the same products were formed in different proportions: 3-bromo-1-cyclooctene, 30%; bromocyclooctane, 3%; trichloromethylcyclooctane, 38%, 1-bromo-2-trichloromethylcyclooctane, 22%; and 1-bromo-4-trichloromethylcyclooctane, 2%. The conversion of cyclooctene into products was 77%, and the combined yield of identified products was 95%.

Selective Dehydrohalogenations of 1-Bromo-2-trichloromethylcyclooctane. A. With AgNO$_3$ in DMF.—A solution of silver nitrate (2.8 g, 0.016 mole) in aqueous dimethylformamide (20 ml, 70% DMF/30% H$_2$O v/v) was added dropwise to a warm (35°), stirred solution of I (0.0325 mole) in DMF (50 ml). Precipitation began quickly, and the mixture was stirred for 4 hr without additional heating. After dilution with water, the mixture was extracted three times with petroleum ether (bp 60–70°). The combined organic material was washed with water, dried, and distilled at reduced pressure. Nmr and gc analyses indicated that a single dehydrohalogenation product, C$_9$H$_{13}$Cl$_3$ (V), was formed and that 54% of the original I was recovered. *Anal.* Calcd for C$_9$H$_{13}$Cl$_3$: C, 47.4; H, 5.8. Found: 47.0; H, 5.9. Spectra of V indicate that it is 3-trichloromethylcyclooctene; nmr −5.7 (2 H, vinyl), −2.7 to −2.0 (5 H, HCCCl$_3$, CH_2C=C, and CH_2CCCl$_3$), and −1.62 ppm (6 H, CH$_2$CH_2CH$_2$). Infrared absorptions were recorded at 3.3 (vinyl C-H), 6.02 (C=C), and 12.6–13.2 μ (intense, CCl$_3$). The gc retention time of V is shorter than those of 4- and 1-trichloromethylcyclooctenes.

The nmr spectrum of the recovered I indicated that the sample was identical, within the experimental precision of the analysis, with the initial I.

B. With KOH in DMSO.—During 1.5 hr, a solution of potassium hydroxide (0.045 mole) in a mixed solvent (20 ml of DMSO, 5 ml of methanol, 5 ml of water) was added to a solution if I (0.065 mole) in DMSO (40 ml) and methanol (10 ml).[2] The mixture was stirred at room temperature for 18 hr longer, poured into 200 ml of water, and extracted three times with petroleum ether. Conventional work-up and distillation of the organic material gave a mixture of products in two fractions and another fraction of essentially pure *trans* I, bp 90–99° (0.12 mm), whose nmr spectrum is reproduced in Figure 1.

The nmr spectra of the first two distillate fractions included signals at −5.1 (complex six-peak multiplet, HCBrC=CCl$_2$), −4.65 (multiplet, HCBr in *trans* I), −3.1 ppm (sharp singlet, OCH_3). Infrared spectra of the same fractions included absorptions at 6.22 and 11.09 (C=CCl$_2$), 9.2 (methyl ether), and 12.7–13.4 μ (CCl$_3$). On the basis of concordant changes in the relative intensities of the absorptions in the nmr and infrared spectra of the distillate fractions, the components (and estimated yields based on initial I) were identified as follows: 1-bromo-2-dichloromethylenecyclooctane (19%), 1-methoxy-2-dichloromethylenecyclooctane (5%), and *trans* I (43%).

C. With *t*-BuOK in *t*-BuOH.—A mixture of potassium *t*-butoxide (0.035 mole), *t*-butyl alcohol (100 ml), methyl alcohol (10 ml), and I (0.052 mole) was stirred for 20 hr at room temperature, diluted with 100 ml of water, and extracted twice with petroleum ether. The combined organic material was washed thoroughly with water, dried with calcium chloride, and distilled. Besides solvent, four fractions (13.4 g total) boiling at 60–92° (0.12 mm) were collected; the final fraction, bp 91–92° (0.12 mm), 3.8 g (0.0123 mole), was virtually pure *trans* I. The fractions which were mixtures were analyzed by nmr and infrared spectroscopy and by gas chromatography. The recordings included nmr signals at −6.51 (well-resolved triplet,[14] J = 8.5 cps) as well as the previously mentioned ones at −5.1 (HCBrC=CCl$_2$) and −4.65 ppm (HCBr in *trans* I), and infrared absorptions at 3.3 and 6.1 (vinyl), 6.25 and 11.08 (C=CCl$_2$), and 12.7–13.4 μ (CCl$_3$). On the basis of concordant changes in the relative intensities of the absorptions in the nmr and infrared spectra and the relative peak areas in the gas chromatograms, the components (and estimated yields based on initial I) were identified as follows: 1-trichloromethyl-1-cyclooctene (19%), 1-bromo-2-dichloromethylenecyclooctane (5.5%), 3-trichloromethyl-1-cyclooctene (1.5%), and *trans* I (total yield 45%). Small amounts of alkoxycyclooctanes (see B above) appeared to be present in the mixtures also.

