added. After stirring for an additional 0.5 hr. the mixture was dried over magnesium sulfate, filtered through Celite, and the filtrate was evaporated under reduced pressure to a colorless oil (3.342 g.). The infrared spectrum of this oil had a weak hydroxyl band at *ca.* 3600 cm.$^{-1}$ and no bands in the carbonyl region. Gas chromatography on SE-30 and Viton A–HV indicated a mixture of at least six olefins (94%) and at least four alcohols (6%). On the basis of retention times the olefin mixture appeared to consist of *cis*-1,2-diphenylcycloöctene (39.5%), compound **8** (6.5%), a component (compound **9**) with a retention time (Viton A–HV) between that of *cis*-1,2-diphenylcycloöctene and compound **8** (8.2%), 2,3-diphenylcycloöctene (1.7%), 4,4- and 5,5-diphenylcycloöctene (43%) and 1,5-diphenylcycloöctene (1%). The alcohol mixture appeared to contain mainly 5,5-diphenylcycloöctanol (75%).

The crude solvolysis mixture (3.300 g.) was chromatographed on 70 g. of neutral alumina (activity I). Eluting with pentane and pentane–methylene chloride (100:1) gave a mixture of olefins (3.076 g.) in twenty-two 100-ml. fractions. Eluting with ether–methanol (10:1) gave a mixture of alcohols (0.232 g.) in two 100-ml. fractions. The yields of olefins and alcohols from the solvolysis were thus 87.6 and 6.2%, respectively. Fractions 6–20 (0.283 g.), containing *cis*-1,2-diphenylcycloöctene (17%), a mixture of 4,4- and 5,5-diphenylcycloöctene (74%) and 1,5-diphenylcycloöctene (9%), were fractionally crystallized from ethanol (1 ml.) to give 63 mg. of 5,5-diphenylcycloöctene, m.p. 91.0–93.2°. The balance of the mixture was separated by gas chromatography on Viton A–HV at 233°. Fraction 1 (12.3 mg.) was shown to be identical with *cis*-1,2-diphenylcycloöctene by comparison of its infrared spectrum with that of an authentic sample. The infrared spectrum of fraction 2 (70.8 mg.) showed all the bands for both 4,4- and 5,5-diphenylcycloöctene and appeared to represent about a 1:1 mixture of these two compounds. The third fraction (10.1 mg.) was shown to be identical with an authentic sample of 1,5-diphenylcycloöctene by comparison of retention times on SE–30 and Viton A–HV and by comparison of ultraviolet and infrared spectra.

Isomerization of 5,5-Diphenylcycloöctene in Trifluoroacetic Acid.—A mixture of 400 mg. of 5,5-diphenylcycloöctene in 50 ml. of trifluoroacetic acid 0.3 *M* in sodium trifluoroacetate was stirred at 0° for 10 hr. The mixture was allowed to stand overnight in a refrigerator, filtered, and the filtrate was evaporated to dryness under reduced pressure at 0°. The combined residues were taken up in ether (50 ml.), dried over potassium carbonate, and evaporated under reduced pressure to an oil (380 mg.). To a portion of this oil (324 mg.) in dry ether (25 ml.) was added 50 mg. of lithium aluminum hydride. The solution was stirred for 0.5 hr., and then poured into 100 ml. of wet ether and stirred for 0.5 hr. longer, then dried over magnesium sulfate and evaporated under reduced pressure. Gas chromatographic analysis of the residual oil (297 mg.) on SE–30 and on Viton A–HV showed a mixture which, on the basis of retention times, consisted of *cis*-1,2-diphenylcycloöctene (33%), compound **9** (3%), 2,3-diphenylcycloöctene (1%), 5,5-diphenylcycloöctene (57%) and 5,5-diphenylcycloöctanol (6%). No trace of ether 1,5-diphenylcycloöctene or compound **8** was detected. Crystallization from ethanol (with seeding) gave 125 mg. of **2** (in two fractions), identified by mixture melting point and the infrared spectrum. Seeding the residue with *cis*-1,2-diphenylcycloöctene (**4**) gave 61 mg., m.p. 58–76.5°, which by gas chromatographic analysis (Viton A-HV) consisted of 94% of **4** and 6% of **2**. Gas chromatography (Viton A–HV) of the residue (82 mg.) from this last crystallization showed the presence of **4** (48%), **9** (9.6%), **5** (3.4%) and **2** (39%). Examination of the infrared spectrum of the **2**, m.p. 85–92°, collected from this gas chromatogram did not indicate the presence of any 4,4-diphenylcycloöctene (**3**).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.

