tained for 5 hours. The hot reaction mixture was poured onto 400 g. of cracked ice, and the resulting mixture was extracted with four 50-ml. portions of ether. The combined ether extracts were washed with dilute hydrochloric acid until the washings were acid to litmus, and then with water. The excess water was removed by passage of the solution through a fluted filter containing 25 g. of anhydrous sodium sulfate. Evaporation of the solvent from the filtrate yielded a dark brown, viscous oil, which was eluted on a column of alumina with petroleum ether. The resulting clear liquid was evaporatively distilled to yield 1.2 g. (57%) of the expected hydrocarbon. The infrared spectrum of this product showed it to be identical with the hydrocarbon obtained *via* the sodium amide cleavage.

Under identical reaction conditions, 1.3 g. (0.004 mole) of optically active ketone having $[\alpha]^{24}_{\mathrm{D}}$ −32 ± 1.5° (*c* 0.843, $CHCl_3$) gave 471 mg. (54%) of pure hydrocarbon, which was shown to be identical with earlier preparations. This material, however, was only 66% optically pure, having $[\alpha]^{23}_{\mathrm{D}}$ +85 ± 2° (*c* 0.392, $CHCl_3$). Racemization to the extent of 34% had occurred during the course of the reaction.

2,2-Diphenylcyclopropylcarbinyl-*p*-toluenesulfonate.—To a solution of 3.8 g. (0.02 mole) of *p*-toluenesulfonyl chloride in 4 ml. of 2,6-lutidine (cooled to 0°) was added a solution of 2.1 g. (0.01 mole) of 2,2-diphenylcyclopropylcarbinol in 4 ml. of lutidine. The mixture was allowed to stand at room temperature for 2 hours, when it had set to a solid mass. Dropwise addition of 2 ml. of water caused the mass to liquefy, and its was poured into 75 ml. of water contained in a separatory funnel. The precipitated solid was extracted with three 50-ml. portions of ether, and the combined ether extracts were washed successively with water, 5% hydrochloric acid, water, 5% potassium hydroxide solution, and water. The ethereal solution was freed of excess water by passage through a fluted filter containing 30 g. of anhydrous sodium sulfate. The solvent was evaporated on the steam-bath, a stream of air being used to keep the temperature below 30°. When the first traces of solid appeared, the flask was removed from the steam-bath, and the residual solvent evaporated by the air stream. Recrystallization from petroleum ether containing a small amount of chloroform yielded 3.1 g. (90%) of the desired tosylate. The decomposition point varied from 58–80°, depending on the rate of heating. No satisfactory elemental analysis was obtained; however, the infrared spectrum showed bands (ascribed to the covalent sulfonate linkage) at 1365 and 1170 cm.$^{-1}$.

In the same manner, 1.2 g. (0.0054 mole) of active carbinol having $[\alpha]^{24}_{\mathrm{D}}$ +167 ± 3° (0.303, $CHCl_3$) gave a quantitative yield of optically active tosylate with $[\alpha]^{23}_{\mathrm{D}}$ +98 ± 4° (0.149, $CHCl_3$) and infrared absorption bands at 1365 and 1170 cm.$^{-1}$.

Methyl-2,2-diphenylcyclopropane.—Three grams of 2,2-diphenylcyclopropylcarbinyl tosylate (0.08 mole) was added rapidly (in the solid phase) to a well-stirred slurry of 3 g. of lithium aluminum hydride and 100 ml. of anhydrous ether. After 5 hours, 20 ml. of tetrahydrofuran was added, and the stirring continued for an additional 19 hours. The reaction was worked up in the usual manner. The liquid product obtained was distilled under vacuum, giving 1.12 g. (67%) of pure methyl-2,2-diphenylcyclopropane, boiling at 122.5° (4 mm.) (bath, 145°). Infrared spectra showed this hydrocarbon to be identical with the 1-methyl-2,2-diphenylcyclopropane obtained in the cleavage reactions.

Similarly, reduction of 1.7 g. (0.0045 mole) of optically active tosylate having $[\alpha]^{29}_{\mathrm{D}}$ +98 ± 4° (0.149 $CHCl_3$) by a weight-equivalent of lithium aluminum hydride, as outlined above, gave 607 mg. (65%) of pure, optically active 1-methyl-2,2-diphenylcyclopropane. Its identity was established by comparison with hydrocarbon prepared by the various procedures, and its specific rotation was $[\alpha]^{26}_{\mathrm{D}}$ +127 ± 2° (*c* 0.388, $CHCl_3$).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.11; H, 7.82.

Metallation of (−)-(R)-1-Bromo-1-methyl-2,2-diphenylcyclopropane.[17]—To 0.7 g. of sodium sand dispersed in 25 ml. of toluene was added 2.0 g. of the bromide, and the mixture was refluxed, with stirring, for 7.5 hours. The reaction mixture was cooled and poured onto a Dry Ice and ether slurry. Upon workup, no acidic material was isolated, but the neutral fraction yielded an oil which was distilled *in vacuo* to give 0.67 g. (46%) of 1-methyl-2,2-diphenylcyclopropane, $[\alpha]^{26}_{\mathrm{D}}$ +78 ± 2° (*c* 5.8, $CHCl_3$), 61% optically pure. The infrared spectrum was identical in all respects with that of an authentic sample.

Repetition of the above using benzene as a solvent produced the hydrocarbon in 49% yield, $[\alpha]^{26}_{\mathrm{D}}$ +89 ± 2° (*c* 1.06, $CHCl_3$), 70% optically pure.

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

Proximity Effects. XXVI. Synthesis and Stereochemistry of Bicyclo[5.1.0]octanols[1,2]

BY ARTHUR C. COPE, SUNG MOON AND CHUNG HO PARK

RECEIVED JUNE 11, 1962

endo- and *exo*-bicyclo[5.1.0]octan-3-ol and *endo*- and *exo*-bicyclo[5.1.0]octan-4-ol have been synthesized and their configurations have been established. In so doing, all six of the methylcycloheptanols were prepared and their configurations were established. Additional evidence for the assignment of configurations to *endo*- and *exo*-bicyclo[5.1.0]octan-2-ol also has been obtained.

endo- and *exo*-bicyclo[5.1.0]octan-2-ol have been obtained as the principal products of the solvolysis of 3-cycloöcten-1-yl brosylate.[3,4] However, *endo*- and *exo*-bicyclo[5.1.0]octan-3-ol and *endo*- and *exo*-bicyclo[5.1.0]octan-4-ol have not been described before, and their syntheses were undertaken in order to investigate the solvolysis of their derivatives. This paper describes the synthesis and stereochemistry of bicyclo[5.1.0]octan-3-ols and bicyclo[5.1.0]octan-4-ols. The stereochemistry of the bicyclo[5.1.0]octan-2-ols is also discussed. The solvolysis of suitable derivatives of the six bicyclo[5.1.0]octanols is described in the following paper.[5]

Preparation of *endo*- and *exo*-Bicyclo[5.1.0]octan-3-ol.—*endo*- and *exo*-bicyclo[5.1.0]octan-3-ol have been synthesized in the following manner. Attempted mono-epoxidation of 1,3-cycloheptadiene[6] with monoperphthalic acid in ether, or with a 40% solution of peracetic acid in glacial acetic acid without additional solvent, yielded only polymeric material. However, when the diene dissolved in ether was treated with 40% peracetic acid solution, 3-cyclohepten-1-one was obtained directly.