Registry No.—*trans* I, 7540-97-8; *cis* I, 7540-98-9; III, 7540-99-0; V, 7541-00-6; 1-bromo-4-trichloromethylcyclooctane, 7541-61-7.

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[14] The nmr spectra of several different 1-substituted cyclooctenes show a clean triplet signal for the single vinyl proton: A. C. Cope and R. B. Kinnel, *J. Am. Chem. Soc.*, **88**, 752 (1966); see in particular footnote 14 of that paper.

Base-Promoted Reactions of Epoxides. II. 3,4- and 5,6-Epoxycyclooctene[1]

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The rearrangement reactions of the title compounds promoted by lithium diethylamide have been examined. 3,4-Epoxycyclooctene produces 3-cyclooctenone and *cis*-bicyclo[3.3.0]oct-7-en-*endo*-2-ol. 5,6-Epoxycyclooctene gives a mixture of 2,4- and 3,5-cyclooctadienol as the initial product. These alcohols undergo facile thermal conversion into 3-cyclooctenone by a pathway involving 1,5-hydrogen migration. The details of the base-initiated rearrangements are discussed in the light of related studies.

In connection with our interest in the reactions of epoxides in strongly basic media, we have examined the transformations of 3,4-epoxycyclooctene (**1**) and 5,6-epoxycyclooctene (**2**) under such conditions. This study was prompted by the earlier work of Cope and co-workers,[2] who observed that *cis*-cyclooctene oxide (**3**) was largely isomerized to bicyclic alcohol **4** upon treatment with lithium diethylamide. This reaction, which is typical for a number of medium-ring epoxides, was demonstrated to proceed by an α-elimination mechanism that presumably involves transannular insertion of a carbenoid intermediate.[3] The present study was initiated to determine the effect of neighboring double bonds on the reactions of medium-ring epoxides with strong bases and, in particular, to ascertain whether intramolecular carbenoid addition to the olefinic bonds would occur. The predominance of transannular insertion reactions in the cyclooctyl system and the availability of the diene precursors of the epoxides directed our attention toward compounds **1** and **2**.

Subjecting **1** to reaction with excess lithium diethylamide in refluxing ether for 1 day resulted in a smooth conversion to a mixture of two products in an 8:92 ratio. The spectroscopic data for the minor component established that it was an unsaturated, non-

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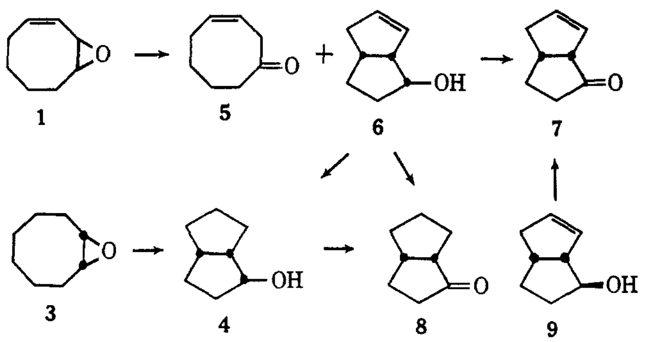
[1] Part I: J. K. Crandall and Luan-Ho Chang, *J. Org. Chem.*, **32**, 435 (1967). A review of base-promoted rearrangements of unfunctionalized epoxides is included in this paper.

[2] A. C. Cope, H. H. Lee, and H. E. Petree, *J. Am. Chem. Soc.*, **80**, 2849 (1958).

