyl singlet at 0.91.

Reaction of 1-*t*-Butylcyclooctene Oxide (22) with *t*-Butyllithium.—The reaction of 1.82 g of **22** in 100 ml of pentane at reflux for 3 days gave 1.62 g (89%) of a colorless oil, bp 90–96° (2 mm). Examination of this material by glpc indicated the presence of three compounds in a 9:46:44 ratio. The first compound decomposed upon preparative glpc and was not identified. It is probably a ketone as indicated by a carbonyl absorption in the infrared spectrum of the glpc isolated material. The last two compounds were identified as 1-*t*-butyl-2-cyclooctenol and 2-*t*-butyl-2-cyclooctenol, respectively.

Reaction of 2-Methylenecycloheptanol (9) with *t*-Butyllithium.—The alcohol (134 mg) was treated with *t*-butyllithium in the usual fashion to give 187 mg of crude product. Analysis by glpc indicated the presence of five components in addition to solvent and some low-boiling material. The first component (4%) was 2-methylcycloheptanone, and the second compound (14%) was unidentified; the next three compounds were 2-methylenecycloheptanol (62%), 2-methyl-2-cycloheptenol (9%), and 1-*t*-butyl-2-methylcycloheptanol (9%).

Registry No.—**5,** 1713-33-3; **8,** 16240-37-2; **9,** 16240-38-3; **11,** 16240-39-4; **12,** 16240-40-7; **15,** 16240-41-8; **16,** 16240-42-9; **18,** 1120-72-5; **19,** 3718-58-9; **22,** 16240-43-0; **23,** 16240-47-4; **24,** 16240-46-3; **25,** 16240-44-1; 1-*t*-butyl-2-methylcycloheptanol, 16240-45-2.

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(18) E. Muller and M. Bauer, *Ann. Chim.*, **554**, 92 (1962).