Proximity Effects. XXIX. Solvolysis of Cycloheptenyl Derivatives[1,2]

BY ARTHUR C. COPE, CHUNG HO PARK AND PETER SCHEINER[3]

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Cycloheptenyl derivatives have been solvolyzed and the products compared with those obtained in the solvolysis of cyclooctenyl derivatives. Solvolysis of 4-cyclohepten-1-yl brosylate in either acetic acid or trifluoroacetic acid gave 4-cyclohepten-1-ol, 3-cyclohepten-1-ol and 1,3- and 1,4-cycloheptadiene in contrast to 4-cycloöcten-1-yl brosylate which gave bicyclic compounds in addition to the normal products. Acetolysis of 3-cyclohepten-1-yl brosylate produced *endo*- and *exo*-bicyclo[4.1.0]heptan-2-ol. The bicyclic alcohols also were prepared by an independent route, and their configurations were established. Solvolysis of 2-cyclohepten-1-yl bromide afforded the expected 2-cyclohepten-1-ol and 1,3-cycloheptadiene.

Previous papers[4–6] in this series described solvolyses of derivatives of the three isomeric cycloöctenols. In acetic acid, 4-cycloöcten-1-yl brosylate gave bicyclo[3.3.0]oct-2-ene and *endo*- and *exo*-bicyclo-[3.3.0]octan-2-ol in addition to the unrearranged 4-cycloöcten-1-ol and 1,4-cycloöctadiene.[4] With trifluoroacetic acid as solvent only bicyclic products were obtained from this brosylate.[5] Similarly, the major products of the acetolysis of 3-cycloöcten-1-yl brosylate were *endo*- and *exo*-bicyclo[5.1.0]octan-2-ol.[4,6] On the other hand, acetolysis of 2-cyclooctene-1-yl bromide gave unrearranged products.[4]

Recent studies have shown that cycloheptane derivatives under appropriate conditions also may form transannular products to a large extent.[7] It was therefore of interest to investigate the solvolytic reactions of derivatives of the isomeric cycloheptenols, and compare the results with those obtained from the solvolysis of the corresponding cycloöctenyl compounds. The solvolyses of 4-cyclohepten-1-yl brosylate, 3-cyclohepten-1-yl brosylate and 2-cyclohepten-1-yl bromide are reported in this paper.

4-Cycloheptene-1-carboxylic acid prepared by the procedure of Stork and Landesman[8] was converted to 4-cyclohepten-1-yl acetate in 70% yield by treatment with lead tetraacetate in acetic acid. The use of lead tetraacetate for the decarboxylation of monocarboxylic acids has been reported by several workers.[9–11] Under the conditions employed

(1) Supported in part by a research grant (NSF-G5055) of the National Science Foundation.

(2) Paper XXVIII, A. C. Cope, P. E. Burton and M. L. Caspar, *J. Am. Chem. Soc.*, **84**, 4855 (1962).

(3) National Institutes of Health Postdoctoral Fellow, 1961–1962.

(4) A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959).

(5) A. C. Cope, J. M. Grisar and P. E. Peterson, *ibid.*, **82**, 4299 (1960).

(6) A. C. Cope, S. Moon and P. E. Peterson, *ibid.*, **84**, 1935 (1962).

(7) A. C. Cope, P. Scheiner and R. L. Talbott, to be published.

(8) G. Stork and H. K. Landesman, *J. Am. Chem. Soc.*, **78**, 5129 (1956).

(9) G. Büchi, R. E. Erickson and N. Wakabayashi, *ibid.*, **83**, 927 (1961).

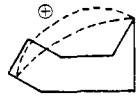
(10) J. Jacques, C. Weidmann and A. Horeau, *Bull. soc. chim. France*, 424 (1959).

(11) G. Büchi and J. T. Marvel, to be published.

in the present work, lead tetraacetate did not attack the double bond. Reduction of 4-cyclohepten-1-yl acetate with lithium aluminum hydride gave the desired 4-cyclohepten-1-ol uncontaminated with other isomeric cycloheptenols as shown by gas chromatography. Catalytic hydrogenation of the alcohol gave cycloheptanol. 3-Cyclohepten-1-ol[12] and 2-cyclohepten-1-yl bromide[13] have been described previously. 3- and 4-cyclohepten-1-ol were converted to the brosylates. The (allylic) brosylate of 2-cyclohepten-1-ol could not be isolated and 2-cyclohepten-1-yl bromide was studied instead.