[3] A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *ibid.*, **82**, 6370 (1960).

conjugated ketone and paved the way for its positive identification as 3-cyclooctenone (**5**) by comparison with an authentic sample.[4] The major product was an unsaturated alcohol which was shown to be *cis*-bicyclo[3.3.0]oct-7-en-*endo*-2-ol (**6**) on the basis of the observations outlined in the following discussion (see Chart I).

CHART I

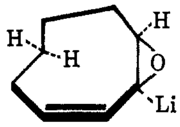


The nmr spectrum of **6** showed the presence of only two olefinic protons, thus indicating a bicyclic structure. Oxidation with chromic acid produced a new ketone (**7**) which was a cyclopentanone as demonstrated by carbonyl absorption in the infrared at 5.76 μ. Furthermore, enhanced $n-\pi^*$ absorption [λ_{max} 298 mμ (ϵ 89)] in the ultraviolet spoke in favor of the double bond being disposed β,γ to the carbonyl group.[5] Catalytic hydrogenation of the rearrangement mixture gave two materials in addition to cyclooctanone. These were readily shown to be bicyclic alcohol **4** and the corresponding ketone **8** by comparison with authentic samples obtained *via* **3**.[2] This experiment demonstrates both the ring system and the position and stereochemistry of the hydroxyl group. Assignment of structure **6** was confirmed by the observation of a strong intramolecular hydrogen bond between the hydroxyl group and the π electrons of the double bond. Finally ketone **7** was shown to be identical with the product obtained by LeBel and Spurlock[6] from the oxidation of an alcohol to which they have assigned structure **9**.

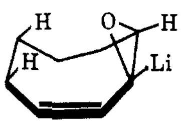
It was somewhat surprising to find substantial amounts of **8** in the catalytic hydrogenation described above. Similar results were observed using either 5% palladium on charcoal or prereduced platinum dioxide. In fact, **8** was the major product under the former conditions. In an attempt to pin down the course of this unusual reaction, the effect of the palladium catalyst on **6** without hydrogen and on **4** both in the presence and absence of hydrogen was determined. However, in none of these experiments was there observed substantial reaction. Consequently, a more involved process than simple dehydrogenation of either starting material or product must be involved. A formally analogous conversion has been observed in the hydrogenation of *trans*-5-cyclodecenol which gives cyclodecanone as a major product.[7]

A comparison of the base-promoted rearrangement of **1** with that of **3** reveals that the double bond in the former epoxide has had little effect on the course of the reaction except to direct formation of the carbenoid center to the allylic carbon atom. Otherwise the reaction of **1** fits nicely into the pattern established earlier for **3** and the other medium-ring epoxides which have been studied. As observed with these prior examples, the transannular insertion reaction is highly specific, as it produces **6** without detectable evidence for the epimeric alcohol **9**. In the appropriate conformation of **1** for formation of the observed product **6** the migrating hydrogen is within about 2.5 A of the incipient carbenoid center. These two facts appear to support the hypothesis of a concerted elimination–insertion mechanism[1,3] and require at the very minimum that transannular insertion be substantially faster than conformational relaxation of any divalent carbon intermediate. The predominance of reaction at the epoxide carbon atom which is also allylic is doubtless attributable to stabilization of the organolithium intermediate which is formed as a prelude to insertion, allylic stabilization in the transition state for decomposition of this species, or both.

Of the two conformations which bring the positionally correct transannular proton within reach of the reactive site, conformation **10** predicts the observed product, whereas **11** would produce the epimeric alcohol **9**. The preference for decomposition from **10** over **11** can be attributed to an inherent stereoelectronic requirement for the concerted reaction which necessitates approach of the transannular carbon–hydrogen bond from the side of the reactive carbon atom *away* from the departing oxygen. An equally plausible explanation is simply that the additional nonbonded interactions of the "axial" oxygen in **11** with the transannular hydrogens destabilize this conformation enough relative to **10**, which has an "equatorial" oxygen, so that only the latter is important in determining reaction products owing to the mirroring of this difference in the respective transition-state energies.



10



11

As proposed for other medium-ring epoxides,[1] the opportunity for β elimination by base attack at the methylene group adjacent to the epoxide function (or the vinylogous position) is probably geometrically inhibited owing to lack of low-energy conformations with the requisite *trans*, coplanar array of the important atoms.[8]

A number of possible pathways leading to ketone **5** can be envisaged and distinction among them is not

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[4] (a) Prepared by chromic acid oxidation of 3-cyclooctenol: A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959). (b) See also N. Heap and G. H. Whitham, *J. Chem. Soc., Phys. Org. Sect.*, 164 (1966).

