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.[13] 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.[13] 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.[13] *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.[13] 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]

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

RECEIVED JUNE 22, 1962

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-

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

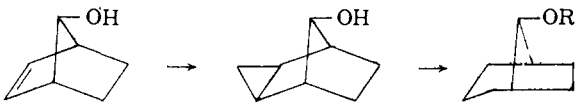
(2) Paper XXIX, A. C. Cope, C. H. Park and P. Scheiner, *J. Am. Chem. Soc.*, **84**, 4862 (1962).

(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).

tion of the corresponding ketone, the rates of oxidation of the epimeric alcohols and a study of the solvolysis products. These lines of evidence involve mechanistic interpretations, and accordingly we have sought completely unambiguous evidence for the configurations. Thus, *exo*-bicyclo[3.2.1]oct-8-yl acetate was synthesized stereospecifically in the following manner. *anti*-7-Norbornenol,[6] a compound of established configuration, was prepared from norbornadiene by the method of Story.[7] *anti*-7-Norbornenol, on treatment with methylene iodide and zinc–copper couple,[8] formed *anti*-7-tricyclo[3.2.1.$0^{2,4}$]octanol in low yield. Although not proved, the methylene group is probably *exo*, as the known addition reactions to norbornene normally occur from the *exo* side. Hydrogenation of cyclopropane derivatives in acetic acid using platinum oxide as a catalyst results in cleavage of the cyclopropane ring, and has been useful in solving other stereochemical problems.[2,9] Hydrogenation of the tricyclic octanol gave two products. The minor product was shown to be *exo*-bicyclo[3.2.1]oct-8-yl



acetate, and gas chromatography showed that there was no detectable amount of *endo*-bicyclo[3.2.1]oct-8-yl acetate. This evidence confirms the configurations previously assigned to these alcohols.[5] The major product from the hydrogenation presumably was 2-methyl-bicyclo[2.2.1]hept-7-yl acetate, but no further work was done to determine the structure of this compound.

Bicyclo[4.2.0]octan-2-ols.—Tentative assignment of configuration to the bicyclo[4.2.0]octan-2-ols[4] was based on the assumption that the hydroxyl group of *endo*-bicyclo[4.2.0]octan-2-ol is more sterically hindered as a result of the restrictions imposed on the bicyclic system by the cyclobutane ring. Thus the isomer which was oxidized faster with chromium trioxide[10,11] and which was obtained as the major product from catalytic hydrogenation[12] of bicyclo[4.2.0]octan-2-one was assigned the *endo* configuration. Furthermore, comparison of the infrared spectra of the two isomers showed that the alcohol which was assigned the *endo* configuration had a much less intense hydrogen-bonded hydroxyl absorption, a fact which was attributed to the shielding of the hydroxyl group of the more hindered alcohol by close-neighboring carbon and hydrogen atoms.

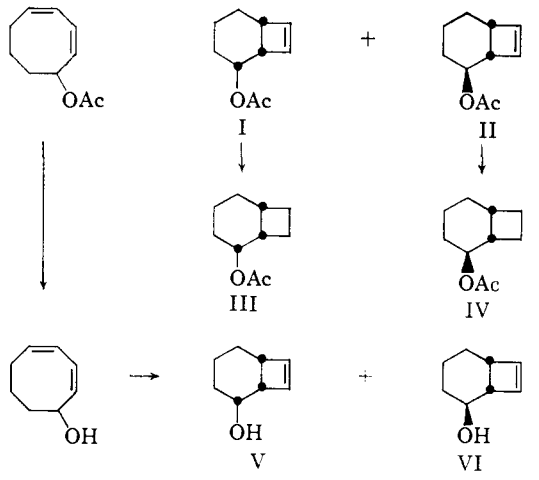
Study of molecular models shows that the hydroxyl group of bicyclo[4.2.0]octan-2-ols can exist in two conformations with the hydroxyl groups in pseudoaxial and in pseudoequatorial positions. Thus, it is possible for both isomers of bicyclo[4.2.0]-octan-2-ol to have the hydroxyl group in the pseudoequatorial position, and it is not clear which isomer would be more hindered. Furthermore, recent observations made in equilibration and reduction experiments with bicyclo[5.1.0]octanols[9] have shown that the *endo* compound is not less stable than the *exo* isomer in all cases. Therefore, it was necessary to obtain independent chemical evidence from which the configurations of these bicyclic alcohols could be assigned. This evidence described below has substantiated the original assignment of stereochemistry.