The structure of 3-cyclohepten-1-one was first tentatively assigned on the basis of spectral data

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

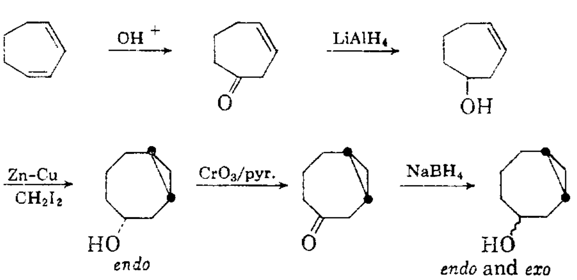
[2] Paper XXV, A. C. Cope and M. J. Youngquist, *J. Am. Chem. Soc.*, **84**, 2411 (1962).

[3] A. C. Cope and P. E. Peterson, *ibid.*, **81**, 1643 (1959).

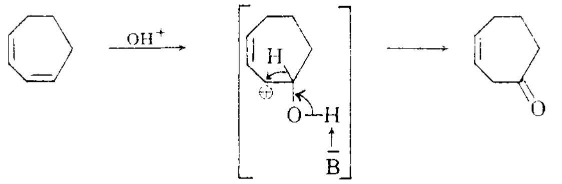
[4] A. C. Cope, S. Moon and P. E. Peterson, *ibid.*, **84**, 1935 (1962).

[5] A. C. Cope, S. Moon and C. H. Park, *ibid.*, **84**, 4850 (1962).

[6] A. C. Cope, T. A. Liss and G. W. Wood, *ibid.*, **79**, 6287 (1957).

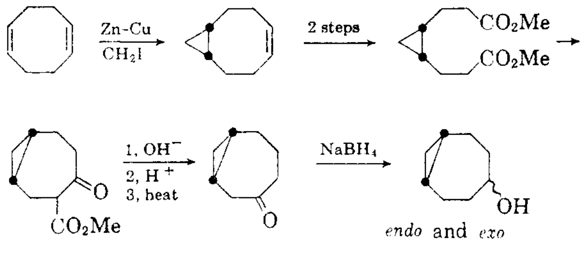


(infrared spectrum, 1650 and 1707 cm.$^{-1}$; ultraviolet, $\lambda_{\max}^{\text{EtOH}}$ 284 mμ, ϵ 80), and confirmed by later experiments. Its 2,4-dinitrophenylhydrazone also exhibits an ultraviolet maximum (360 mμ, ϵ 22,000) characteristic of these derivatives of non-conjugated ketones. The alcohol obtained by reduction of the ketone with lithium aluminum hydride followed by isolation by silver nitrate extraction was shown to be homogeneous by gas chromatography. In addition, a mixture consisting of the alcohol and authentic 2-cyclohepten-1-ol[6] showed two peaks with different retention times on gas chromatography, indicating that none of the conjugated ketone was present in 3-cyclohepten-1-one obtained by the attempted epoxidation of 1,3-cycloheptadiene. A possible route for the transformation can be written in which the diene is attacked by hydroxonium ion to form more stable allylic carbonium ion, followed by the removal of the hydroxyl hydrogen atom with 1,2-hydride shift of the hydrogen atom α to the hydroxyl group. Alternatively the epoxide could be formed as an intermediate and undergo acid-catalyzed rearrangement to the ketone.

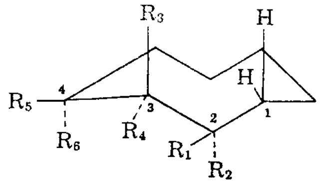


endo-Bicyclo[5.1.0]octan-3-ol was obtained in good yield (89%) from 3-cyclohepten-1-ol by treatment with methylene iodide and zinc–copper couple.[7,8] Chromic anhydride oxidation of the bicyclic alcohol gave bicyclo-[5.1.0]octan-3-one, which on reduction with sodium borohydride yielded a mixture containing 30% of *endo*- and 70% of *exo*-bicyclo[5.1.0]octan-3-ol. The isomeric alcohols were separated by elution chromatography on alumina, or by gas chromatography.

Preparation of *endo*- and *exo*-Bicyclo[5.1.0]octan-4-ol.—Bicyclo-[6.1.0]non-4-ene, obtained in 37% yield from 1,5-cyclooöctadiene by reaction with methylene iodide and zinc–copper couple, was oxidized to *cis*-1,2-cyclopropanedipropionic acid with potassium permanganate in acetone. An attempted preparation of bicyclo[5.1.0]octan-4-one directly from the barium salt of the dicarboxylic acid was unsuccessful, and its dimethyl ester was cyclized instead (67% yield) by the use of a modified[9–11] Dieckmann condensation procedure. Saponification of the resulting β-keto ester with dilute sodium hydroxide followed by decarboxylation in a slightly acidic medium gave bicyclo[5.1.0]octan-4-one in 97% yield. The ketone was reduced with sodium borohydride to give a mixture of 35% of *endo*- and 65% of *exo*-bicyclo[5.1.0]octan-4-ol, which was separated by chromatography on alumina.



Stereochemistry of Bicyclo[5.1.0]octan-2-ols.—A number of lines of evidence concerning the stereochemistry of *endo*- and *exo*-bicyclo[5.1.0]octan-2-ol have been discussed previously.[4] In the present investigation, additional evidence was obtained based on n.m.r. spectra, reaction of methylene iodide and zinc–copper couple with 2-cyclohepten-1-ol and catalytic hydrogenation of the cyclopropane rings in the bicyclic alcohols.



Examination of models shows that the proton α to the hydroxyl group in *exo*-bicyclo[5.1.0]octan-2-ol (Fig. 1, R_1 = OH, $R_2 = R_3 = R_4 = R_5 = R_6$ = H) is axially oriented forming bond angles of approximately 180° with two adjacent axial hydrogen atoms (R_3 and the C_1–hydrogen atom), whereas in the *endo* isomer (R_2 = OH, $R_1 = R_3 = R_4 = R_5 = R_6$ = H), the proton α to the hydroxyl group is equatorially located forming bond angles of approximately 30–90° with adjacent hydrogen atoms. It has been shown[12] that the peak due to an axial proton α to an oxygen atom in the cyclohexane series is observed at a higher field with a broader band width in the n.m.r. spectrum than its equatorial counterpart. Therefore, it is reasonable to expect the peak due to the C_2–hydrogen atom of the *exo* isomer to come at higher field with broader band width than that of the *endo* isomer. Indeed, the peak due to the hydrogen atom of the *exo* isomer was observed at τ = 6.7 with a width at half-height of 15 c.p.s., whereas the peak due to the hydrogen atom of the *endo* isomer was observed at τ = 5.8 with a width at half-height of 10 c.p.s., supporting the assigned configurations.