[5] A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," The Macmillan Co., New York, N. Y., 1964, pp 75–77.

[6] N. A. LeBel and L. A. Spurlock, *Tetrahedron*, **20**, 215 (1964). We wish to thank Professor LeBel for kindly supplying us with the infrared spectra of **7** and **9**.

[7] A. C. Cope, R. J. Cotter, and G. G. Roller, *J. Am. Chem. Soc.*, **77**, 3594 (1955). Note, however, that the possibility of an intramolecular hydrogen migration, which appears reasonable for *trans*-5-cyclodecenol, is precluded for **6** because of the geometry of this molecule.

[8] D. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., New York, N. Y., 1963; J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Cook Co., Inc., New York, N. Y., 1962, Chapter VIII; J. F. Bunnett, *Angew. Chem. Intern. Ed. Engl.*, **1**, 225 (1962).

possible with the available data. The most likely possibility is that this transformation is related to the conversion of several saturated alicyclic epoxides to ketones.[1] However, it is also possible that **5** arises by a pathway related to that discussed below for the genesis of this same material from **2**.

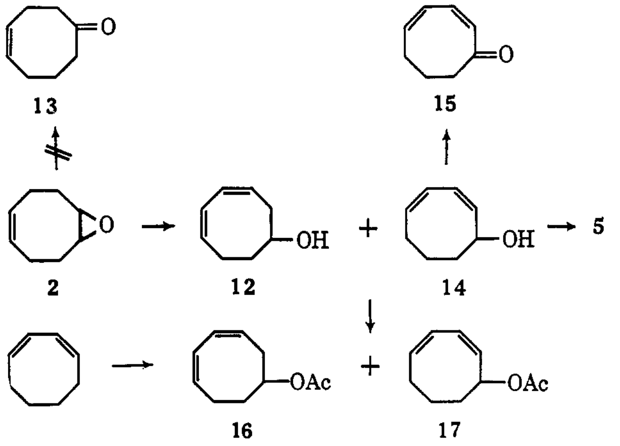
5,6-Epoxycyclooctene (**2**) was exposed to excess lithium diethylamide in refluxing ether for 2 days. Distillation of the resulting product yielded two fractions of widely differing boiling point. The lower boiling fraction was shown to contain 1,3,5-cyclooctatriene[9] along with varying quantities of the valence tautomers of this compound.[10] Careful investigation was not performed to establish this point, but it is likely that the latter materials are secondary products which are formed during the distillation and preparative gas chromatographic separation procedures. Preparative gas chromatography on the higher boiling fraction yielded two major components in roughly a 2:1 ratio. The first of these compounds was again recognized as 3-cyclooctenone (**5**). The other material was a monocyclic alcohol as indicated by hydroxyl absorption in the infrared and the appearance of four olefinic protons in the nmr spectrum. A conjugated diene system was shown to be present by ultraviolet absorption at 230 mμ (ϵ 6600).[11] Finally, an nmr double-resonance experiment demonstrated that the olefinic protons were not spin coupled to the proton on the hydroxyl-bearing carbon, thus allowing assignment of structure **12** to this rearrangement product.

The direct rearrangement of **2** to a ketone in a fashion analogous to that observed for saturated alicyclic epoxides should yield **13** (in the form of its lithium enolate) rather than the observed ketone **5**. The possibility of isomerization during the reaction was considered, but control experiments demonstrated that **13** was recovered unchanged from the reaction conditions, thus eliminating the possibility that **13** is an intermediate in the reaction.

At this point it was observed that the ratio of ketone to alcohol progressively increased from crude product, to distilled product, to gas chromatographically separated material. This information suggested the possibility of a thermal conversion of **12** to **5**, a transformation which was subsequently verified.

