Base-Promoted Reactions of Epoxides. VI. Bicyclo[2.2.1]heptene and Bicyclo[2.2.2]octene Oxides[1,2a]

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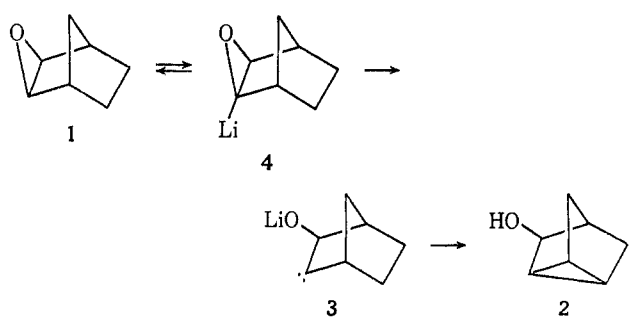
The details of the previously observed lithium diethylamide isomerization of 2,3-epoxybicyclo[2.2.1]heptane to nortricyclanol have been examined. By deuterium labeling methods, it has been shown that reversible metalation occurs at the epoxide ring and that base attack does not remove the exo hydrogens of the transannular bridge. These observations support a carbenoid mechanism for the rearrangement. The *endo*-5-methyl derivative **5** is transformed into the analogous tricyclic alcohol **7**, whereas epoxide **6**, with both transannular endo positions blocked with methyl groups, isomerizes to bicyclic ketone **9**. Bornylene oxide gives camphor, epicamphor, and tricyclic alcohols **13** and **14**. 2,3-Epoxybicyclo[2.2.2]octane gives ketone **19** along with minor amounts of tricyclic alcohol **20**. 2,3-Epoxybicyclo[3.3.0]octane yields allylic alcohol **25** as well as lesser amounts of ketones **23** and **24**. These results are used to outline the scope of the base-promoted isomerization of epoxides as a source of products derived from carbenoid insertion into transannular C–H bonds.

In connection with our interest in carbenoid reactions of epoxides,[3] we have reported on the base isomerization of *exo*-2,3-epoxybicyclo[2.2.1]heptane (**1**), which was found to rearrange smoothly to nortricyclanol (**2**).[4] The suggested mechanistic pathway for this transformation invoked carbene **3** or its carbenoid[5] equivalent as a key intermediate.[6] In the present work further aspects of the strong-base isomerization of 2,3-epoxybicyclo[2.2.1]heptanes and related epoxides have been examined.



1 4 3 2

Support for the proposed α-elimination–insertion reaction over a γ-elimination route was obtained by deuterium labeling techniques. Epoxide **1** specifically labeled with deuterium at the exo 5,6 positions was prepared from the corresponding olefin.[7] Isomerization of this material with lithium diethylamide yielded tricyclic alcohol **2** which retained all of the deuterium label as evidenced by nmr and mass spectral analysis. This result clearly demonstrates that γ elimination involving the more accessible exo hydrogens of the transannular carbons does not take place.

Direct evidence for metalation at the epoxide ring was secured by performing the isomerization in the presence of an excess of *N*,*N*-dideuteriocyclohexylamine. The reaction was halted prior to completion, and both the starting material and the product were examined for deuterium incorporation by nmr. In this fashion it was ascertained that recovered **1** had exchanged 83% of its epoxy protons while 69% deuterium was present at the carbinol position of alcohol **2**. This experiment shows unequivocally that the organolithium species **4** is generated reversibly during the course of the rearrangement, and it is most reasonable to assume that **4** is an intermediate on the mechanistic pathway to tricyclic alcohol **2**.[8] Taken together then, these experiments provide strong support for the carbenoid mechanism described above.