In the reaction of methylene iodide and zinc–copper couple with unsaturated cyclic alcohols, the addition of the methylene group to the double bond

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(7) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(8) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

(9) F. F. Blicke, J. Azuara, N. J. Doorenbos and E. B. Hotelling, *J. Am. Chem. Soc.*, **75**, 5418 (1953).

(10) N. J. Leonard and C. W. Schimelpfenig, Jr., *J. Org. Chem.*, **23**, 1708 (1958).

(11) N. J. Leonard and R. C. Sentz, *J. Am. Chem. Soc.*, **74**, 1704 (1952).

(12) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider, *ibid.*, **80**, 6098 (1958).

occurs from the same side of the double bond as the hydroxyl group, probably due to complex formation between the attacking iodomethylzinc iodide and the hydroxyl group.[13] Thus, the addition of a methylene group to 2-cyclopenten-1-ol,[14] 3-cyclopenten-1-ol[13] and, as shown later in this paper, 3-cyclohepten-1-ol gave predominantly the corresponding *endo*-bicyclic alcohol in each case. Accordingly, it was expected that the *endo* isomer would be the major product from the reaction of methylene iodide and zinc–copper couple with 2-cyclohepten-1-ol, and this was found to be the case.

Finally, cleavage of cyclopropane rings in the bicyclo[5.1.0]octan-2-ols by catalytic hydrogenation gave unequivocal evidence concerning their structures. The reaction was carried out under sufficiently mild conditions so as to avoid any change in the configuration at the carbon atom bearing the hydroxyl group. As expected, hydrogenation of *endo*-bicyclo[5.1.0]octan-2-ol yielded *cis*-2-methylcycloheptanol and *cis*-3-methylcycloheptanol. In the same manner, the *exo* isomer yielded *trans*-2-methylcycloheptanol and *trans*-3-methylcycloheptanol. It has been reported[15] that pure *cis*-2-methylcycloheptanol was obtained by catalytic reduction of 2-methylcycloheptanone in acetic acid containing a trace of hydrochloric acid, while mostly *trans*-2-methylcycloheptanol was obtained by the reduction of the ketone with sodium in alcohol. Equilibration of *cis*-2-methylcycloheptanol under Meerwein–Ponndorf conditions gave a mixture containing 14% of 2-methylcycloheptanone and mostly *trans*-2-methylcycloheptanol with less than 10% of the *cis* isomer, estimated by gas chromatography. *trans*-2-Methylcycloheptanol, uncontaminated by any of the *cis* isomer, was also obtained[16] from the hydroboration of 1-methylcycloheptene, as expected by the stereospecific *cis* addition mechanism proposed by Brown.[17] Finally, the geometry of the 2-methylcycloheptanols was demonstrated by the formation of *trans*-2-methylcycloheptanol from the reaction of cycloheptene oxide with dimethylmagnesium. The reaction of dimethylmagnesium with cyclohexene oxide was reported[18] to give *trans*-2-methylcyclohexanol.

Stereochemistry of Bicyclo[5.1.0]octan-3-ols.—Configurations of bicyclo[5.1.0]octan-3-ols have been assigned on the basis of the following evidence. Study of models shows that the hydroxyl group of the *endo* isomer (Fig. 1, $R_4 = OH$, $R_1 = R_2 = R_3 = R_5 = R_6 = H$) is equatorially oriented, and is much less hindered than that of the *exo* isomer (Fig. 1, $R_3 = OH$, $R_1 = R_2 = R_4 = R_5 = R_6 = H$) in which the hydroxyl group is axially oriented. As shown in the cases of bicyclo[5.1.0]octan-2-ols[4] and others,[19-21] the hindered nature of an axial hydroxyl substituent compared to an equatorial substituent would cause an axial alcohol to be more weakly adsorbed on alumina than its equatorial epimer. Therefore, *exo*-bicyclo[5.1.0]octan-3-ol would be expected to be eluted more easily than the *endo* isomer by chromatography on alumina. Thus, the isomer which was eluted more easily was assigned the *exo* configuration.

It is also expected that the *endo* isomer would be thermodynamically more stable than the *exo* isomer also due to the orientation of the hydroxyl groups in the two epimeric alcohols. As predicted, equilibration of the *exo* isomer under Meerwein–Ponndorf conditions yielded a mixture containing 18% of the *exo* and 82% of the *endo* isomer. Equilibration of the *endo* isomer under the same conditions yielded a mixture containing 25% of the *exo* and 75% of the *endo* isomer.

Another fact supporting the assignment of these configurations comes from the catalytic reduction of bicyclo[5.1.0]octane-3-one. It has been reported[22] that the thermodynamically less stable (axial-equatorial) isomers were obtained predominantly from the corresponding methylcyclohexanones by catalytic hydrogenation in acetic acid containing a trace of mineral acid. Thus, *cis*-2-methylcyclohexanol, *trans*-3-methylcyclohexanol and *cis*-4-methylcyclohexanol were obtained as the principal products from the corresponding ketones. Hydrogenation of bicyclo[5.1.0]octan-3-one under similar conditions yielded a mixture containing 8% of the more stable *endo* isomer (equatorial hydroxyl group) and 92% of the less stable *exo* isomer (axial hydroxyl group).

Infrared spectra of the two isomeric alcohols also supported the assignment of configurations. The spectrum of the *endo* isomer showed a much larger peak corresponding to a hydrogen-bonded hydroxyl group than did that of the *exo* isomer.

The reaction of methylene iodide and zinc–copper couple with 3-cyclohepten-1-ol gave only *endo*-bicyclo[5.1.0]octan-3-ol in line with the other examples described previously. As expected, addition of the methylene group to the double bond of 3-cyclohepten-1-yl acetate was less stereospecific, probably due to the absence of the hydroxyl group which forms a complex with iodomethylzinc iodide in the process of the addition. Thus, *endo*- and *exo*-bicyclo[5.1.0]oct-3-yl acetate were obtained in a ratio of 63 to 37% from the reaction of methylene iodide and zinc–copper couple with 3-cyclohepten-1-yl acetate.

Finally, hydrogenation of *endo*-bicyclo[5.1.0]-octan-3-ol gave *cis*-3-methylcycloheptanol and *cis*-4-methylcycloheptanol. *trans*-3-Methylcycloheptanol and *trans*-4-methylcycloheptanol were obtained from catalytic reduction of the *exo* isomer. The 3-methylcycloheptanols were identified by gas chromatography and by comparison of their infrared spectra with the spectra of the 3-methylcycloheptanols obtained previously from the reduction of *endo*- and *exo*-bicyclo[5.1.0]octan-2-ol.