The stereochemistry of the bicyclo[4.2.0]octan-2-ols and bicyclo[4.2.0]octan-3-ols were interrelated in the following manner. Epoxidation of bicyclo-[4.2.0]oct-2-ene produced two isomeric epoxides in relative amounts of 75% and 25%. On treatment with lithium aluminum hydride, the epoxide obtained in major yield, later shown to be the *exo* isomer and purified by gas chromatography, gave a mixture of *exo*-bicyclo[4.2.0]octan-2-ol and *exo*-bicyclo[4.2.0]octan-3-ol, separated by gas chromatography and identified as the acetates. Similar treatment of the *endo*-epoxide with lithium aluminum hydride gave a mixture of the *endo*-alcohols, which could not be separated by gas chromatography, either as alcohols or as acetates. However the infrared spectrum of the alcohol mixture showed that it contained principally *endo*-bicyclo[4.2.0]-octan-3-ol.

The recent discovery[13] that 1,3-cyclooctadiene can be converted to bicyclo[4.2.0]oct-7-ene by irradiation suggested the possible syntheses of the bicyclo[4.2.0]oct-7-en-2-ols by photoisomerization of 2,4-cyclooctadien-1-ol or a derivative.

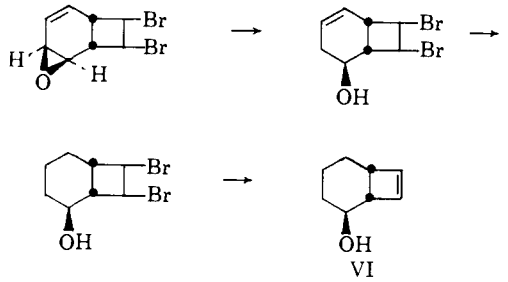
Irradiation of 2,4-cyclooctadiene-1-yl acetate, prepared from 1,3-cyclooctadiene as described in the Experimental section, afforded a mixture of *endo*-bicyclo[4.2.0]oct-7-en-2-yl acetate (I) and *exo*-bicyclo-[4.2.0]oct-7-en-2-yl acetate (II) (in a 3-to-1 ratio) which could be separated by preparative gas chromatography. The bicyclic skeletons of I and II were established by catalytic hydrogenation to the corresponding *endo*- and *exo*-bicyclo-[4.2.0]oct-2-yl acetates. Compound I was hydrogenated to III which was prepared by acetylation of the bicyclo[4.2.0]octan-2-ol that was assigned the *endo* configuration in the earlier work.[4] Hydrogenation of II afforded IV which was identical with the sample prepared by acetylation of the bicyclo-[4.2.0]octan-2-ol which was originally assigned the *exo* configuration.[4] The irradiation of 2,4-cyclooctadiene-1-ol gave a mixture of the photoisomers V and VI, which were partially separated by gas chromatography and could be more conveniently separated through their acetates, which were shown to be identical with the ones obtained from the irradiation of 2,4-cyclooctadien-1-yl acetate. The ratio of I to II obtained from the photoproducts of 2,4-cyclooctadien-1-ol followed by acetylation also was found to be 3 to 1. The rate of photoisomerization of 2,4-cyclooctadiene-1-yl acetate was much faster than that of the corresponding alcohol.

(6) S. Winstein and M. Shatavsky, *J. Am. Chem. Soc.*, **78**, 592 (1956).
(7) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).
(8) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959); R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).
(9) A. C. Cope, S. Moon and C. H. Park, *J. Am. Chem. Soc.*, **84**, 4843 (1962).
(10) J. Schrieber and A. Eschenmoser, *Helv. Chim. Acta*, **38**, 1529 (1955).
(11) H. Kwart and P. S. Francis, *J. Am. Chem. Soc.*, **81**, 2116 (1959).
(12) W. Klyne, "Progress in Stereochemistry," W. Klyne, Ed., Academic Press, Inc., New York, N. Y., 1954, p. 74.
(13) W. G. Dauben and R. L. Cargill, *J. Org. Chem.*, **27**, 1910 (1962).



The pure alcohols V and VI were obtained by reducing I and II, respectively, with lithium aluminum hydride. Gas chromatography on a 1,2,3-tris-(2-cyanoethoxy)-propane column showed that, although the retention times of V and VI were very similar, the *exo* isomer VI was eluted before V. It has been reported in several cases[14,15] that an *endo* compound is eluted before its *exo* epimer, suggesting intramolecular hydrogen bonding between the hydroxyl proton and the double bond of the *endo* molecule.