In order to determine if insertion could occur into a C–H bond more remote from the reactive center or possibly into a C–C bond,[9] methyl-substituted epoxides **5** and **6** were prepared and subjected to base treatment. The epoxides were synthesized by peracid oxidation of the corresponding bicyclo[2.2.1]heptenes of established stereochemistry and can be assigned the exo stereochemistry at the epoxy ring with confidence.[10] The monomethyl derivative **5** was isomerized to tricyclic alcohol **7** and two unidentified minor products. The structure of **7** follows from its spectroscopic properties and conversion to tricyclanone **8** by chromic acid oxidation.[11] Thus, the major reaction for **5** is analogous to that of **1**. Selective reaction at one of the epoxide carbons is in agreement with reversible metalation and selective insertion into the single C–H bond in the requisite position for reaction. This particular possibility is, of course, not available to the dimethyl derivative **6** in which both transannular endo hydrogens have been replaced by methyl groups. In this instance an entirely different type of transformation led to bicyclic

(1) Part V: J. K. Crandall and L. C. Lin, *J. Org. Chem.*, **33**, 2375 (1968).

(2) (a) Supported by a research grant from the National Science Foundation; (b) Alfred P. Sloan Research Fellow, 1968–1970; (c) National Science Foundation Undergraduate Research Participant.

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

(4) J. K. Crandall, *J. Org. Chem.*, **29**, 2830 (1964).

(5) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **6**, 41 (1967).

(6) Independent examination of the simple carbene of this system has shown just this behavior: J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959); R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *J. Amer. Chem. Soc.*, **89**, 1442 (1967); W. Reusch, M. W. DiCarlo, and L. Traynor, *J. Org. Chem.*, **26**, 1711 (1961).

(7) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Amer. Chem. Soc.*, **87**, 2596 (1965).

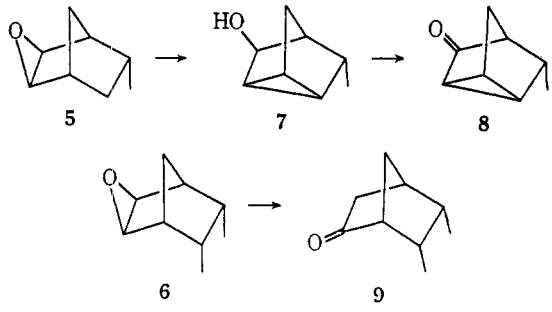
(8) The possibility that a reactive species may be formed but not lie along the reaction pathway has been emphasized: R. Breslow, *Tetrahedron Lett.*, 399 (1964). Irrelevant exchange of the epoxide hydrogens would allow for γ elimination with specific removal of an endo transannular proton by the base as a possible mechanism. See A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 3915 (1967).

(9) Such a rearrangement has been reported for the copper-catalyzed decomposition of a diazo ketone of this ring system: P. Yates and S. Danishefsky, *ibid.*, **84**, 879 (1962).

(10) The endo methyl substituents should increase the preference for exo epoxidation: H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963).

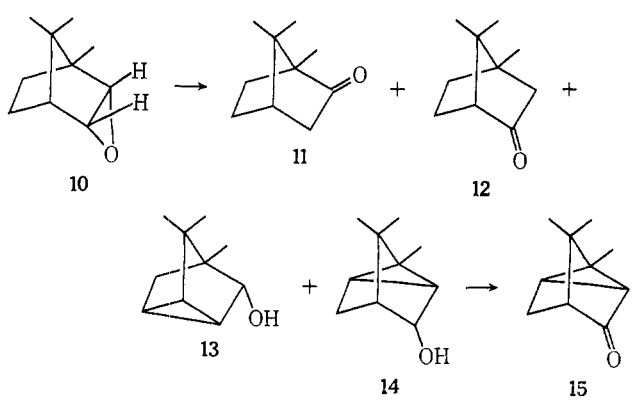
(11) B. C. Henshaw, D. W. Rome, and B. L. Johnson, *Tetrahedron Lett.*, 6049 (1968).

ketone **9** as the sole product. Similar base isomerizations of epoxides to ketones have been observed previously.[3] No evidence was obtained for products resulting from transannular insertion into the methyl C–H bonds or into the C–CH_3 bond. Failure to observe such products suggests that there may be severe restrictions on the insertion reaction.[12]