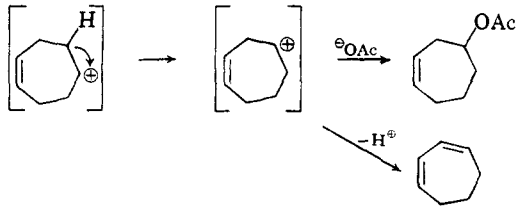
Solvolysis of 4-Cyclohepten-1-yl Brosylate.—The crystalline brosylate was solvolyzed under conditions similar to those employed for the solvolysis of 4-cycloöcten-1-yl brosylate.[4] When the solvolysis was carried out in acetic acid containing sodium acetate at 80° for 6 hours, the products (after lithium aluminum hydride reduction) were 4-cyclohepten-1-ol (71%), 3-cyclohepten-1-ol (12%), 1,4-cycloheptadiene (12%) and 1,3-cycloheptadiene (5%), isolated by gas chromatography and identified by comparison of their infrared spectra with those of authentic samples. When the solvolysis was carried out in acetic acid at room temperature for 26 hours, the starting brosylate was recovered unchanged. Solvolysis in trifluoroacetic acid, however, was complete after two hours at room temperature. The product was reduced with lithium aluminum hydride and gave a mixture containing 70% of 4-cyclohepten-1-ol, 20% of 3-cyclo-hepten-1-ol, 9% of 1,4-cycloheptadiene and 1% of 1,3-cycloheptadiene.

Winstein and Carter[14] recently suggested the possibility of formation of the non-classical carbonium ion A from 4-cycloheptenyl derivatives. In the present investigation bicyclo[3.2.0]hept-2-yl derivatives were not isolated. Although the formation of such derivatives from the solvolysis of 4-cyclohepten-1-yl brosylate would be an indication that the ion A was a possible intermediate, absence of them does not rule out such a possibility.

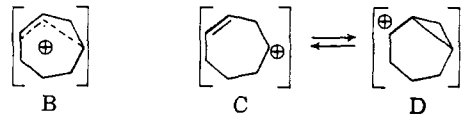


A

Formation of the rearranged products, 3-cyclohepten-1-ol and 1,3-cycloheptadiene can be explained by a simple 1,2-hydride shift.



Solvolysis of 3-Cyclohepten-1-yl Brosylate.—The solvolysis in acetic acid was carried out under conditions similar to those employed for the solvolysis of 3-cycloöcten-1-yl brosylate.[4] The mixture of alcohols obtained (after saponification of the acetates) was shown to consist of 22% *exo*- and 78% *endo*-bicyclo[4.1.0]heptan-2-ol. No hydrocarbons were present. Possible mechanisms for the formation of these products may be written similar to those proposed[4,6] for the solvolysis of 3-cyclooctenyl-1-yl brosylate. The *endo* isomer would be expected as the principal product if the reaction proceeded either by a concerted mechanism or through the non-classical carbonium ion intermediate B. However, since the *endo* isomer (see later) is thermodynamically the more stable one, it would also be expected as the major product if the solvolysis proceeded through classical carbonium ion intermediates (C and D). This result therefore does not permit a decision between the three possible mechanisms.