The inaccessibility of the pure V and VI prompted a search for other more practical syntheses so that one pure isomer could be isolated in substantial quantity. Bicyclo[4.2.0]oct-4-en-2-ol-7,8-dibromide, previously described,[4,16,17] was transformed to *exo*-bicyclo[4.2.0]oct-7-en-2-ol (VI) by catalytic

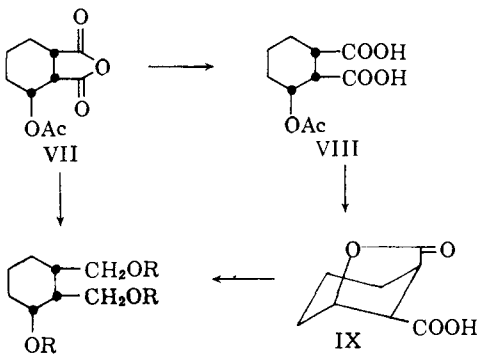


hydrogenation followed by treatment with a zinc–copper couple. This sample of VI was shown to be identical with the one obtained by irradiation and to be free from contamination by V.

It was hoped that infrared spectroscopic studies of hydrogen bonding, both intramolecular and intermolecular, of V and VI might shed some light on their stereochemistry. It has been shown by Lord and Evans[18] that the infrared spectrum of an unsaturated *endo*-alcohol shows less intermolecular hydrogen bonding than its *exo* isomer. Schleyer and co-workers[19] had also observed that the free hydroxyl band of an unsaturated *endo*-alcohol was partially split into two bands due to the intramolecular interaction of the hydroxylic proton and the double bond. However, Winstein and Piccolini[20] pointed out that even simple saturated non-hydrogen bonded alcohols showed splitting, probably due to conformational heterogeneity of the molecule. Molecular models show that some of the possible conformations of V, but not of VI, can allow substantial interaction between the hydroxyl function and the double bond. However, high resolution infrared spectra[21] of 2% solutions of V and VI in carbon tetrachloride showed no significant differences in intramolecular and intermolecular hydrogen bonding.

The nuclear magnetic resonance spectrum of V showed two olefinic protons at 3.80 τ, two bridgehead protons at 6.95 τ, the C-2 proton at 6.10 τ and six methylene protons at 8.42 τ. The spectrum of VI revealed the two olefinic protons at 3.86 τ, two bridgehead protons at 7.24 and 7.00 τ, the C-2 proton at 6.10 τ and six methylene protons at 8.41 τ. The olefinic protons of both V and VI appeared as a singlet while the other protons formed a broad band or multiplet. Thus the nuclear magnetic resonance spectra of V and VI do not favor one assignment of configuration over the other. Chapman and co-workers[14] have suggested that intramolecular hydrogen bonding causes the olefinic protons of *endo*-bicyclo[3.2.0]hept-6-en-3-ol to appear at a lower field than those of the *exo* isomer. The nuclear magnetic resonance and infrared spectra of V and VI, in addition to their similar behavior on gas chromatography, suggest that V may adopt a more energetically favorable conformation in which the hydroxyl group is pseudoequatorial, and intramolecular hydrogen bonding is made impossible by the distance separating the hydroxyl function and the double bond.

Successful elucidation of the stereochemistry of V and VI by degradation is based on the known stereochemistry of *cis*-3-acetoxycyclohexane-*cis*-1,2-dicarboxylic anhydride (VII) and the corresponding



Xa, R = H
b, R = Ac
c, R = *p*-$O_2NC_6H_4CO$

(14) O. L. Chapman, D. J. Pasto, G. W. Borden and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962).

(15) C. H. DePuy and P. R. Story, *Tetrahedron Letters*, **No. 6**, 20 (1959).

(16) A. C. Cope and M. Burg, *J. Am. Chem. Soc.*, **74**, 168 (1952).

(17) W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

(18) M. V. Evans and R. C. Lord, *J. Am. Chem. Soc.*, **83**, 3409 (1961).

(19) P. von R. Schleyer, D. S. Trifan and R. Bacskai, *ibid.*, **80**, 6691 (1958).

(20) R. Piccolini and S. Winstein, *Tetrahedron Letters*, **No. 13**, 4 (1959).

(21) These spectra were taken with a Perkin-Elmer single beam spectrophotometer, model 112, equipped with a lithium fluoride prism. Acknowledgment is made to Professor R. C. Lord and Dr. M. Falk for obtaining the spectra.

dicarboxylic acid VIII.[22] The anhydride VII was prepared from a Diels–Alder reaction of 1,3-butadien-1-yl acetate and maleic anhydride followed by catalytic reduction.[22] Hydrolysis of the anhydride VII with water afforded the acid VIII. The s ereochemistry of VII and VIII was proved by Nazarov and collaborators on the basis of the general scheme of the Diels–Alder reaction and by the observation that VII and VIII could be converted easily to the γ-lactone IX, which is possible only if the acetoxyl group and the carboxyl group are *cis*.