5 7 8 6 9

Attention was next focused on the influence of the epoxide stereochemistry by examining the reaction of bornylene oxide (**10**), a compound known to possess an endo epoxy group.[13] Four products were formed in the ratio of 41:33:12:16 under the usual reaction conditions. The first three of these materials were identified as camphor (**11**), epicamphor (**12**), and tricyclanol **13** by comparison with authentic samples. The remaining compound was assigned structure **14** on the basis of its spectroscopic properties and those of the corresponding ketone **15** which was obtained by chromic acid oxidation. Thus, transannular insertion can also ensue from base isomerization of an endo epoxide, although the major rearrangement pathway results in conversion of the epoxy function into a carbonyl group. Consequently, it is concluded that, although the exo configuration of the epoxide facilitates transannular reaction relative to ketone formation, it is not an absolute requirement in order for this transformation to proceed. This result has some bearing on earlier work[3a,14] with flexible systems, for example, cycloheptene oxide. It was suggested[3a] that the *observed specificity* for reaction through a transition state array as indicated in **16** (backside attack) over that of **17** (frontside attack) could have arisen owing to a stereoelectronic requirement for the former.[15] The present results appear to rule out such an argument, since **10** can only give tricyclic alcohols by way of a geometry analogous to **17**.



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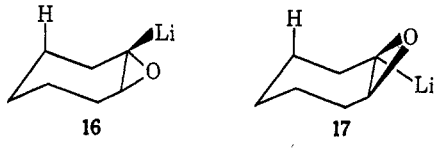
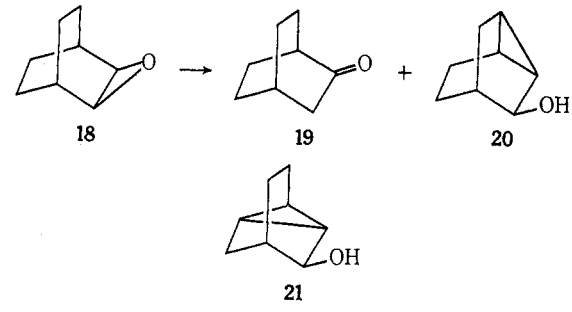


16 17

Thus, it seems that an alternate explanation[3a] based on conformational interactions in the respective transition states best accounts for the preference for **16** in flexible systems.

Reaction of 2,3-epoxybicyclo[2.2.2]octane[16] (**18**) also gave mainly the corresponding ketone **19**.[17] However, about 5% of *endo*-tricyclo[2.2.2.$0^{2,6}$]octan-3-ol[18] (**20**) was also isolated from the reaction mixture. None of the epimeric exo alcohol[18] (**21**) was found, although as little as 0.5% would have been detected. Interestingly, the less-strained bicyclic skeleton of **18** leads to less transannular reaction than its lower homolog **1**. A similar but less dramatic difference in reaction propensities is observed for the simple carbenes of these systems.[6,19] This effect is almost certainly a result of the greater distance between the reactive center and the transannular C–H bond.[20] A second point of concern is the preference for the production of alcohol **20** over **21**. In the more symmetrical bicyclo[2.2.2]octane system where both modes of transannular insertion can occur without substantial bias (the oxygen stereochemistry is the only important difference), the favored process is that corresponding to **17**, the unfavorable one for cycloheptene oxide. This observation confirms the conclusions drawn above and, in fact, points toward a preference for the "frontside" process when other things are equal.



18 19 20 21

Finally, the isomerization of *exo*-2,3-epoxybicyclo[3.3.0]octane[21] (**22**) yielded ketones **23** and **24** in addition to allylic alcohol **25** (14:10:76 ratio). The ketones were identical with authentic samples;[22] **25** was converted to the known saturated alcohol[23] for comparison. Noteworthy here is the absence of carbenoid

(12) A recent report notes a substantial predominance for reaction with a methine position (exo substituent) over a methylene group: E. J. Corey and R. S. Glass, *J. Amer. Chem. Soc.*, **89**, 2600 (1967).

(13) A. Suzuki, M. Miki, and M. Itoh, *Tetrahedron*, **23**, 3621 (1967).

(14) A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev. Chem. Soc.*, **20**, 119 (1966).