When the rearrangement of **2** was performed at room temperature, only 7 hr was required for complete utilization of the starting material. The crude product of this reaction showed a strong alcohol band but no carbonyl absorption in its infrared spectrum. Examination of this material by thin layer chromatography demonstrated the presence of two compounds of similar mobility in addition to some polymeric material. Distillation of the alcohol mixture at 55° (0.1 mm) separated the alcohols from the higher boiling materials accompanied by only a small amount of ketone formation. Heating the mixture to 180° for 1 hr, however, resulted in a relatively clean conversion to **5**. Spectroscopic examination of the rearrangement product indicated that the previously identified **12** was the more abundant component. Oxidation of the mixture with manganese dioxide gave a crude product which displayed infrared absorption indicative of a conjugated ketone at 6.04, 6.17, and 6.29 μ[12] and new ultraviolet absorption at 279 mμ (ϵ 4300)[13] in addition to the characteristics of the starting material. These observations suggest that the second component was the allylic dienol **14** and that the manganese dioxide oxidation had selectively converted this alcohol to dienone **15**. Confirming support for the proposed nature of the alcohol mixture was provided by acetylation of the crude alcohol mixture. This procedure gave a gas chromatographically inseparable mixture of acetates **16** and **17** (for details see the Experimental Section). Ultraviolet absorption at 228 mμ (ϵ 5900) assures that both of the major components of this mixture are conjugated dienes and hence only structures **16** and **17** are possible since the spectral data will not accommodate enol acetate isomers. A similar mixture of acetates was obtained by selenium dioxide oxidation of 1,3-cyclooctadiene in refluxing acetic anhydride. Apparently the thermal conditions of the selenium dioxide reaction were sufficient to cause isomerization of **17**, the probable primary oxidation product, to **16**. (See Chart II).

CHART II



With this information in hand the details of the base-promoted reaction of **2** can now be formulated. The initial step probably involves a β elimination that forms the nonconjugated dienol **18** (in the form of its lithium salt). A subsequent base-catalyzed isomerization converts this material substantially to the more stable mixture of conjugated dienols **12** and **14**. Presuming this explanation to be correct, **2** becomes the only medium-ring (C_7–C_{10}) epoxide thus far studied which has not generated at least some transannular insertion product. The prominence of insertion reactions found with this class of compounds has been attributed[1] to a combination of (a) the lack of proper conformations for β elimination, the common reaction pathway for most epoxides, and (b) the availability of transannular hydrogens which are held quite near the reactive carbon atom by the molecular framework. Examina-

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[9] A. C. Cope, A. C. Haven, Jr., F. L. Ramp, and E. R. Trumbull, *J. Am. Chem. Soc.*, **74**, 4867 (1952).

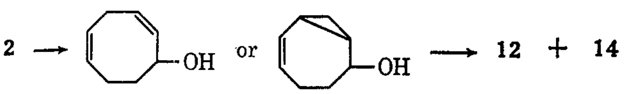
[10] W. R. Roth and B. Peltzer, *Ann.*, **685**, 56 (1965).

[11] Cyclooctadiene shows λ_{max} 228 mμ (ϵ 5600): A. C. Cope and L. L. Estes, Jr., *J. Am. Chem. Soc.*, **72**, 1128 (1950).

[12] R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966, pp 143–144, 162–163.

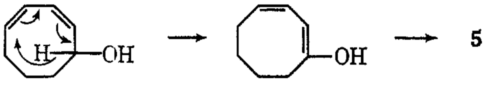
[13] Compare with H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1964, pp 213–217. It is difficult to predict the ultraviolet spectrum of **15** because of the conformational effects of the eight-membered ring on the chromophoric system.

tion of a Dreiding model of **2** suggests that in all of the relatively stable conformations there is a transannular hydrogen in reasonable proximity to the reactive center. The conformations with the necessary *trans*, coplanar arrangement of the important atoms for a normal β elimination have substantial nonbonded interaction between the interior 2- and 7-hydrogen atoms in a manner analogous to *cis*-cyclooctene oxide. However, the presence of the double bond in **2** reduces the congestion in the middle of the ring and possibly this increased flexibility aids the β elimination enough to make it the predominant reaction. In addition, the conformational picture is such that the stereoelectronic requirements for a *cis* β elimination[14] are easily met and the possibility of reaction by this pathway cannot be discounted. Finally, it may be that transannular insertion did obtain, but that the resulting product (**19**, as the lithium alkoxide) was isomerized to the observed dienol mixture under the reaction conditions. While the latter explanation is less appealing, a control experiment with **19** has not been performed to check on this point.