Attempts to oxidize either I or II to the corresponding dicarboxylic acid by various methods were unsuccessful. The anhydride VII was reduced with lithium aluminum hydride to the triol Xa which was characterized as its triacetate Xb and its tris-*p*-nitrobenzoate Xc. The stereochemical integrity of VII should not be affected by this series of transformations and therefore Xb and Xc must possess the same stereochemistry as their precursor VII. The γ-lactone IX also was converted to Xc after reduction with lithium aluminum hydride, confirming the retention of configuration in the lactonization of the acid VIII.

Ozonization of *exo*-bicyclo[4.2.0]oct-7-en-2-yl acetate (II) followed by treatment with lithium aluminum hydride produced 3-hydroxy-*cis*-1,2-cyclohexanedimethanol (XIIa), which was shown to be different from the authentic sample of *cis*-3-hydroxy-*cis*-1,2-cyclohexanedimethanol (Xa) by comparison of their tris-*p*-nitrobenzoates and triacetates.

The fact that derivatives of the ozonization product were not identical with the corresponding derivatives of *cis*-3-hydroxy-*cis*-1,2-cyclohexanedimethanol suggested that the original structural assignments to the bicyclo[4.2.0]octan-2-ols were correct. However, in order to obtain positive proof, pure *endo*-bicyclo[4.2.0]oct-7-en-2-yl acetate was prepared by the following sequence, and ozonized.

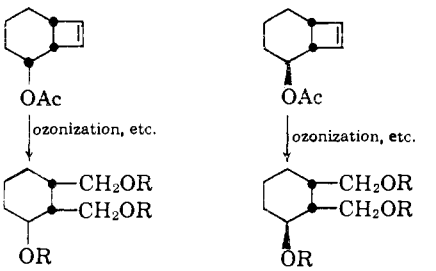
Oxidation[23] of a mixture of bicyclo[4.2.0]oct-7-en-2-ols (largely the *exo* isomer) followed by sodium borohydride reduction and treatment with acetic anhydride gave a mixture of *endo*- and *exo*-bicyclo-[4.2.0]oct-7-en-2-yl acetate containing principally the *endo* isomer. Pure *endo*-bicyclo[4.2.0]oct-7-en-2-yl acetate (I) was isolated by preparative gas chromatography and ozonized and reduced in a manner similar to that described for the *exo* isomer.

The triol XIa obtained from the ozonization was shown to be identical with *cis*-3-hydroxy-*cis*-1,2-cyclohexanedimethanol (Xa) by comparison of their triacetates and tris-*p*-nitrobenzoates.

These results unequivocally prove the stereochemistry of I and II, establish the stereochemical relationship among the compounds I, II, III, IV, V and VI, and confirm the original assignments of configuration to the bicyclo[4.2.0]octan-2- and 3-ols.

Experimental[24]

Catalytic Reduction of Tricyclo[3.2.1.0^{2,4}]octan-8-ol to *exo*-Bicyclo[3.2.1]oct-8-yl Acetate.—According to the procedure of Story,[7] 4.8 g. (3%) of *anti*-7-norbornenol was prepared from 149 g. of norbornadiene. A mixture of 2 g. of zinc–copper couple,[8] 2 ml. of methylene iodide and 20 ml. of ether was refluxed with stirring for 30 min., and to this mixture was added 0.45 g. of *anti*-7-norbornenol. After refluxing overnight, the mixture was filtered, the filtrate washed with 3% hydrochloric acid, water, 10% sodium bicarbonate, water, and dried over magnesium sulfate. Removal of the solvent gave 0.8 g. of material. The tricyclic alcohol was collected by gas chromatography on 1,2,3-tris-(2-cyanoethoxy)-propane (TCEP) at 140°. Thirty-five milligrams of *exo*-tricyclo[3.2.1.0^{2,4}]octan-8-oi in 5 ml. of glacial acetic acid and 3 drops of concd. hydrochloric acid was hydrogenated at room temperature using 200 mg. of platinum oxide as catalyst. Hydrogen uptake was complete in 6 hr. The catalyst was removed by filtration and the filtrate was diluted with water and extracted with ether. The combined extracts were washed with 10% sodium carbonate solution, then water, dried over magnesium sulfate, and concentrated. Gas chromatography on TCEP at 115° showed two peaks in the ratio of 15:85. The minor product was isolated by gas chromatography, and was shown to be *exo*-bicyclo[3.2.1]oct-8-yl acetate by comparison of its retention time on gas chromatography and its infrared spectrum with the spectrum of a sample previously prepared.[5] The major product was probably 2-methyl-bicyclo[2.2.1]hept-7-yl acetate; its infrared spectrum is comparatible with that structure. Gas chromatography of the product showed that there was no detectable amount of *endo*-bicyclo-[3.2.1]oct-8-yl acetate.