(15) This discussion assumes that C–H insertion is concerted with α elimination, a situation which appears to be required by the available data.[3,14]

(16) H. M. Walborsky and D. F. Loncrini, *J. Amer. Chem. Soc.*, **76**, 5396 (1954).

(17) O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **478**, 137 (1930); R. Zbinden and H. K. Hall, *J. Amer. Chem. Soc.*, **82**, 1215 (1960).

(18) N. A. LeBel and J. E. Huber, *ibid.*, **85**, 3193 (1963).

(19) C. A. Grob and J. Hostynek, *Helv. Chim. Acta*, **46**, 1676 (1963).

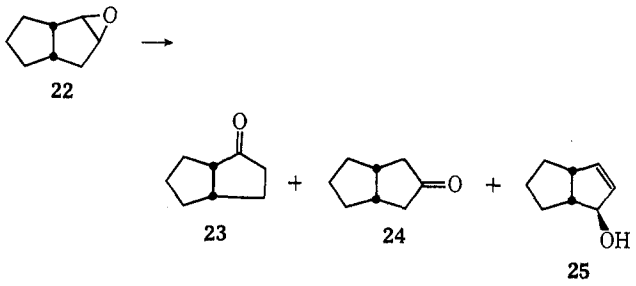
(20) J. F. Chiang, C. F. Wilcox, and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 3149 (1968); O. Ermer and J. D. Dunitz, *Chem. Commun.*, 567 (1968).

(21) A. C. Cope, S. Moon, and C. H. Park, *J. Amer. Chem. Soc.*, **84**, 4850 (1962).

(22) H. C. Brown and W. J. Hammar, *ibid.*, **89**, 6378 (1967).

(23) A. C. Cope, H. H. Lee, and H. E. Petree, *ibid.*, **80**, 2849 (1958).

insertion products paralleling the reaction of the unadorned carbene.[24] The major product is derived from β elimination, normally an important pathway where not precluded by structural features.[3,25]



In summary, while the C–H insertion reaction proceeds cleanly in favorable cases, it appears to be restricted in scope to molecules with special geometric features. A guide for predicting where this reaction mode will obtain is the behavior of the corresponding carbene generated by conventional means. In instances where transannular reactions are not effective and β elimination is impossible, base rearrangement of epoxides produces isomeric ketones. This transformation has been discussed previously,[3] but experimental evidence bearing on the mechanism of this interesting rearrangement is unavailable as yet.

Experimental Section

General.—Nuclear magnetic resonance (nmr) spectra were taken in carbon tetrachloride solution with tetramethylsilane as internal standard with Varian A-60 or HA-100 spectrometers. Infrared spectra (ir) were obtained with Perkin–Elmer Model 137 and 137G Infracord spectrophotometers on neat samples, unless otherwise noted. Gas chromatography (glpc) was performed on Aerograph A600, A1200 (analytical, hydrogen flame detector), and A700 (preparative) instruments. Analytical columns were 10 ft × 3/8 in. 15% Carbowax 20M on 60–80 Chromosorb W; preparative columns were 20 ft × 3/8 in. 15% SE-30 or 20 ft × 3/8 in. 15% Carbowax on 60–80 Chromosorb W. Percentage composition data were estimated by peak areas and are uncorrected. Anhydrous magnesium sulfate was used for all drying operations. Microanalyses were performed by Midwest Microlabs, Inc., Indianapolis, Ind., and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Preparation of Epoxides.—Epoxides were prepared by the buffered peracetic acid method.[3] The following epoxides were prepared by this method.

2,3-Epoxy-*cis*-bicyclo[3.3.0]octane (90% yield) was shown by glpc to contain 13% of the endo and 87% of the exo epoxide.[21] Separation by preparative glpc gave the pure endo isomer [ir 9.6, 9.8, 10.9, and 11.8 μ; 100-MHz nmr δ 1.1–2.2 (m, 8), 2.41 (m, 2, bridgehead CH), 3.22 (broad s, 1, epoxide CH), and 3.31 (broad s, 1, epoxide CH)] and the pure exo isomer (**22**) [ir 9.8, 9.9, 10.8, and 11.9 μ; 100-MHz nmr δ 1.1–1.9 (m, 7), 2.0–2.7 (m, 3), 3.12 (d, 1, J = 2 Hz, epoxide CH), and 3.28 (t, 1, J = 2 Hz, epoxide CH)].