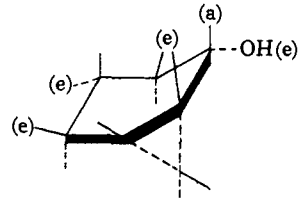


B C D

Authentic samples of *endo*- and *exo*-bicyclo[4.1.0]heptan-2-ol were prepared by reaction of methylene iodide and zinc–copper couple[15,16] with 2-cyclohexen-1-ol. The configurations have been assigned on the basis of the identities of the isomeric methylcyclohexanols obtained by hydrogenolysis of the cyclopropane ring in each case. Catalytic hydrogenation of *endo*-bicyclo[4.1.0]heptan-2-ol gave *cis*-2-methylcyclohexanol (75%), *cis* - 3 - methylcyclohexanol (11%) and cycloheptanol (14%); hydrogenation of the *exo* isomer gave *trans*-2-methylcyclohexanol (*ca.* 50%) and *trans*-3-methylcyclohexanol (*ca.* 50%). The stereochemistry of the methylcyclohexanols has been determined previously.[17-21] Equilibration of either the *endo* or the *exo* isomer under Meerwein–Ponndorf conditions gave a mixture of the same composition: 67% *endo*, 33% *exo*. The mixture of bicyclo[4.1.0]heptan-2-ols obtained by the reaction of methylene iodide and zinc–copper couple with 2-cyclohexene-1-ol consisted largely (75%) of the *endo* isomer. This result was expected, since addition of the methylene group to a double bond is known[12,22] to occur principally from the same side of the double bond as a hydroxyl group, probably due to complex formatio by attacking iodomethylzinc iodide with the hydroxyl group. Although the alcohols could not be separated cleanly by elution chromatography on alumina, the *exo* isomer was eluted slightly mo e easily than the *endo* isomer, indicating that the hydroxyl group of *exo* isomer is more hindered. All this evidence indicates that the *endo* isomer is thermodynamically more stable and less hindered than the *exo* isomer. Examination of models shows that, in a

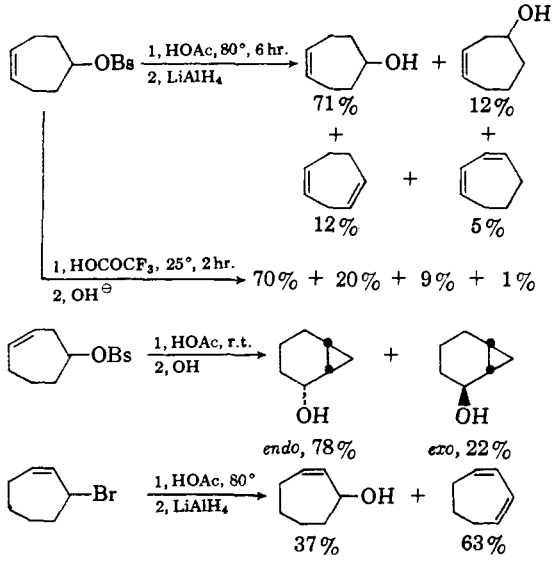
(12) A. C. Cope, S. Moon and C. H. Park, *J. Am. Chem. Soc.*, **84**, 4843 (1962).
(13) A. C. Cope, T. A. Liss and G. W. Wood, *ibid.*, **79**, 6287 (1957).
(14) S. Winstein and P. Carter, *ibid.*, **83**, 4485 (1961).
(15) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).
(16) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).
(17) P. D. Bartlett and C. M. Berry, *J. Am. Chem. Soc.*, **56**, 2683 (1934).
(18) W. G. Dauben, G. J. Fonken and D. S. Noyce, *ibid.*, **78**, 2579 (1956).
(19) E. L. Eliel and C. A. Lukach, *ibid.*, **79**, 5986 (1957).
(20) H. C. Brown and G. Zweifel, *ibid.*, **81**, 247 (1959).
(21) S. Brownstein and R. Miller, *J. Org. Chem.*, **24**, 1886 (1959).
(22) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961).

conformation such as is shown in Fig. 1, the *endo* isomer is quite likely to be less hindered than the *exo* isomer due to its equatorially oriented hydroxyl group. However, this conformation is not a rigid one, and the *endo* and *exo* isomers may assume other conformations.



Solvolysis of 2-Cyclohepten-1-yl Bromide.—The acetolysis of 2-cyclohepten-1-yl bromide was conducted at 80° for 32 hours. The product (after lithium aluminum hydride reduction) consisted of 2-cyclohepten-1-ol (37%) and 1,3-cycloheptadiene (63%). As expected, rearrangement or hydride shift, which would destroy the resonance stabilization of the allylic carbonium ion intermediate, was not encountered in this case.

The results of solvolysis of the cycloheptenyl derivatives are summarized in Fig. 2.



Experimental[23,24]

4-Cyclohepten-1-yl Acetate.—To a solution of 2.39 g. of 4-cyclohepten-1-carboxylic acid[8] and 16.4 g. of anhydrous potassium acetate in 45 ml. of glacial acetic acid heated at 70 ± 3° was added 11.5 g. of commercial lead tetraacetate in three portions with stirring during 0.5 hour. A moderate evolution of carbon dioxide was observed. After an additional 0.5 hour of stirring at 70° the evolution of gas had ceased. The pale yellow solution was cooled to room temperature, diluted with 40 ml. of water, and extracted with six 20-ml. portions of pentane. The combined pentane extracts were washed with 5% sodium bicarbonate solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure yielded 1.85 g. (70%) of 4-cyclohepten-1-yl acetate which was shown to be homogeneous by gas chromatography on TCEP at 117°. An analytical sample, $n^{25}D$ 1.4837, was collected by gas chromatography (TCEP, 117°).