XIa, R = H
b, R = Ac
c, R = *p*-O₂NC₆H₄CO

XIIa, R = H
b, R = Ac
c, R = *p*-O₂NC₆H₄CO

Bicyclo[4.2.0]oct-2-ene was prepared by the pyrolysis of the S-methyl xanthates (13.5 g., 95%) obtained from 8.3 g. of the isomeric bicyclo[4.2.0]octan-2-ols, in the manner described for the preparation of bicyclo[5.1.0]oct-3-ene.[25] The xanthate mixture was pyrolyzed without purification. Decomposition started at 140° and the olefin distilled at *ca.* 120°. The temperature of the oil-bath was maintained at 170–180° during the first 1.5 hr. and finally was raised to 210° for 0.5 hr. The distillate was diluted with 50 ml. of ether, and washed successively with 20% sodium hydroxide, water and saturated sodium chloride solution. After drying over magnesium sulfate, the solvent was removed, and the residue was passed through a column of 70 g. of base-washed alumina (activity II) in pentane, giving 4.7 g. of colorless liquid. The liquid was distilled and the fractions boiling at 55–56° (50 mm.) were collected (3.3 g., 50%). Bicyclo-[4.2.0]oct-2-ene, n^{25}D 1.4795 (lit.[26] n^{20}D 1.4810) thus obtained, was homogeneous on gas chromatography (silicone oil at 80°).

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.70; H, 11.25.

Bicyclo[4.2.0]oct-2-ene Oxide.—To a solution of 370 mg. of bicyclo[4.2.0]oct-2-ene in 2 ml. of acetic acid, 1 g. of commercial 40% peracetic acid (after its sulfuric acid content was neutralized with 250 mg. of sodium acetate trihydrate) was added at such a rate that the temperature of the reaction mixture was maintained at 26–27°. The flask was cooled in

(22) V. F. Kucherov, N. Ya. Grigor'eva and I. N. Nazarov, *Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, 849 (1959); *C. A.*, **54**, 1349h (1960).

(23) K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(24) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses. Footnote 24 of A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959), describes the conditions and equipment used for gas chromatography.

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

(26) A. T. Blomquist and J. Kwiatek, *ibid.*, **73**, 2098 (1951).

an ice–water-bath when necessary. After the addition had been completed, the mixture was maintained at 25–27° for an additional 25 min. and then diluted with 30 ml. of water and extracted with four 15-ml. portions of ether. The combined ether extracts were successively washed with water, saturated sodium bisulfite, water, 5% sodium carbonate solution, water, and sodium chloride solution. After drying over magnesium sulfate, the solvent was removed, giving 370 mg. (87%) of a mixture of epoxides which was later shown to contain 20% of *endo*- and 80% of *exo*-bicyclo[4.2.0]oct-2-ene oxide. Samples collected by gas chromatography (TCEP at 116°) were analyzed.

endo-Bicyclo[4.2.0]oct-2-ene oxide, $n^{25}D$ 1.4811: *Anal.* Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.29; H, 9.91.

exo-Bicyclo[4.2.0]oct-2-ene oxide, $n^{25}D$ 1.4838: *Anal.* Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.08; H, 9.77.

In another preparation on a larger scale, 2.8 g. (84%) of the mixture of epoxides was obtained from 2.9 g. of the olefin by treatment with 6.5 g. of the 40% peracetic acid and 1.5 g. of sodium acetate trihydrate in 10 ml. of acetic acid.

The isomeric epoxides were partially separated by elution chromatography on alumina. The mixture of the epoxides was placed on a column of 90 g. of base-washed alumina (activity II) in pentane, and eluted with pentane. The first 200 ml. of the eluent contained a mixture enriched in the *endo* isomer, the next 100 ml. of the eluent contained both of the isomers in comparable amounts and the third 600 ml. of the eluent contained mostly the *exo* isomer. Finally, the last 1500 ml. of the eluent contained the pure *exo* isomer. The pure *endo* isomer was collected by gas chromatography.