2,3-Epoxybicyclo[2.2.2]octane (**18**) was prepared in 82% yield: ir (CCl_4) 8.1, 10.5, 11.6, and 11.8 μ; nmr δ 1.4–1.8 (m, 8), 2.04 (m, 2, bridgehead CH), and 3.05 (broad s, 2, epoxide CH).[16]

exo-2,3-Epoxy-*endo*-*cis*-5,6-dimethylbicyclo[2.2.1]heptane (**6**) was prepared from the corresponding olefin[26] (71% yield): bp 107–112° (20 mm); mp 75–77°; ir (CCl_4) 3.27, 9.9, and 11.7 μ; nmr δ 0.90 (d, 6, CH_3), 0.97 (broadened AB quartet, 2, $\Delta\nu$ = 37 Hz, J = 9 Hz, CH_2), 2.2 (m, 2), 2.25 (m, 2), and 3.04 (s, 2, epoxide CH).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.5; H, 10.2.

exo-2,3-Epoxy-*endo*-5-methylbicyclo[2.2.1]heptane (**5**) was prepared from *endo*-5-methylbicyclo[2.2.1]hept-2-ene in 87% yield: bp 88–90° (100 mm); mp 50.5–52°; ir 3.27, 9.9, and 11.7 μ; nmr δ 0.5–2.0 (m, 5), 1.02 (d, 3, J = 7 Hz, CH_3), 2.21, 2.35 (broad s, 2, bridgehead protons), and 3.02 (m, epoxide CH).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.1; H, 9.6.

***endo*-5-Methylbicyclo[2.2.1]hept-2-ene.**—A modification of the literature procedure was utilized.[27] Ethyl bicyclo[2.2.1]hept-2-ene-*endo*-5-carboxylate was obtained from the highly stereoselective aluminum chloride catalyzed Diels–Alder reaction of ethyl acrylate and cyclopentadiene.[28] This was reduced with lithium aluminum hydride to the alcohol, converted to the crystalline *p*-toluenesulfonate (mp 42–44°), and reduced again with lithium aluminum hydride to give the desired olefin.[27]

Bicyclo[2.2.2]oct-2-ene.—The decarboxylation procedure of Cimarusti and Wolinsky[29] was used. After oxygen was bubbled through 20 ml of pyridine (distilled from BaO) for 20 min, 2.00 g of dried bicyclo[2.2.2]octane-2,3-dicarboxylic acid[17] and 15.0 g of lead tetraacetate (dried over KOH *in vacuo*) were added, and the flask was immersed in an oil bath maintained at 65°. The mechanical stirrer was started and after 2 min a vigorous evolution of carbon dioxide was observed. The mixture was heated for 5 min after all evidence of gas evolution had ceased, then removed from the bath, and cooled to room temperature. The mixture was poured into excess dilute nitric acid and extracted with ether. The ether was washed with saturated sodium bicarbonate solution, saturated salt solution, and dried. Removal of the solvent gave a light yellow oil which was placed on 30 g of Merck neutral alumina and eluted with pentane to yield 0.66 g (60%) of bicyclo[2.2.2]octene as a volatile white solid, mp 109–111° (lit.[30] 111–112°).

Bornylene Oxide (10).—The epoxide was prepared from α-pinene following the literature procedure, mp 169–171° (lit.[31] 170–171°).