Stereochemistry of Bicyclo[5.1.0]octan-4-ols.—Configurations of bicyclo[5.1.0]octan-4-ols have been assigned on the basis of evidence similar to that employed for the assignment of configurations

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[13] S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961).

[14] W. R. Moore and R. L. Thornton, to be published.

[15] M. Godchot and G. Cauquil, *Compt. rend.*, **190**, 642 (1930).

[16] A. C. Cope and J. K. Hecht, *J. Am. Chem. Soc.*, **84**, 4872 (1962).

[17] H. C. Brown and G. Zweifel, *ibid.*, **81**, 247 (1959).

[18] P. D. Bartlett and C. M. Berry, *ibid.*, **56**, 2683 (1934).

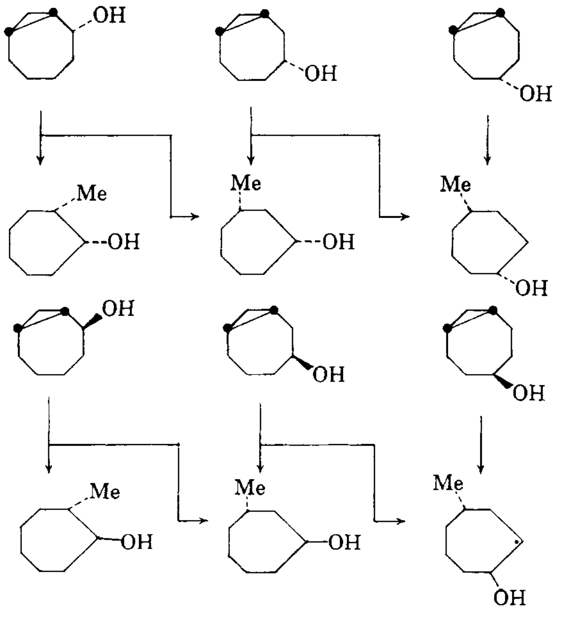
[19] S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

[20] D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

[21] K. Savard, *J. Biol. Chem.*, **202**, 457 (1953).

[22] E. L. Eliel and C. A. Lukach, *J. Am. Chem. Soc.*, **79**, 5986 (1957).

to bicyclo[5.1.0]octan-3-ols. Examination of models shows that the *endo* isomer (Fig. 1, R_6 = OH, R_1 = R_2 = R_3 = R_4 = R_5 = H) possesses an axially oriented hydroxyl group, whereas the *exo* isomer (Fig. 1, R_5 = OH, R_1 = R_2 = R_3 = R_4 = R_6 = H) possesses an equatorially oriented hydroxyl group. Therefore, contrary to the case of the bicyclo[5.1.0]-octan-3-ols, *endo*-bicyclo[5.1.0]octan-4-ol is expected to be more hindered and thus thermodynamically less stable than the *exo* isomer. In fact, equilibration of the *endo* isomer under Meerwein–Ponndorf conditions gave 35% of the *endo* and 65% of the *exo* isomer. Equilibration of the *exo* isomer under the same conditions yielded 33% of the *endo* and 67% of the *exo* isomer. The *endo* isomer was also eluted more easily than the *exo* isomer on chromatography on alumina, and catalytic hydrogenation of bicyclo[5.1.0]octan-4-one in acetic acid containing a trace of hydrochloric acid produced the *endo* and *exo* isomers in a ratio of 91 to 9%. In agreement with other lines of evidence, the infrared spectrum of the *exo* isomer showed a stronger band corresponding to a hydrogen-bonded hydroxyl group than did the *endo* isomer. Hydrogenation of the cyclopropane ring of the *endo* isomer yielded *cis*-4-methylcycloheptanol identical with the compound previously obtained from the hydrogenation of *endo*-bicyclo[5.1.0]octan-3-ol. *trans*-4-Methylcycloheptanol was obtained from the hydrogenation of *exo*-bicyclo[5.1.0]octan-4-ol. The hydrogenation of all six of the bicyclo[5.1.0]octanols is summarized in the equations



Since *exo*-bicyclo[5.1.0]octan-4-ol possesses an axially oriented C_4–hydrogen atom (Fig. 1, R_6), while the *endo* isomer possesses an equatorially oriented C_4–hydrogen atom (Fig. 1, R_5), the n.m r. spectrum of the *exo* isomer would be expected to show signals due to the hydrogen atom at higher field and split more than the spectrum of the *endo* isomer. The peak due to the C_4–hydrogen atom of the *exo* isomer was observed at τ = 6.5 with a width at half height of 22 c.p.s., while that of the *endo* isomer was observed at τ = 5.9 with a width at half height of 8 c.p.s.

Experimental[23,24]

3-Cyclohepten-1-ol.—To a solution of 24.6 g. of 1,3-cycloheptadiene[6] in 200 ml. of ether, 50 g. of commercial 40% peracetic acid solution (after the sulfuric acid present was neutralized with 11.5 g. of sodium acetate trihydrate) was added at such a rate that the reaction mixture was maintained under gentle reflux. After the reaction subsided, the ether layer was washed with water, and then with 0.5 *N* sodium thiosulfate solution until the washings no longer colored potassium iodide in acetic acid solution. The ether solution was washed with 5% sodium carbonate followed by water, and dried over magnesium sulfate. Removal of the solvent gave 18 g. of a crude product which showed one major peak on gas chromatography on silicone oil at 140°; however, a large portion of the product remained in the column, indicating that the crude product contained a considerable amount of polymeric material. An attempt to purify the product by distillation resulted in extensive polymerization. Therefore, the crude product was used for the subsequent reaction without further purification. A pure sample of 3-cyclohepten-1-one was collected by gas chromatography on silicone oil at 140°, $n^{25}\text{D}$ 1.4811. The ketone exhibits infrared absorption at 1650 cm.$^{-1}$ (C=C) and 1707 cm.$^{-1}$ (C=O) with an ultraviolet maximum[25] at 284 mμ (ε 80).

Anal. Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.31; H, 9.21.

Its 2,4-dinitrophenylhydrazone was prepared by the experimental procedure used for the preparation of 2,4,6-cycloheptatriene - 1 - carboxaldehyde 2,4 - dinitrophenylhydrazone.[26] The 2,4-dinitrophenylhydrazone formed brown needles. and had m.p. 147.0–147.5° after three recrystallizations from 95% ethanol. It exhibits an ultraviolet maximum[25] at 360 mμ (ε 22,000).

Anal. Calcd. for $C_{13}H_{14}O_4N_4$: C, 53.79; H, 4.86. Found: C, 53.82; H, 4.93.

The semicarbazone of the ketone had m.p. 154–155° (lit.[27] m.p. 155–156°).