18 **19**

There may be some conversion of the **12**–**14** mixture to 3-cyclooctenone by the basic reaction medium, but most of this transformation is undoubtedly thermally induced and almost certainly involves 1,5-hydrogen migrations. Such changes allow interconversion of **12** and **14** (as well as **16** and **17**) and lead to **20**, the enol related to **5**, as illustrated below. Tautomerization of **20** irreversibly shifts the system in favor of **5** in accordance with the known properties of this species.[4b,15] Since the importance of 1,5-hydrogen migrations in diene systems was first recognized several years ago, there has been ample documentation of this process, particularly in medium-ring dienes.[16] Thus the witnessed transformation is well founded in precedent, although it does represent the first example of ketone formation resulting from a 1,5-hydrogen shift in a diene with an allylic hydroxyl.[17]



14 **20**

In summary neither **1** nor **2** has shown any evidence for carbenoid reactions involving addition to an intramolecular double bond in their base-induced decompositions. However, it should be noted that unfavorable geometrical features in the starting materials and the strained nature of the expected carbene addition products may have contributed substantially to this result. Consequently, such reactions are perhaps still to be expected under more propitious circumstances.

Experimental Section

General.—Nmr spectra were recorded on a Varian A-60 spectrometer using carbon tetrachloride as solvent. The data are given in parts per million downfield from internal standard tetramethylsilane. Gas chromatography (gc) was performed on Aerograph A600 (analytical) and A700 (preparative) instruments. The analytical column was 5 ft × $^1/_8$ in. of 15% Carbowax 20 M; the preparative column was 20 ft × $^3/_8$ in. with 20% of the same liquid phase. Percentage composition data were obtained by peak areas and are uncorrected. Microanalyses were performed by the Midwestern Microanalytical Laboratories.

Rearrangement of 3,4-Epoxycyclooctene.[15]—The isomerization of 5.30 g of **1** in 300 ml of ether at reflux temperatures for 22 hr was performed and worked up according to the previously described procedure.[1] After distillation there was obtained 3.75 g (71%) of a light yellow oil, bp 93–96° (20 mm), which contained two components in an 8:92 ratio by gc analysis. Preparative gc provided pure samples of the two materials for identification. The minor component was 3-cyclooctenone (**5**) as demonstrated by spectral comparison with an authentic sample.[4] The major material was a colorless liquid assigned as *cis*-bicyclo[3.3.0]oct-7-en-*endo*-2-ol (**6**): infrared 2.9, 3.26 μ; nmr two-proton multiplet at δ 5.74 ($CH{=}CH$), one-proton multiplet at 4.16 ($CHOH$), and the remaining nine protons spread out from 3.5 to 1.0. A concentration study of the hydroxyl region of the infrared spectrum in carbon tetrachloride was performed on a Perkin-Elmer Model 137 G spectrometer. At concentrations down to 0.058 *m* two hydroxyl peaks ($\Delta\nu$ = 33 cm^{-1}) were observed, the relative intensities ($\sim$1:1) of which did not change as a function of concentration, thus indicating a hydrogen bond between the hydroxyl group and the π electrons of the double bond.[18]

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.11; H, 9.76.

In a second experiment with a 2-day reflux period there was obtained an 88% yield of product which contained about 4% of a third product. This material was a bicyclic alcohol with an nmr spectrum very similar to that of **6**. It was shown not to be **9** by infrared comparison and is probably the double-bond isomer, *cis*-bicyclo[3.3.0]-oct-6-en-*endo*-2-ol, formed from **6** under the reaction conditions.

Oxidation of 6.—To an ice-cold solution of 137 mg of gc-purified alcohol in 10 ml of acetone was added dropwise with stirring 0.5 ml of 6 *N* chromic acid solution. The reaction mixture was stirred until the acetone layer became clear, poured into water, and extracted three times with ether. The combined extracts were washed with water, saturated sodium bicarbonate solution, and water again. After drying over anhydrous magnesium sulfate, removal of the solvent gave 85 mg of crude **7**. The infrared spectrum of this material was superimposable with that of an authentic sample.[6] Additional quantities of **7** were obtained by chromic acid oxidation of the rearrangement mixture. Partial oxidation of **6** was also effected by active manganese dioxide.[19] Compound **7** showed the following spectral properties: infrared 3.24 and 5.75 μ; nmr a two-proton multiplet at δ 5.55 ($CH{=}CH$) and a complex pattern from 1.0 to 3.3; ultraviolet (95% ethanol) λ_{max} 298 mμ (ϵ 89).