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.85; H, 9.24.

(23) Melting points are corrected and boiling points are uncorrected.

(24) Reference 4, footnote 24, describes the conditions and equipment used for gas chromatography.

4-Cyclohepten-1-ol.—4-Cyclohepten-1-yl acetate (28.4 g.) was reduced with lithium aluminum hydride in ether at room temperature for 0.5 hour to give 19.5 g. (95%) of crude 4-cyclohepten-1-ol. The product was distilled at 83–84° (11 mm.) and yielded 13.9 g. of 4-cyclohepten-1-ol, $n^{25}D$ 1.4937, which was shown to be homogeneous by gas chromatography on TCEP (117°) and silicone grease (159°). An analytical sample was collected by gas chromatography (silicone grease, 159°).

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.21; H, 10.73.

A sample of 4-cyclohepten-1-ol (0.229 g.) in 14 ml. of ethyl acetate was hydrogenated in the presence of 30 mg. of 5% palladium-on-charcoal at room temperature under atmospheric pressure. It absorbed 97.3% of the calculated amount of hydrogen and yielded cycloheptanol, identified by gas chromatography on TCEP (130°) and silicone grease (162°) and by comparison of its infrared spectrum with that of an authentic sample.

Preparation of the Brosylates.—The brosylates were prepared from the corresponding alcohols by the procedure described for the brosylates of 3- and 4-cyclooctene-1-ol.[4]

4-Cyclohepten-1-yl brosylate, prepared in 65% yield, was analyzed after three recrystallizations from pentane, m.p. 45.5–46.5°.

Anal. Calcd. for $C_{13}H_{15}O_3SBr$: C, 47.13; H, 4.57. Found: C, 47.13; H, 4.46.

3-Cyclohepten-1-yl brosylate, obtained in 49% yield, was rather unstable at room temperature, and was therefore analyzed immediately after one recrystallization from an ether–pentane mixture; m.p. 53–54° dec.

Anal. Calcd. for $C_{13}H_{15}O_3SBr$: C, 47.13; H, 4.57. Found: C, 47.40; H, 4.53.

Although considerably more stable than 3-cyclohepten-1-yl brosylate, 4-cyclohepten-1-yl brosylate decomposed slowly on standing at room temperature for several days.

Solvolysis of 4-Cyclohepten-1-yl Brosylate. (a).—A mixture of 1.519 g. of 4-cyclohepten-1-yl brosylate, 10.0 ml. of 0.5 *M* sodium acetate in acetic acid and 6.6 ml. of acetic acid was heated at 80 ± 2° for 6 hours. The mixture was cooled, 100 ml. of water was added, and the solution was extracted with five 30-ml. portions of ether. The combined extracts were washed with 5% sodium carbonate solution until the washings became basic, and were dried over magnesium sulfate. Removal of the solvent at 40°, followed by evaporation at room temperature under reduced pressure, yielded 0.433 g. of liquid containing 17% of hydrocarbons and 83% of acetates as determined by gas chromatography (TCEP, 115°). Reduction of the acetate fraction (separated by gas chromatography) with lithium aluminum hydride in ether at room temperature for 0.5 hour yielded a mixture containing 85% 4-cyclohepten-1-ol and 15% 3-cyclohepten-1-ol, identified by gas chromatography (TCEP, 115°) and by comparison of their infrared spectra with those of authentic samples. The hydrocarbon fraction was shown to contain 72% 1,4- and 28% of 1,3-cycloheptadiene by gas chromatography (TCEP, 42°) and by comparison of their infrared spectra with those of authentic samples.

(b).—4-Cyclohepten-1-yl brosylate (0.331 g.) was added in small portions to a solution of 0.103 g. of anhydrous sodium acetate in 2.3 g. of trifluoroacetic acid. The deep red solution was allowed to stand at room temperature for 2 hours. The mixture was then diluted with 10 ml. of ether and washed with eight 25-ml. portions of water, two 10-ml. portions of 10% sodium carbonate solution and 10 ml. of water. The ether was evaporated and the residue was saponified by stirring with 10 ml. of 10% sodium hydroxide solution at room temperature for 2.5 hours. The mixture was extracted with five 5-ml. portions of ether and the combined extracts were washed with 10 ml. of water and dried over magnesium sulfate. Removal of the solvent afforded 74 mg. of an oil which contained 70% of 4-cyclohepten-1-ol, 20% of 3-cyclohepten-1-ol, 9% of 1,4-cycloheptadiene and 1% of 1,3-cycloheptadiene, identified as described previously.