The crude 3-cyclohepten-1-one (16 g.) was reduced with lithium aluminum hydride in ether at room temperature for 30 minutes and the pure 3-cyclohepten-1-ol (4.6 g., 16% on the basis of 1,3-cycloheptadiene) was isolated by silver nitrate extraction.[3] The alcohol so obtained had a different retention time from that of 2-cyclohepten-1-ol[6] on gas chromatography on TCEP at 110°. An analytical sample, $n^{25}\text{D}$ 1.4903, was collected by gas chromatography (silicone oil, 140°).

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.65; H, 10.63.

3-Cyclohepten-1-yl phenylurethan was recrystallized four times from *n*-pentane; m.p. 98–99°.

Anal. Calcd. for $C_{14}H_{17}O_2N$: C, 72.70; H, 7.41. Found: C, 72.46; H, 7.38.

3-Cyclohepten-1-yl acetate (0.65 g.) was prepared from 0.57 g. of 3-cyclohepten-1-ol, 1.2 g. of acetic anhydride and 1 g. of dry pyridine according to the procedure described for the preparation of 3-cycloöcten-1-yl acetate.[4] A sample collected by gas chromatography (silicone oil, 170°) was analyzed.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.40; H, 9.32.

When the reaction of 1,3-cycloheptadiene with 40% peracetic acid was carried out without ether as solvent, extensive polymerization took place and none of the desired product was isolated. The reaction of the diene with monoperphthalic acid in ether at 0° or at room temperature also gave only polymeric material.

Bicyclo[5.1.0]octan-3-ols.—A mixture containing methylene iodide (57.5 g.), iodine (0.15 g.), zinc–copper couple

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

(24) Reference 3, footnote 24, describes the conditions and equipment used for gas chromatography.

(25) Determined as a solution in 95% ethanol.

(26) A. C. Cope, N. A. Nelson and D. S. Smith, *J. Am. Chem. Soc.*, **76**, 1100 (1954).

(27) E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 614 (1954).

(17.5 g., prepared by the procedure of Shank and Shechter[8]) and anhydrous ether (165 ml.) was heated under reflux with stirring for 0.5 hour. External heating was discontinued and a solution of 4 g. of 3-cyclohepten-1-ol in 10 ml. of anhydrous ether was added at such a rate that the mixture was maintained under gentle reflux. Heating was resumed, and after 24 hours, the mixture was treated as described by Shank and Shechter[8] to give 4.0 g. (89%) of product which later was shown to be *endo*-bicyclo[5.1.0]octane-3-ol. The product showed one major peak on gas chromatography (TCEP at 140°). A sample collected by gas chromatography on silicone oil at 140° exhibited infrared absorption at 3050 cm.$^{-1}$ (cyclopropane ring), 3330 and 3600 cm.$^{-1}$ (OH).

In two other runs conducted under the same conditions, the bicyclic alcohol was obtained in 89–90% yield. An analytical sample, $n^{25}\mathrm{D}$ 1.4892, was collected by gas chromatography on silicone oil at 142°.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.23; H, 11.25.

endo-Bicyclo[5.1.0]oct-3-yl phenylurethan was recrystallized twice from *n*-hexane; m.p. 98.0–98.5°.

Anal. Calcd. for $C_{15}H_{19}O_2N$: C, 73.44; H, 7.81. Found: C, 73.37; H, 7.93.

When 3-cyclohepten-1-yl acetate (0.5 g.) was treated with an equivalent amount of methylene iodide and 25% excess of zinc–copper couple, a mixture containing mostly the original acetate and *ca.* 10% of *endo* - and *exo*-bicyclo[5.1.0]oct-3-yl acetate in the ratio of 63 to 37% was obtained. The products were identified (after saponification) as the corresponding alcohols by gas chromatography on TCEP at 150° and by comparison of their infrared spectra with those of authentic samples.

endo-Bicyclo[5.1.0]octan-3-ol (2 g.) was oxidized to bicyclo[5.1.0]octan-3-one (1.73 g., 85%) with 9 g. of chromic anhydride in 65 ml. of pyridine according to the procedure[3] described for the preparation of bicyclo[5.1.0]octan-2-one. A sample collected by gas chromatography on silicone oil at 140° was analyzed; $n^{25}\mathrm{D}$ 1.4798.

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.03; H, 9.70.

The 2,4-dinitrophenylhydrazone of bicyclo[5.1.0]octan-3-one formed yellow needles and was analyzed after three recrystallizations from 95% ethanol; m.p. 119.5–120.5°.

Anal. Calcd. for $C_{\;4}H_{16}O_4N_4$: C, 55.25; H, 5.38. Found: C, 55.53; H, 5.32.

To 100 mg. of bicyclo[5.1.0]octan-3-one dissolved in 5 ml. of 95% ethanol 0.5 g. of sodium borohydride was added, and the mixture was heated on a steam-bath for 1 hour. The cooled mixture was diluted with 50 ml. of water and extracted with ether. The combined ether extracts were washed with water, dried, and the solvent was removed to give 80 mg. of material, which was later shown to contain 30% of *endo*- and 70% of *exo*-bicyclo[5.1.0]octan-3-ol, estimated by gas chromatography on TCEP at 140°. In another run conducted in the same manner, 1.7 g. of the ketone yielded 1.4 g. of a mixture containing 26.5 % of the *endo* and 73.5% of the *exo* isomer. When bicyclo[5.1.0]octan-3-one was reduced with lithium aluminum hydride in ether at room temperature for 0.5 hour, the product contained 35% of the *endo* and 65% of the *exo* isomer.

The mixture of *endo*- and *exo*-bicyclo[5.1.0]octan-3-ol (1.4 g.) was passed through a column (35 × 1.8 cm., with a water-cooled jacket) of 100 g. of alumina, (acid-washed, activity II) packed in pentane. The column was eluted with pentane and the eluent was gradually changed to 10, 20, 30, 40 and 50% ether–pentane mixtures. The pure *exo* isomer was obtained when the column was eluted with 30% ether in pentane, followed by the *endo* isomer. An analytical sample of *exo*-bicyclo[5.1.0]octan-3-ol, $n^{25}\mathrm{D}$ 1.4934, was collected by gas chromatography (silicone oil, 140°).

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.13; H, 11.09.

exo-Bicyclo[5.1.0]oct-3-yl phenylurethan was recrystallized three times from *n*-hexane; m.p. 76–77°.

Anal. Calcd. for $C_{15}H_{19}O_2N$: C, 73.44; H, 7.81. Found: C, 73.38; H, 7.92.