Hydrogenation of the Rearrangement Product of 1.—A solution of 1.24 g of the rearrangement mixture in 50 ml of methanol was hydrogenated at atmospheric pressure using 100 mg of Adams catalyst. The catalyst was removed by filtration and the filtrate was poured into water and extracted three times with pentane. After drying over anhydrous magnesium sulfate the solvent was removed from the extracts and the residue was distilled to give 0.98 g of product. Two major products were obtained by preparative gc and shown to be *cis*-2-bicyclo[3.3.0]-octanone (**8**) and *endo*,*cis*-2-bicyclo[3.3.0]octanol (**4**) by spectral comparison with authentic samples.[2] While **4** was the major product under these conditions, a similar reaction using 5% palladium on carbon gave a 2:1 ratio of **8** to **4**. No change oc-

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[14] C. H. DePuy, G. F. Morris, J. S. Smith, and R. J. Smat, *J. Am. Chem. Soc.*, **87**, 2421 (1965); N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *ibid.*, **85**, 3199 (1963); J. Zavada, M. Svoboda, and J. Sicher, *Tetrahedron Letters*, 1627 (1966).

[15] Equilibration of the double bond in 2- and 3-cyclooctenones under various conditions was considered by Heap and Whitham.[4b]

[16] For a leading reference, see D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Letters*, 999 (1966).

[17] See, however, R. L. Cargill and D. M. Pond, *J. Org. Chem.*, **31**, 2414 (1966), for an example probably involving such an intermediate compound in a pyrolytic conversion.

[18] For a comprehensive review of hydrogen-bonding studies utilizing infrared spectroscopy, see M. Tichy, *Advan. Org. Chem.*, **5**, 115 (1965).

[19] R. M. Evans, *Quart. Rev.* (London), **13**, 61 (1959).

curred when **6** was stirred with 5% palladium on carbon in methanol in the absence of hydrogen. Likewise **4** was unchanged under these conditions or in a similar reaction with a hydrogen atmosphere.

Rearrangement of 5,6-Epoxycyclooctene.[20]—The reaction was carried out on 5.0 g of **2** in 300 ml of ether at room temperature for 7 hr, at which time thin layer chromatography (tlc) indicated complete utilization of starting material. After work-up the crude product showed a strong hydroxyl but no carbonyl by infrared examination. Tlc revealed two spots in addition to polymeric material at the origin. Distillation gave 1.6 g of colorless oil, bp 55° (0.1 mm), which now contained a small amount of ketone **5** as demonstrated by a small carbonyl band in the infrared and comparative tlc. This product displayed ultraviolet absorption (95% ethanol) with λ_{max} 228 mμ (ε ~5000).[11]

A 50-mg sample of the alcohol mixture enriched in the minor component by column chromatography on silica gel was stirred for 16 hr at room temperature with 0.6 g of active manganese dioxide[19] in 10 ml of pentane. Removal of the solid by filtration and evaporation of the solvent gave 47 mg of crude product. In addition to hydroxyl absorption the infrared indicated a strong conjugated carbonyl (6.04 μ) and a conjugated double bond system (6.17 and 6.29 μ). The ultraviolet spectrum (95% ethanol) of the crude product showed absorption at 228 mμ (ε 3700) and 279 mμ (ε 4300). These data are in accord with a mixture of **12** and **15** with the former predominating. The original alcohol mixture thus probably contained a similar ratio of **12** and **14**.[21]

A rearrangement of 5.0 g of **2** in 600 ml of ether for 2 days gave 0.95 g of a low-boiling fraction and 2.18 g of a fraction boiling at 105–110° (20 mm). The low-boiling fraction contained 1,3,5-cyclooctatriene[9] as the major product along with variable amounts of the valence tautomers of this hydrocarbon which are probably formed during the gc isolation procedure. Preparative gc of the high-boiling fraction yielded 3-cyclooctenone and 3,5-cyclooctadienol (**12**) in roughly a 2:1 ratio. Compound **12** showed the following spectroscopic properties: infrared 3.0 and 3.30 μ; ultraviolet (95% ethanol) λ_{max} 230 mμ (ε 6600); nmr a complex, four-proton signal at δ 5.6 (olefinic hydrogens), one proton at 3.9 (O*H*), a one-proton quintet at 3.73 (C*H*OH), four allylic protons as a complex multiplet at 2.3, and two methylene protons as a complex multiplet at 1.7. A double-resonance experiment demonstrated that there was no coupling between the olefinic protons and the hydrogen adjacent to the hydroxyl group.