Acetates of *endo*- and *exo*-Bicyclo[4.2.0]octan-2-ol and *endo*- and *exo*-Bicyclo[4.2.0]octan-3-ol.—The acetates were prepared from the corresponding alcohols by treatment with acetic anhydride in pyridine at room temperature.

endo-Bicyclo[4.2.0]oct-2-yl acetate (52 mg., 87%), $n^{25}D$ 1.4636, was collected from a TCEP column at 120°: *Anal.* Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.14; H, 9.60.

exo-Bicyclo[4.2.0]oct-2-yl acetate (55 mg., 83%), $n^{25}D$ 1.4632, was collected from a TCEP column at 120°: *Anal.* Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.38; H, 9.58.

endo-Bicyclo[4.2.0]oct-3-yl acetate (80 mg., 86%), $n^{25}D$ 1.4628, was collected from a silicone oil column at 130°: *Anal.* Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.24; H, 9.66.

exo-Bicyclo[4.2.0]oct-3-yl acetate (64 mg., 80%), was collected from a silicone oil column at 130°: *Anal.* Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.31; H, 9.56.

Reduction of *endo*-Bicyclo[4.2.0]oct-2-ene Oxide with Lithium Aluminum Hydride.—Fifty-eight milligrams of *endo*-bicyclo[4.2.0]oct-2-ene oxide and 0.1 g. of lithium aluminum hydride in 5 ml. of ether was heated under reflux for 0.5 hr. The product (50 mg., 85%) showed a single peak on gas chromatography on TCEP at 120°. The infrared spectrum of the product was practically identical with the spectrum of an authentic sample of *endo*-bicyclo[4.2.0]-octan-3-ol obtained as described previously,[4] indicating that the product contained principally *endo*-bicyclo[4.2.0]octan-3-ol and very little *endo*-bicyclo[4.2.0]octan-2-ol.

Reduction of *exo*-Bicyclo[4.2.0]oct-2-ene Oxide with Lithium Aluminum Hydride.—A mixture of 220 mg. of *exo*-bicyclo[4.2.0]oct-2-ene oxide and *ca.* 200 mg. of lithium aluminum hydride in 10 ml. of ether was heated under reflux for 0.5 hr. The mixture of alcohols isolated (220 mg., 98%) was converted to the corresponding acetate mixture (85%) by treatment with acetic anhydride in pyridine. It was shown to contain 84% of *exo*-bicyclo[4.2.0]oct-2-yl acetate and 16% of *exo*-bicyclo[4.2.0]oct-3-yl acetate, separated and identified by gas chromatography on TCEP at 120° and by comparison of their infrared spectra with the spectra of the authentic samples prepared as described above.

5-Bromo-1,3-cycloöctadiene.—A mixture of 30 g. of *cis*, *cis*-1,3-cycloöctadiene, 49.5 g. of N-bromosuccinimide and 0.4 g. of benzoyl peroxide in 300 ml. of carbon tetrachloride was heated on a steam-bath under a nitrogen atmosphere. After refluxing for 3 hr., no sign of reaction was observed. An additional 0.5-g. portion of benzoyl peroxide was added and the mixture was refluxed for an additional 3 hr., but no reaction was observed. Another addition of 0.5 g. of N-bromosuccinimide was necessary to initiate the reaction. The mixture was refluxed overnight. The succinimide was separated by filtration and the filtrate was washed with sodium bicarbonate solution and water, and dried over magnesium sulfate. After concentration of the solvent under reduced pressure, the residue was distilled through a semi-micro column, giving 28.4 g. (52%) of 5-bromo-1,3-cycloöctadiene, b.p. 52–54° (1.1 mm.), $n^{27.5}D$ 1.5500. The ultraviolet spectrum showed λ_{max}^{EtOH} 223 mμ (ε 4,800).

Anal. Calcd. for $C_8H_{11}Br$: C, 51.36; H, 5.93. Found: C, 51.69; H, 5.82.

2,4-Cycloöctadiene-1-yl Acetate.—A slurry of 29 g. of silver acetate in 50 ml. of acetic acid was added with cooling to a mixture of 25 g. of 5-bromo-1,3-cycloöctadiene and 50 ml. of acetic acid. The mixture was allowed to stand at room temperature overnight. The silver bromide that formed was separated by filtration and the filtrate was concentrated under reduced pressure. The additional silver bromide that precipitated was separated, and the filtrate was distilled under reduced pressure through a semi-micro column, giving 15.2 g. (68%) of 2,4-cycloöctadien-1-yl acetate, b.p. 56–57° (0.6 mm.), $n^{27}D$ 1.4873. The ultraviolet spectrum showed λ_{max}^{EtOH} 223 mμ (ε 5,900).

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.98; H, 8.66.