Bicyclo[6.1.0]non-4-ene.—Bicyclo[6.1.0]non-4-ene was prepared from 1,5-cycloöctadiene by the procedure used by Shank and Shechter[8] for the preparation of *n*-hexylcyclopropane from 1-octene. The crude reaction product contained 51% of the unchanged starting material, 37% of bicyclo-[6.1.0]non-4-ene and 12% of tricyclo[7.1.0.0^{4,6}]decanes (isomer A and isomer B in yields of 7 and 5%), estimated by gas chromatography on silicone oil at 110°. When the reaction was carried out with two equivalents of methylene iodide and zinc–copper couple, the composition of the products was found to be 27% of the starting material, 35% of the bicycloölefin and 38% of the tricyclodecanes (isomer A and isomer B in yields of 21 and 17%; isomer A has the shorter retention time on the silicone oil column). Presumably A and B are *cis* and *trans* isomers. The starting material was removed from the products by silver nitrate extraction[3] and the remainder was distilled under reduced pressure. The fraction boiling at 68–75° (22 mm.) contained 71% of bicyclo[6.1.0]non-4-ene and 29% of the tricyclodecanes, and the fraction boiling at 75–85° (22 mm.) contained 20% of the bicyclic olefin and 80% of the tricyclodecanes. An analytical sample of bicyclo[6.1.0]non-4-ene, $n^{25}\mathrm{D}$ 1.4933, was collected by gas chromatography (silicone oil, 120°).

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.53; H, 11.50.

A sample of tricyclo[7.1.0.0^{4,6}]decane (isomer A) was collected by gas chromatography (silicone oil, 120°), m.p. 41.5–42.0°.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.18; H, 12.01.

An analytical sample of tricyclo[7.1.0.0^{4,6}]decane (isomer B) was also collected by gas chromatography (silicone oil, 120°), $n^{25}\mathrm{D}$ 1.4880.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.24; H, 11.84.

cis-**1,2-Cyclopropanedipropionic Acid.**—Fifty grams of the mixture containing 71% of bicyclo[6.1.0]non-4-ene and 29% of tricyclo[7.1.0.0^{4,6}]decanes dissolved in 3.3 l. of acetone was stirred in the presence of 26 g. of sodium bicarbonate. Then 133 g. of granulated potassium permanganate was added in small portions. The mixture became warm (up to 54°) and, after addition was complete, the mixture was stirred until it returned to room temperature (*ca.* 4–5 hours). The mixture was filtered and the acetone in the filtrate was removed under reduced pressure. The residue was dissolved in 100 ml. of ether and extracted with three 20-ml. portions of 5% sodium carbonate and two 20-ml. portions of water. The ether solution was dried, and the solvent was removed to give 10 g. of the unchanged tricyclo[7.1.0.0^{4,6}]decanes. The cake of manganese dioxide was washed with the aqueous basic solution employed to wash the ether solution and with an additional 2 l. of 3% sodium carbonate solution. The basic extracts were concentrated to *ca.* 700 ml. under reduced pressure. The resulting basic solution was washed with three 200-ml. portions of ether and acidified to congo red with 20% sulfuric acid at 0–10°. The aqueous solution was saturated with sodium chloride and extracted with four 250-ml. portions of ether. The combined ether extracts were washed with three 100-ml. portions of saturated sodium chloride solution, and dried over magnesium sulfate. Evaporation of the ether yielded 36 g. (67%) of a yellow oil which solidified on standing. One gram of the crude dicarboxylic acid was dissolved in 3 ml. of ethyl acetate and the solution was treated with Norit. The filtered solution was concentrated to 2 ml. and allowed to stand at *ca.* 3° overnight. The colorless solid was collected on a filter and recrystallized from a benzene–pentane mixture to give 0.6 g. of the pure dicarboxylic acid, m.p. 78–79°.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.83; H, 7.54.

Bicyclo[5.1.0]octan-4-one.—A mixture of 35 g. of *cis*-1,2-cyclopropanedipropionic acid, 200 ml. of absolute methanol and 10 drops of 6 *M* hydrochloric acid was stirred at room temperature for 27 hours. The excess methanol was removed under reduced pressure, and the residue was dissolved in 800 ml. of ether. The ether solution was washed successively with 200 ml. of water, three 200-ml. portions of 5% sodium carbonate, three 200-ml. portions of water and 200 ml. of saturated sodium chloride solution. After drying (magnesium sulfate), removal of the solvent yielded 35 g. (87%) of the crude dimethyl ester. The pure *cis*-1,2-cyclopropanedipropionic acid dimethyl ester distilling at 100–104° (0.7 mm.) weighed 31 g. (77%). A fraction boiling at 103° (0.7 mm.) was analyzed, $n^{25}\mathrm{D}$ 1.4481.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.36; H, 8.45.

A 3-necked, 500-ml. Morton flask was fitted with a high speed stirrer, a nitrogen inlet and a high dilution apparatus.[11] Eleven grams of commercial 50% sodium hydride in mineral oil was placed in the flask and washed with four 25-ml. portions of xylene (distilled from sodium). After the whole apparatus had been filled with dry nitrogen, 234 ml. of xylene was added. A very slow stream of nitrogen was passed through the apparatus throughout the experiment. The suspension was stirred rapidly and 0.2 ml. of absolute methanol was added. The flask was heated and as soon as the mixture refluxed vigorously, 20 g. of the dimethyl ester dissolved in 168 ml. of xylene was added during a period of 20 hours. The mixture was refluxed for 1 hour after addition was complete, and then allowed to cool to room temperature. The nitrogen inlet was replaced by a dropping funnel, and 14 g. of acetic acid was added to the stirred solution at such a rate that the reaction mixture did not become warm. After the mixture had been stirred for 1 hour, 13.4 ml. of water was added slowly. A few crystals of sodium acetate were added with cooling in order to induce precipitation of the sodium acetate in the mixture. The precipitate was collected and washed with xylene. The xylene solution was successively washed with 200 ml. of 5% sodium carbonate, three 200-ml. portions of water and 200 ml. of saturated sodium chloride solution. The solution was dried over magnesium sulfate, and the solvent was removed at 41–42° (18 mm.). The residue was fractionated through a semi-mico column to give 11.4 g. (67.5%) of the β-keto ester, b.p. 85–91° (0.2 mm.). The infrared spectrum of the β-keto ester exhibited cyclopropane absorption bands at 3050 and 1029 cm.$^{-1}$ and carbonyl absorption bands at 1740 and 1700 cm.$^{-1}$ along with slight shoulders at 1650 and 1630 cm.$^{-1}$. A fraction distilling at 89° (0.2 mm.) was analyzed; n^{25}D 1.4843.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.84; H, 7.62.

A mixture of 14.2 g. of 3-carbomethoxy-bicyclo[5.1.0]-octan-4-one and 177 ml. of 5.3% sodium hydroxide solution was stirred at room temperature for 4 hours. It became homogeneous during the first 0.5 hour. The mixture was carefully acidified to congo red with 6 *M* hydrochloric acid, and stirred for 0.5 hour. The aqueous solution was then heated on a steam-bath for 0.5 hour. The cooled mixture was extracted with four 70-ml. portions of ether and the combined ether extracts were washed successively with 100 ml. of water, two 100-ml. portions of 5% sodium carbonate, three 100-ml. portions of water and 100 ml. of saturated sodium chloride solution. After drying over magnesium sulfate, the solvent was removed to give 9.4 g. (97%) of the product which was shown to be homogeneous by gas chromatography (silicone oil, 130°). An analytical sample, n^{25}D 1.4798, was collected by gas chromatography.