***exo*-2,3-Epoxybicyclo[2.2.1]heptane-*exo*-5,6-d_2.**—The catalytic reduction of 46 g of norbornadiene with deuterium gas was performed according to the procedure of Arnold.[7] The crude product was fractionated on a spinning-band column to give a 9.5-g fraction boiling at 95–101°. Eight grams of this material was epoxidized by the standard procedure, the solvent was removed by distillation through a Vigreux column, and the residue was sublimed to give 2.1 g of volatile epoxide. A pure sample was obtained by preparative glpc. The nmr spectrum integrated for two less protons in the δ 1.0–1.6 ppm region when compared with the spectrum of undeuterated material but was otherwise identical. Analysis by mass spectrometry indicated the following distribution of deuterated species: 4.0% d_1, 94.6% d_2, and 1.4% d_3.[32]

Rearrangement of *exo*-2,3-Epoxybicyclo[2.2.1]heptane-*exo*-5,6-d_2.—The crude product from the previous experiment (1.5 g) was treated with lithium diethylamide according to the usual procedure to yield 0.85 g of a white solid which was purified by preparative glpc to give nortricyclanol (**2**), mp 109–110°. The nmr spectrum was identical with that of an authentic sample except for changes in the δ 1.0–1.5 ppm region which integrated for four protons rather than six. Mass spectral examination of this material showed the following distribution of deuterated species: 4% d_1, 95% d_2, and 1% d_3.[32]

Dideuteriocyclohexylamine.—Cyclohexylamine (270 ml) and deuterium oxide (108 ml) were stirred under a nitrogen atmosphere for 3 hr, 200 ml of benzene was added, and the benzene–water azeotrope was removed by distillation. This procedure was repeated twice more. The remaining benzene was removed and the product purified by distillation through a spinning-band column to yield 250 ml (92%) of a colorless liquid, bp 132–133°.

(24) W. Kirmse and L. Ruetz, *Justus Liebigs Ann. Chem.*, **726**, 36 (1969).

(25) B. Rickborn and R. P. Thummel, *J. Org. Chem.*, **34**, 3583 (1969); *J. Amer. Chem. Soc.*, **92**, 2064 (1970).

(26) H. N. Miller and K. W. Greenlee, *J. Org. Chem.*, **26**, 3734 (1961).

(27) J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Amer. Chem. Soc.*, **83**, 3986 (1961).

(28) T. Inukai and T. Kojima, *J. Org. Chem.*, **31**, 2032 (1966).

(29) C. M. Cimarusti and J. Wolinsky, *J. Amer. Chem. Soc.*, **90**, 113 (1968).

(30) K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **514**, 1 (1934); K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964).

(31) L. Borowiecki and Y. C. Bessiere, *Bull. Chim. Soc. Fr.*, 2364 (1967); M. Vilkas, *ibid.*, 1401 (1959).

(32) We thank Drs. P. J. Kropp and J. H. Collins of Procter and Gamble for this measurement.

Nmr integration indicated 93% replacement of the amino hydrogens.

Rearrangement of Norbornene Oxide.—To a predried flask cooled to 0° under a nitrogen atmosphere was added 9.2 g of dideuteriocyclohexylamine in 50 ml of benzene and 3.75 ml of 1.6 *M* *n*-butyllithium solution in hexane. After stirring for 30 min, the ice bath was removed, a solution of 1.0 g of norbornene oxide in 10 ml of benzene was added, and the reaction mixture was heated to reflux for 12 hr. The mixture was cooled and poured into water, the layers were separated, and the aqueous layer was extracted with ether. The organic portions were washed with 1 *N* hydrochloric acid, saturated sodium bicarbonate solution, water, and dried. Glpc analysis showed that 60% rearrangement to nortricyclanol had occurred. The remaining starting material and rearranged product were collected by glpc. The deuterium content of recovered norbornene oxide was determined by nmr which showed a slightly simplified spectrum and integrated for 17% hydrogen in the epoxide ring. The rearranged product, nortricyclanol, was similarly shown to contain 31% hydrogen at the carbinol position.

A model experiment with dideuterioamine alone showed that no hydrogens were exchanged on norbornene oxide. Similarly, lithium deuteriocyclohexylamide did not exchange either the carbinol or cyclopropyl hydrogens of nortricyclanol.