Solvolysis of 3-Cyclohepten-1-yl Brosylate.—A mixture of 0.4 g. of the crystalline brosylate, 4.0 ml. of 0.5 *M* sodium acetate in acetic acid and 2.4 ml. of glacial acetic acid was allowed to stand at room temperature for 24 hours. Crystalline sodium *p*-bromobenzenesulfonate was removed by filtration and the filtrate was diluted with 10 ml. of water and extracted with three 10-ml. portions of ether. The combined ether extracts were washed with water and 5% sodium

carbonate solution. Removal of solvent followed by saponification with 15% sodium hydroxide in methanol–water yielded 0.1 g. (74%) of a mixture which was shown to contain 22% of *exo*- and 78% of *endo*-bicyclo[4.1.0]heptan-2-ol by gas chromatography (TCEP, 117°) and by comparison of their infrared spectra with those of authentic samples.

Solvolysis of 2-Cyclohepten-1-yl Bromide.—Freshly distilled 2-cyclohepten-1-yl bromide[12] (2.0 g.) in 26 ml. of glacial acetic acid 0.5 *M* in sodium acetate was heated at 80–85° for 32 hours. The mixture was then poured into 120 ml. of water and extracted with three 40-ml. portions of ether. The combined ether extracts were washed with 5% sodium bicarbonate solution until the washings were basic and dried over magnesium sulfate. Removal of the solvent afforded 0.8 g. which (after reduction with lithium aluminum hydride) contained 37% of 2-cyclohepten-1-ol and 63% of 1,3-cycloheptadiene, identified as described previously for the solvolysis of 4-cyclohepten-1-yl brosylate in acetic acid.

1,4-Cycloheptadiene.—In a stream of nitrogen 210 μl. of 4-cyclohepten-1-yl acetate was passed through a Pyrex tube (25 × 1 cm.) packed with glass helices and heated to 550 ± 10°. The pyrolysate was condensed in a trap cooled to −70° to give two components in yields of 82 and 18% as determined by gas chromatography (TCEP, 113°). The minor component had a retention time and infrared spectrum identical to those of 1,3-cycloheptadiene. 1,4-Cycloheptadiene, the major product isolated by gas chromatography (TCEP, 113°), was analyzed.

Anal. Calcd. for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 88.98; H, 10.84.

A 15-mg. sample of 1,4-cycloheptadiene in 5 ml. of pentane was hydrogenated for 4 hours at room temperature and atmospheric pressure with 28 mg. of platinum dioxide. After filtration the solution was concentrated (*ca.* 0.2 ml.) by distilling the solvent through a semi-micro column. Gas chromatography on silicone grease (78°) showed the product to be cycloheptane, identified by comparison of its infrared spectrum and retention time with an authentic sample.

Preparation of *endo*- and *exo*-Bicyclo[4.1.0]heptan-2-ol.—A mixture of bicyclo[4.1.0]heptan-2-ols was obtained from 2-cyclohexen-1-ol (24% yield) by the same procedure used for the preparation of *endo*-bicyclo[5.1.0]octan-3-ol from 3-cyclohepten-1-ol.[12] The alcohols were obtained in a ratio of 1:3 estimated by gas chromatography (TCEP, 105°). The preponderant isomer was found to be *endo*. In two other preparations conducted under the same conditions, the ratio of *endo* to *exo* isomer was found to be 79 to 21 and 88 to 12.

The mixture of *endo*- and *exo*-bicyclo[4.1.0]heptan-2-ol was partially separated by elution chromatography on alumina. It was passed through a column of acid-washed alumina (activity II) packed in pentane and eluted with ether–pentane mixtures. The fractions eluted with 25% ether–pentane mixtures contained largely the *exo* isomer with a trace of *endo*, and the fractions eluted with 30% ether–pentane mixtures contained both isomers in comparable amounts (estimated by gas chromatography). Finally, the fractions eluted with 40–100% ether–pentane mixture contained the pure *endo* isomer. Samples collected by gas chromatography (TCEP, 105°, followed by silicone oil, 120°) were analyzed.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found for the *endo* isomer: C, 74.94; H, 10.78. Found for the *exo* isomer: C, 74.64; H, 10.75.