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.31; H, 9.74.

Bicyclo[5.1.0]octan-4-one 2,4-dinitrophenylhydrazone was recrystallized twice from 95% ethanol as bright orange needles, m.p. 137.0–137.6°.

Anal. Calcd. for $C_{14}H_{16}O_4N_4$: C, 55.25; H, 5.38. Found: C, 55.19; H, 5.15.

Bicyclo[5.1.0]octan-4-ols.—To a solution of 5 g. of bicyclo[5.1.0]octan-4-one in 50 ml. of 95% ethanol was added 1 g. of sodium borohydride. The mixture became warm and, after 10 minutes, 50 ml. of water was added and the mixture was heated to the boiling point. The cooled solution was diluted with 250 ml. of water and extracted with four 100-ml. portions of ether. The combined ether extracts were washed with three 100-ml. portions of water and 100 ml. of saturated sodium chloride solution. After drying, the solvent was removed to give 4.8 g. (94%) of a mixture which was later shown to contain 35% of *endo*- and 65% of *exo*-bicyclo[5.1.0]octan-4-ol, estimated by gas chromatography on TCEP at 125°. The mixture was placed on a column of 100 g. of alumina (acid-washed, activity II) packed in pentane. The column was eluted with pentane, and then with 5, 10, 20, 30, 40 and 50% ether–pentane mixtures. The fractions eluted with a 20% ether–pentane mixture contained the pure *endo* isomer and the fractions eluted with a 30% ether–pentane mixture contained both the *endo* and *exo* isomers. Finally, the fractions eluted with 40–100% ether–pentane mixtures contained the pure *exo* isomer.

endo-Bicyclo[5.1.0]octan-4-ol was recrystallized twice from *n*-pentane; m.p. 48–49°: *Anal.* Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.09; H, 11.04.

endo-Bicyclo[5.1.0]oct-4-yl phenylurethan was recrystallized twice from *n*-hexane; m.p. 114.0–114.5°: *Anal.* Calcd. for $C_{15}H_{19}O_2N$: C, 73.44; H, 7.81. Found: C, 73.47; H, 7.82.

exo-Bicyclo[5.1.0]octan-4-ol was recrystallized four times from *n*-pentane; m.p. 54–55°: *Anal.* Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.97; H, 11.23.

exo-Bicyclo[5.1.0]oct-4-yl phenylurethan was recrystallized once from *n*-hexane and again from *n*-pentane; m.p. 134.0–134.5°: *Anal.* Calcd. for $C_{15}H_{19}O_2N$: C, 73.44; H, 7.81. Found: C, 73.41; H, 7.89.

Reaction of 2-Cyclohepten-1-ol with Methylene Iodide and Zinc–Copper Couple.—2-Cyclohepten-1-ol was treated with methylene iodide and zinc–copper couple as described for the preparation of *endo*-bicyclo[5.1.0]octan-3-ol from 3-cyclohepten-1-ol. Starting with 2.87 g. of methylene iodide, 0.87 g. of zinc–copper couple, 200 mg. of 2-cyclohepten-1-ol and 10 ml. of ether, 150 mg. of a mixture was obtained. It contained 91% of *endo*- and 9% of *exo*-bicyclo[5.1.0]octan-2-ol, identified by gas chromatography on TCEP at 130°, and by comparison of infrared spectra with those of authentic samples.

Equilibration of the Bicyclic Alcohols.—Equilibration of the alcohols was carried out in the following manner. A mixture of 50 mg. of a pure sample of the appropriate alcohol, 100 mg. of freshly distilled aluminum isopropoxide, 1 ml. of dry isopropyl alcohol and 0.07 ml. of anhydrous acetone was heated under reflux for 7 days (at the end of this time the mixture had not necessarily reached equilibrium). The cooled mixture was then diluted with 2 ml. of water, and 20% sulfuric acid was added dropwise until the mixture became clear. The clear solution was extracted with four 2-ml. portions of ether, and the combined ether extracts were washed successively with three 3-ml. portions of water, 2 ml. of 5% sodium carbonate and 3 ml. of saturated sodium chloride solution. After drying over magnesium sulfate, the solvent was removed and the mixture was identified by gas chromatography on TCEP at 110–140°, and by comparison of the infrared spectra of the alcohols (separated by gas chromatography) with those of authentic samples.

Equilibration of *endo*-bicyclo[5.1.0]octan-3-ol gave 75% of the *endo* and 25% of the *exo* isomer; equilibration of *exo*-bicyclo[5.1.0]octan-3-ol gave 82% of the *endo* and 18% of the *exo* isomer. Equilibration of *endo*-bicyclo[5.1.0]octan-4-ol gave 35% of the *endo* and 65% of the *exo* isomer; equilibration of *exo*-bicyclo[5.1.0]octan-4-ol gave 33% of the *endo* and 67% of the *exo* isomer.

Catalytic Reduction of Bicyclo[5.1.0]octan-3-one.—Bicyclo[5.1.0]octan-3-one (62 mg.) in 10 ml. of acetic acid containing one drop of concentrated hydrochloric acid was hydrogenated in the presence of pre-reduced platinum oxide (*ca.* 30 mg.) at room temperature under atmospheric pressure. In 1 hour, 109% of the calculated amount of hydrogen was absorbed. The catalyst was removed by filtration, and the filtrate was diluted with 50 ml. of water and extracted with four 10-ml. portions of ether. The combined ether extracts were washed with three 15-ml. portions of water, two 40-ml. portions of 5% sodium carbonate and 10 ml. of saturated sodium chloride solution. After drying over magnesium sulfate, the solvent was removed to give 58 mg. of product which, after saponification with 15% sodium hydroxide in 50% methanol–water at room temperature for 24 hours, yielded 45 mg. of a mixture containing bicyclo[5.1.0]octan-3-ols in the ratio of 8 (*endo*) to 92% (*exo*) estimated by gas chromatography on TCEP at 140°. The isomers were identified by comparison of their infrared spectra with the spectra of authentic samples.

Catalytic Reduction of Bicyclo[5.1.0]octan-4-one.—Bicyclo[5.1.0]octan-4-one was hydrogenated by the same procedure employed for the hydrogenation of bicyclo[5.1.0]-octan-3-one. Starting with 66 mg. of the ketone in 5 ml. of acetic acid containing 1 drop of concentrated hydrochloric acid, 58 mg. of product was obtained after 140% of the calculated amount of hydrogen had been absorbed. The product was shown to contain 40% of *cis*-4-methylcycloheptanol, 55% of *endo*-bicyclo[5.1.0]octan-4-ol and 5% of *exo*-bicyclo-[5.1.0]octan-4-ol, estimated by gas chromatography on TCEP at 127°. The identities of the components were proved by comparison of their infrared spectra with those of authentic samples.