General Procedure for Rearrangement of Epoxides by Lithium Diethylamide.—To a predried flask cooled to 0° under a nitrogen atmosphere was added 2.5 equiv of diethylamine in anhydrous ether and 2.5 equiv of 1.6 *N* *n*-butyllithium in hexane solution. After stirring for 15 min, a solution of 1 equiv of the appropriate epoxide in anhydrous ether was added, the ice-bath was removed, and the solution was heated to reflux for the specified time or until the starting material was consumed. The reaction mixture was cooled and quenched carefully with water, and the layers were separated. The aqueous layer was extracted with ether, and the combined organic layers were washed with 1 *N* hydrochloric acid, saturated sodium bicarbonate solution, water, and dried. The solvent was removed by distillation and the residue purified by distillation. If the product was a mixture, further purification was performed by preparative glpc.

Rearrangement of 5.—The rearrangement was carried out on 1.0 g of **5** in benzene. Glpc examination of the crude product showed one major product accounting for 95% of the volatile material. Two minor peaks constituted the remainder but were not separated or identified other than noting absorption for OH and C=O (5.73 μ, probably bicyclo[2.2.1]heptanone)[33] in the ir. The major product was collected by preparative glpc and assigned as *syn*-5-methyltricyclo[2.2.1.$0^{2,6}$]heptan-*anti*-3-ol (**7**):[11] ir 3.0, 3.3, 9.2, 9.3, 9.6, 9.7, 12.3, and 12.4 μ; nmr δ 0.92 (d, 3, CH_3), 1.0–2.0 (m, 7), 4.10 (broad s, 1, CHOH), and 4.39 (s, 1, OH).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.1; H, 10.0.

Oxidation with chromic acid in acetone gave *syn*-5-methyltricyclo[2.2.1.$0^{2,6}$]heptan-3-one:[11] ir 5.68, 8.7, 8.9, 11.6, and 11.9 μ; 2,4-DNP, mp 190.5–191° (lit.[11] mp 192–194°).

Rearrangement of 6.—**6** (1 g) was treated in the usual fashion in 50 ml of ether. The crude product (0.91 g) was shown to be greater than 95% one product by glpc. Sublimation gave a pure sample assigned as *endo-cis*-5,6-dimethylbicyclo[2.2.1]heptan-2-one (**9**): mp 65–65.5°; ir (CCl_4) 5.73 μ;[33] nmr δ 0.78 (d, 3), 0.89 (d, 3), 1.66 (s, 2), 1.86 (m, 2), and 2.30 (m, 4).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.3; H, 10.1.

Rearrangement of 10.—Refluxing 1.33 g of **10** in 40 ml of benzene for 12 hr according to the normal procedure gave 1.05 g (79%) of a yellow oil. Glpc analysis indicated the presence of four components which were isolated by preparative glpc in a ratio of 41:33:12:14. The two major components were identified as camphor (**11**) and epicamphor (**12**), respectively, by comparison with authentic samples.

The third product (12%) was identified as *endo*-isocyclanol (**13**) by comparison with an authentic sample:[34] 100-MHz nmr δ 0.79 (s, 3), 0.81 (s, 6), 1.10 (m, 3), 1.47 (AB quartet, 2, $\Delta\nu$ = 30 Hz, J = 11 Hz), 3.06 (s, 1, OH), and 3.70 (s, 1, CHOH).

The fourth product (14%) was assigned as *endo*-1,7,7-trimethyltricyclo[2.2.1.$0^{2,6}$]heptan-3-ol (**14**): mp 56–58°; ir (CCl_4) 2.76, 3.00, 3.28 (cyclopropyl CH),[35] and 9.6 μ (broad); 100-MHz nmr δ 0.84 (s, 3), 0.90 (s, 3), 1.00 (s, 3), 1.30 (m, 3), 1.68 (broad s, 2), 2.07 (s, 1, OH), and 4.12 (t, 1, J = 2 Hz, CHOH).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.2; H, 10.9.

When the same reaction was conducted at room temperature for 12 hr, glpc analysis indicated the same four products were formed in a ratio of 35:26:24:15.