Nmr comparison indicated that the preponderant alcohol in the mixture obtained in the first experiment described above was **12**.

Thermal Rearrangement of the Dienol Mixture.—Heating 1.0 g of the mixture of **12** and **14** to 180° for 1 hr resulted in almost complete disappearance of hydroxyl absorption in the infrared. Distillation gave 0.5 g of pure 3-cyclooctenone.

Attempted Base Isomerization of 4-Cyclooctenone.—When 1.0 g of **13** was treated with lithium diethylamide in 75 ml of ether at reflux temperature for 20 hr, there was obtained 0.68 g of distilled product containing essentially only starting material. In a similar experiment run in the presence of 1.0 g of **2** essentially all of the 4-cyclooctenone was recovered.

Acetylation of the Rearrangement Product of 2.—A room-temperature rearrangement was carried out on 2.5 g of **2** as described above. The crude product was heated with 8 ml of acetic anhydride and 20 ml of pyridine on a steam bath for 2 hr. The reaction mixture was poured into ice–water containing 20 ml of concentrated hydrochloric acid and extracted with three portions of ether. The combined extracts were washed with sodium bicarbonate solution and water and dried over anhydrous magnesium sulfate. Removal of the solvent and distillation gave 0.55 g of an oil, bp 68–76° (7 mm) which showed three peaks in the ratio 91:3:6. The major peak was isolated by preparative gc: infrared 3.30, 5.76, 6.00, 6.13, and 8.1 μ; ultraviolet (95% ethanol) λ_{max} 228 mμ (ε 5900). The nmr spectrum of this material showed complex multiplets at δ 5.7, 4.8, and 2.0 with a sharp singlet at 1.96. However, the integral of the δ 4.8 peak (C*H*OAc) was less than one proton relative to the rest of the spectrum. This suggested that the material was a mixture of **16** and **17**[21] and that the proton on the acetoxyl-bearing carbon of **17** was shifted downfield into the region of the olefinic protons. A lithium aluminum hydride reduction was performed on gc-purified material and the crude alcohol subjected to tlc examination which revealed two spots of similar intensity and mobility. The infrared spectrum of the crude product was essentially identical with that of the rearrangement mixture from **2**.

Selenium Dioxide Oxidation of 1,3-Cyclooctadiene.—A mixture of 10.0 g of 1,3-cyclooctadiene, 10.0 g of freshly sublimed selenium dioxide, and 60 ml of acetic anhydride was heated to reflux overnight. The reaction mixture was cooled and poured into water, and the acetic acid formed was neutralized with sodium carbonate and the resulting mixture was steam distilled. The distillate was extracted twice with ether and the extracts were dried over anhydrous magnesium sulfate. After removal of the solvent through a Vigreux column the residue was distilled to give 4.32 g (31%) of product, bp 108° (15 mm), containing more than 90% of a major gc peak. A pure sample of this material was isolated by gc. It was spectroscopically identical with the major product obtained by acetylation of the crude rearrangement product as described above.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.59; H, 8.55.

Lithium aluminum hydride reduction of this acetate followed by tlc of the crude alcohol again indicated the presence of two major materials of similar mobility. The infrared spectrum was also very similar to that of the alcohol mixture from **2**.

Registry No.—**1**, 6690-12-6; **2**, 637-90-1; **6**, 10095-77-9; **7**, 10095-78-0; **12**, 10095-79-1; **15**, 10095-80-4; **16**, 10095-81-5; **17**, 10095-82-6.

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[20] The preparation of this material will be described in a forthcoming paper from these laboratories.

[21] A. C. Cope, S. Moon, C. H. Park, and G. L. Woo, *J. Am. Chem. Soc.*, **84**, 4865 (1962).