2,4-Cycloöctadien-1-ol.—A solution of 13.2 g. of 2,4-cycloöctadien-1-yl acetate in 150 ml. of anhydrous ether was added dropwise to 3.0 g. of lithium aluminum hydride in 50 ml. of ether. The solution was refluxed for 4 hr. and hydrolyzed by adding dropwise 20 ml. of water and 50 ml. of saturated ammonium chloride. The ether layer was separated and the aqueous layer was extracted with ether. The combined extracts were washed with water, saturated ammonium chloride solution and water, and dried over magnesium sulfate. The solution was concentrated and the residue was distilled through a semi-micro column, giving 7.1 g. (72%) of 2,4-cycloöctadien-1-ol, b.p. 57.5–58.5° (0.7 mm.), $n^{24}D$ 1.5184. The ultraviolet spectrum showed λ_{max}^{EtOH} 223 mμ (ε 5,600).

Anal. Calcd. for $C_8H_{10}O$: C, 77.37; H, 9.74. Found: C, 77.65; H, 10.02.

The phenylurethan was recrystallized twice from *n*-hexane; m.p. 110.0–110.8°.

Anal. Calcd. for $C_{15}H_{17}O_2N$: C, 74.05; H, 7.04. Found: C, 74.09; H, 7.18.

The *p*-nitrobenzoate was obtained by treating the alcohol with *p*-nitrobenzoyl chloride in pyridine at room temperature for 0.5 hr. and was recrystallized twice from ethanol; m.p. 114.0–115.0°.

Anal. Calcd. for $C_{15}H_{15}O_4N$: C, 65.92; H, 5.53. Found: C, 65.78; H, 5.33.

Regeneration of 2,4-Cycloöctadien-1-ol from 2,4-Cycloöctadien-1-yl *p*-Nitrobenzoate.—A solution of 2.7 g. of 2,4-cycloöctadien-1-yl *p*-nitrobenzoate in 180 ml. of ethanol and 1.5 g. of sodium hydroxide in 5 ml. of water was stirred at room temperature under a nitrogen atmosphere overnight. The solution was concentrated to about 70 ml. at room temperature under reduced pressure and diluted with 50 ml. of water. The solution was extracted with three 70-ml. portions of ether. Concentration of the dried (magnesium sulfate) extract and distillation through a semi-micro column gave 0.67 g. (56%) of a product, b.p. 59–60° (0.7 mm.), $n^{25}D$ 1.5186, λ_{max}^{EtOH} 223 mμ (ε 5,750). The infrared spectrum of the product was identical with that of 2,4-cycloöctadien-1-ol obtained by hydrolysis of the acetate described above.

Oxidation of 2,4-Cycloöctadien-1-ol with Chromium Trioxide.—A solution of 220 mg. of 2,4-cycloöctadien-1-ol in 2 ml. of anhydrous pyridine was added to 300 mg. of chromium trioxide in 3 ml. of pyridine cooled in an ice-bath. The mixture was stirred for 2 hr. at room temperature and poured into 30 ml. of ice-water. The precipitate formed was separated by filtration through Celite, and the filtrate was extracted with four 40-ml. portions of ether, washed with four 50-ml. portions of 1 *N* hydrochloric acid, water, sodium bicarbonate solution and water, and dried over magnesium sulfate. The ketone was not isolated but was converted into its 2,4-dinitrophenylhydrazone by treatment with a solution of 2,4-dinitrophenylhydrazine hydrochloride in methanol. Three recrystallizations from ethanol gave red needles, m.p. 179.5–181.0°.

Anal. Calcd. for $C_{14}H_{14}N_4O_4$: C, 55.62; H, 4.67. Found: C, 55.68; H, 4.82.

Irradiation of 2,4-Cycloöctadien-1-ol.—A solution of 5.27 g. of 2,4-cycloöctadien-1-ol in 500 ml. of anhydrous ether was irradiated with a Hanau H-81 high pressure mercury arc lamp (Quarzlampen Gesellschaften, Hanau, West Germany) which was connected in series to two 120-ohm Dividohm resistances (Ohmite, 200 watts) connected in turn to a 110–220 volt transformer. The solution was agitated gently by a slow stream of nitrogen. After 8 days the reaction was found to be 84% complete by gas chromatography. Distillation through a semi-micro column afforded 1.744 g. (30.5%) of a colorless liquid, b.p. 65–72° (0.9 mm.). The residue was polymeric. The mixture of bicyclo[4.2.0]oct-7-en-2-ols was separated from the starting material by gas chromatography on a silicone oil column (132°). The isomeric alcohols could be partially resolved on a TCEP column (120°) and were more conveniently separated by way of their acetates as described below.

Irradiation of 2,4-Cycloöctadien-1-yl Acetate.—A solution of 4.52 g. of 2,4-cycloöctadien-1-yl acetate was irradiated as described for the corresponding alcohol. After 7 days the reaction was complete and gave 1.32 g. (29%) of the crude acetates, b.p. 84–87° (7 mm.). Gas chromatography on a TCEP column (120°) showed that the ratio of the *endo* to the *exo* isomer was 3 to 1.