Oxidation of 14.—To an ice-cold solution of 70 mg of glpc purified **14** in 10 ml of acetone was added dropwise with stirring 1.6 ml of 0.67 *N* chromic solution. The reaction mixture was stirred until the acetone layer became clear, poured into water, and extracted with ether. The combined extracts were washed with water, saturated sodium bicarbonate solution, water, and dried. Distillation of the solvent gave 55 mg of crude solid. Isolation by preparative glpc gave 1,7,7-trimethyltricyclo[2.2.1.$0^{2,6}$]heptan-3-one (**15**) as a white solid: mp 97.5–100°; ir (CCl_4) 5.68 μ;[33] 100-MHz nmr δ 0.97 (s, 6), 1.00 (s, 1), 1.12 (s, 3), 1.31 (s, 1), and 1.5–2.0 (m, 3).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.8; H, 9.2.

Rearrangement of 18.—Isomerization of 1.00 g of **18** in refluxing ether for 20 hr gave 0.95 g (95%) of a yellow solid. Analysis by glpc indicated two products in a ratio of 95:5. Column chromatography using 50 g of Merck neutral alumina (activity I) and pentane–ether as eluent separated the two components easily. The major product was identified as bicyclo[2.2.2]-octan-2-one (**19**): mp 177–178° (lit. 178–179°); ir compares with the published spectra;[17] nmr δ 1.6–1.9 (m, 7) and 2.0–2.3 (m, 5).

The minor product was identified as *endo*-tricyclo[2.2.2.$0^{2,6}$]-octan-3-ol (**20**) by comparison with an authentic sample. None of the epimeric alcohol **21** was detectable in the crude reaction mixture by nmr; less than 0.5% was present by glpc.

Tricyclo[2.2.2.$0^{2,6}$]octan-3-ol.—A mixture of 0.842 g of tricyclo[2.2.2.$0^{2,6}$]octan-3-one[36] and 4.0 g of sodium metal in 35 ml of absolute ethanol was refluxed for 19 hr. The mixture was diluted with 30 ml of 95% ethanol, poured into 200 ml of water, and extracted with ether. The ether layer was dried and concentrated to give 1.5 g of crude yellow liquid of which 1.0 g was placed on 80 g of Merck neutral alumina. Elution with increasing amounts of ether in pentane afforded 70 mg of unreacted ketone, 100 mg of pure *exo*-tricyclo[2.2.2.$0^{2,6}$]octan-3-ol[18] (**21**) [mp 154–156° (lit. 156.5–158.2°); ir identical with the published spectra; nmr δ 0.7–2.1 (m, 10), 3.02 (s, 1, OH), and 4.30 (broad m, 1, CHOH)], 290 mg of a mixture of alcohols, and 50 mg of pure *endo*-tricyclo[2.2.2.$0^{2,6}$]octan-3-ol[18] (**20**) [mp 124–126° (lit.125–127.1°); ir identical with that reported; 100-MHz nmr δ 0.7–2.1 (m, 11) and 3.83 (s, 1, CHOH)].

Rearrangement of 22.—Refluxing 0.5 g of **22** in an ethereal solution of lithium diethylamide for 48 hr gave a 72% yield of a colorless liquid. Analysis by glpc indicated the presence of three products in a ratio of 14:10:76. The minor products were identified as *cis*-bicyclo[3.3.0]octan-2-one (**23**) and *cis*-bicyclo[3.3.0]-octan-3-one (**24**) by comparison of glpc retention times and ir data with those of authentic samples.[22] The major product was identified as *exo-cis*-bicyclo[3.3.0]octen-2-ol (**25**): ir 3.05, 3.31, and 6.15 μ; nmr δ 1.2–1.7 (m, 6), 2.38 (m, 1, bridgehead CH), 3.23 (m, 1, allylic bridgehead CH), 4.30 (m, 1, CHOH), 4.57 (broad s, 1, OH), and 5.62 (broad s, 2, olefinic CH).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.3; H, 9.6.

Hydrogenation of 120 mg of **25** in methanol using Adams catalyst gave *exo*-bicyclo[3.3.0]octan-2-ol identical with an authentic sample.[23]

Registry No.—**1**, 3146-39-2; **5**, 27141-82-8; **6**, 27141-83-9; **7**, 27141-84-0; **9**, 27141-85-1; **14**, 27141-86-2; **15**, 27150-45-4; *exo*-**22**, 24454-42-0; *endo*-**22**, 24454-41-9; **25**, 27141-89-5.

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