Preparation of *cis*- and *trans*-2-Methylcycloheptanol.—*cis*-2-Methylcycloheptanol was prepared according to the procedure of Godchot and Cauquil.[16] 2-Methylcycloheptanone[16] (92 mg.) in 5 ml. of glacial acetic acid containing one drop of concentrated hydrochloric acid was hydrogenated in the presence of pre-reduced platinum oxide (100 mg.) at room temperature (30°) under atmospheric pressure. In 1 hour, 112% of the calculated amount of hydrogen was absorbed. The mixture was treated as described for the catalytic reduction of bicyclo[5.1.0]octan-3-one. *cis*-2-Methylcycloheptanol (80 mg.) thus obtained was shown to be homogeneous by gas chromatography on TCEP at 120°.

Equilibration of 50 mg. of *cis*-2-methylcycloheptanol by the procedure described previously gave 40 mg. of a mixture containing 14% of 2-methylcycloheptanone and mostly *trans*-2-methylcycloheptanol with less than 10% of the *cis* isomer, estimated by gas chromatography on TCEP at 120°. The components were identified by comparison of their infrared spectra with those of authentic samples.

An ether solution of halide-free dimethylmagnesium was prepared[28] from 2.7 g. of magnesium, 15.8 g. of methyl iodide, 100 ml. of ether and 38 ml. of dioxane. To one-quarter of the solution 0.5 g. of cycloheptene oxide in 10 ml. of ether was added. The solvent was distilled and the residue was heated on a steam-cone for 1 hour. The mixture was poured into 100 ml. of ice-water, and 6 *N* hydrochloric acid was added dropwise until the cloudiness disappeared. The organic material was extracted with four 20-ml. portions of ether and the combined ether layers were washed successively with two 20-ml. portions of water, 15 ml. of saturated sodium bicarbonate and 20 ml. of saturated sodium chloride solution. After drying (magnesium sulfate), evaporation of the solvent yielded 0.45 g. of a mixture containing 5% of *trans*-2-methylcycloheptanol and 95% of the unchanged starting material, identified by gas chromatography on TCEP at 140° and by comparison of their infrared spectra with the spectra of authentic samples.

Catalytic Reduction of the Bicyclic Alcohols.—*endo*-Bicyclo[5.1.0]octan-2-ol (126 mg.) in 7.5 ml. of glacial acetic acid was hydrogenated in the presence of pre-reduced platinum oxide (*ca.* 100 mg.) at 44 ± 1° under atmospheric pressure. In 0.5 hour, 103% of the calculated amount of hydrogen was absorbed. The catalyst was removed by filtration and the filtrate was treated as described for the catalytic reduction of bicyclo[5.1.0]octan-3-one to give 85 mg. of crude product. The product was then reduced with lithium aluminum hydride in ether at room temperature for 0.5 hour to give 60 mg. of a mixture containing 16% of *cis*-2-methylcycloheptanol, 18% of an unknown alcohol and 66% of unchanged starting material, estimated by gas chromatography on TCEP at 120°. The unknown alcohol was first tentatively assigned the structure of *cis*-3-methylcycloheptanol, and its identity was proved by the subsequent hydrogenation of *endo*-bicyclo[5.1.0]octan-3-ol, since *cis*-3-methylcycloheptanol is the only alcohol expected to be formed from the reduction of both *endo*-bicyclo[5.1.0]octan-2-ol and *endo*-bicyclo[5.1.0]octan-3-ol. The identities of the components of the hydrogenation products were proved by comparison of their infrared spectra.

Catalytic reduction of *exo*-bicyclo[5.1.0]octan-2-ol under the same conditions (after 105% of the calculated amount of hydrogen had been absorbed in 25 minutes) gave a mixture containing 91% of *trans*-2-methylcycloheptanol and 9% of *trans*-3-methylcycloheptanol.

Catalytic reduction of *endo* - bicyclo[5.1.0]octan-3-ol yielded 6% of unchanged starting material and 94% of an alcohol mixture whose infrared spectrum was identical with that of an authentic mixture of 50% of *cis*-3-methylcycloheptanol and 50% of *cis*-4-methylcycloheptanol.

Catalytic reduction of *exo*-bicyclo[5.1.0]octan-3-ol (after 117% of the calculated amount of hydrogen had been absorbed in 20 minutes) yielded a mixture containing 42% of *trans*-3-methylcycloheptanol and 58% of *trans*-4-methylcycloheptanol.

endo-Bicyclo[5.1.0]octan-4-ol (after 106% of the calculated amount of hydrogen had been absorbed in 20 minutes) yielded *cis*-4-methylcycloheptanol (90%); no other product was present.

exo - Bicyclo[5.1.0]octan - 4 - ol (after 109% of the calculated amount of hydrogen had been absorbed in 30 minutes) gave *trans*-4-methylcycloheptanol in 87% yield; and no other product was formed.

Analytical samples of *cis*-and *trans*-3-methylcycloheptanol were collected by gas chromatography (TCEP, 120°). *Anal.* Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found for the *cis* isomer: C, 74.74; H, 12.76. Found for the *trans* isomer: C, 74.85; H, 12.68.

An analytical sample of *cis*-4-methylcycloheptanol, n^{25}_D 1.4680, was collected by gas chromatography (TCEP, 135°). *Anal.* Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 75.06; H, 12.35.

An analytical sample of *trans*-4-methylcycloheptanol, n^{25}_D 1.4658, was collected by gas chromatography (TCEP, 135°). *Anal.* Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.79; H, 12.61.

cis- and *trans*-3-methylcycloheptanol were also obtained from sodium borohydride reduction of 3-methylcycloheptanone[16] according to the procedure described for the reduction of bicyclo[5.1.0]octan-4-one. Starting from 100 mg. of 3-methylcycloheptanone, 100 mg. of a mixture containing 47% of *cis*- and 53% of *trans*-3-methylcycloheptanol was obtained, estimated by gas chromatography on TCEP at 120°. Infrared spectra of the isomers collected by gas chromatography were identical with those of *cis*- and *trans*-3-methylcycloheptanol obtained from the catalytic reduction of *endo*- and *exo*-bicyclo[5.1.0]octan-2-ol and *endo*- and *exo*-bicyclo[5.1.0]octan-3-ol.

cis-4-Methylcycloheptyl acetate (50 mg., 94%) was prepared from the corresponding alcohol (40 mg.) by the pyridine–acetic anhydride method, and an analytical sample was collected by gas chromatography (TCEP, 130°).

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.41; H, 10.92.

trans-4-Methylcycloheptanol (60 mg.) was converted to the corresponding acetate (73 mg., 91%) in the same manner.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.83; H, 10.75.

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