Equilibration of *endo*- and *exo*-Bicyclo[4.1.0]heptan-2-ol.—The bicyclic alcohols were equilibrated in the same manner as were the bicyclo[5.1.0]octanols.[12] Equilibration of *endo*-bicyclo[4.1.0]heptan-2-ol yielded a mixture of 67% *endo* isomer and 33% *exo* isomer. Equilibration of the *exo* isomer under the same conditions gave the same result.

Catalytic Hydrogenation of *endo*- and *exo*-Bicyclo[4.1.0]-heptan-2-ol.—The bicyclic alcohols were hydrogenated according to the procedure described for the bicyclo[5.1.0]-octanols.[12] *endo*-Bicyclo[4.1.0]heptan-2-ol (after it had taken up 140% of the calculated amount of hydrogen in 10 minutes) yielded a mixture containing 75% of *cis*-2-methylcyclohexanol, 11% of *cis*-3-methylcyclohexanol and 14% of cycloheptanol, identified by gas chromatography (TCEP, 120°) and by comparison of their infrared spectra with the spectra of authentic samples. The *exo* isomer (after it had absorbed 103% of the calculated amount of hydrogen in 15 minutes) yielded a mixture containing *ca.* 50% of *trans*-2-methylcyclohexanol and *ca.* 50% of *trans*-3-methylcyclohexanol, identified by gas chromatography (TCEP, 120°) and by comparison of the infrared spectrum of the mixture with the spectrum of an authentic mixture containing 50% of *trans*-2-methylcyclohexanol and 50% of *trans*-3-methylcyclohexanol.

Preparation of the Methylcyclohexanols.—Authentic samples of *cis*- and *trans*-2-methylcyclohexanol and *cis*- and *trans*-3-methylcyclohexanol were prepared by reduction of the corresponding ketones with sodium borohydride according to the procedure described for bicyclo[5.1.0]octan-4-one.[12] Starting with 1 g. of 2-methylcyclohexanone, 1 g. of a mixture containing 37% of *cis*- and 63% of *trans*-2-methylcyclohexanol was obtained. The reduction of 3-methylcyclohexanone (1 g.) yielded 1 g. of a mixture containing 83% of *cis*- and 17% of *trans*-3-methylcyclohexanol. The pure isomers were separated by gas chromatography (TCEP, 120°), and their identities were proved by comparison of their infrared spectra with the reported spectra.[19]

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

Proximity Effects. XXX. Stereochemistry of Bicyclo[3.2.1]octan-8-ols and Bicyclo-[4.2.0]octan-2- and 3-ols[1,2]

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The original assignment of configurations to the epimeric bicyclo[3.2.1]octan-8-ols has been confirmed by an unambiguous synthesis of *exo*-bicyclo[3.2.1]octan-8-ol. The configurations of *endo*- and *exo*-bicyclo[4.2.0]octan-2-ols also were confirmed by interrelating the stereochemistry of bicyclo[4.2.0]oct-7-en-2-ol by ozonization to a cyclohexane derivative of established configuration. The configurations of *endo*- and *exo*-bicyclo[4.2.0]octan-3-ols were related to the corresponding 2-ols, and thereby established unequivocally.

During a study of the solvolysis of bicyclo[4.2.0]-octanol derivatives,[3] isolation of an unexpected product led us to review critically the evidence for the assignment of configurations to the bicyclo-[4.2.0]octan-2-ols[4] and bicyclo[3.2.1]octan-8-ols.[5] This paper presents unambiguous evidence supporting the original assignments.[4,5]

Bicyclo[3.2.1]octan-8-ols.—The configurations of the bicyclo[3.2.1]octan-8-ols originally were assigned on the basis of the results obtained in reduc-

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(2) Paper XXIX, A. C. Cope, C. H. Park and P. Scheiner, *J. Am. Chem. Soc.*, **84**, 4862 (1962).

(3) A. C. Cope, R. W. Gleason, S. Moon and C. H. Park, to be published.

(4) A. C. Cope and R. W. Gleason, *J. Am. Chem. Soc.*, **84**, 1928 (1962).

(5) A. C. Cope, J. M. Grisar and P. E. Peterson, *ibid.*, **82**, 4299 (1960).