Separation of *exo*- and *endo*-Bicyclo[4.2.0]oct-7-en-2-yl Acetates.—A solution of 447 mg. of bicyclo[4.2.0]oct-7-en-2-ols in 1.25 ml. of dry pyridine was treated with 1 ml. of acetic anhydride to give 541 mg. (89%) of the crude corresponding acetates, consisting (by gas chromatography) of 95% of the *exo*- and *endo*-acetates (1-to-3 ratio) and 5% of a third component.

The *exo*- and *endo*-acetates were first separated by gas chromatography on a GE XF-1150 nitrile silicone fluid column (140°) to give the pure *exo* compound and the impure *endo* isomer which was further purified on a 1,2,3-tris-(2-cyanoethoxy)-propane column (120°).

exo- and *endo*-bicyclo[4.2.0]oct-7-en-2-yl acetates from the irradiation of 2,4-cycloöctadien-1-yl acetate were separated in the same manner and found to be identical with those obtained from irradiation of the alcohol followed by acetylation.

The *exo* isomer was eluted before the *endo* on TCEP or on GE XF-1150 nitrile silicone fluid. The *exo*- and the *endo*-bicyclo[4.2.0]oct-7-en-2-yl acetates recollected through a silicone grease column (170°) were analytically pure.

***endo*-Bicyclo[4.2.0]oct-7-en-2-yl acetate (I)** had $n^{25.5}D$ 1.4733: *Anal.* Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.40; H, 8.47.

***exo*-Bicyclo[4.2.0]oct-7-en-2-yl acetate (II)** had $n^{25}D$ 1.4716: *Anal.* Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.30; H, 8.44.

Hydrogenation of *exo*-Bicyclo[4.2.0]oct-7-en-2-yl Acetate (II).—A mixture of 7 mg. of II and 33 mg. of platinum oxide in 2 ml. of ether was hydrogenated until uptake of hydrogen ceased. The product (4 mg.) obtained by gas chromatography on a GE XF-1150 nitrile silicone oil column (140°) was homogeneous, as also shown on a TCEP column (120°). Its retention time on gas chromatography and infrared spectrum were identical with those of the acetate prepared from the bicyclo[4.2.0]octan-2-ol which had been assigned the *exo* configuration previously.[4]

Hydrogenation of *endo*-Bicyclo[4.2.0]oct-7-en-2-yl Acetate (I).—The hydrogenation of 8 mg. of I by the procedure described above afforded 4.4 mg. of a homogeneous product which had the same retention time on gas chromatography and an infrared spectrum identical with the spectrum of the acetate prepared from the bicyclo[4.2.0]octan-2-ol which had been assigned the *endo* configuration previously.[4]

***endo*-Bicyclo[4.2.0]oct-7-en-2-ol (V) from *endo*-Bicyclo[4.2.0]oct-7-en-2-yl Acetate (I).**—*endo*-Bicyclo[4.2.0]oct-7-en-2-yl acetate (I) (56 mg.) was reduced with 53 mg. of lithium aluminum hydride in 2 ml. of dry ether. Excess hydride was decomposed with 100 μl. of water and enough saturated ammonium chloride solution was added to dissolve the precipitate. After 4 ml. of water was added, the layers were separated and the aqueous layer was extracted with two additional 3-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate. *endo*-Bicyclo-[4.2.0]oct-7-en-2-ol (V), collected by gas chromatography (27 mg., 63.5%) on a silicone oil column (179°), was homogeneous and had m.p. 42.3–44.2.°

In another similar experiment, the hydride reduction of 169 mg. of I afforded 105 mg. of crude V which after purification by gas chromatography on a silicone grease column (140°) weighed 54 mg., m.p. 47.5–49.1°. Recrystallization from pentane (Dry Ice–acetone temperature) afforded analytically pure *endo*-bicyclo[4.2.0]oct-7-en-2-ol (V), m.p. 51.6–53.2°

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.54; H, 9.85.

***exo*-Bicyclo[4.2.0]oct-7-en-2-ol (VI) from *exo*-Bicyclo-[4.2.0]oct-7-en-2-yl Acetate (II).**—The hydride reduction of 35 mg. of II was carried out by the method described above. Gas chromatography of the crude product on a silicone grease column afforded 17 mg. (64%) of pure *exo*-bicyclo[4.2.0]-oct-7-en-2-ol identical with that obtained from cycloöctatetraene (see below).

Cycloöctatetraene Dibromide Monoepoxide.—Cycloöctatetraene dibromide was prepared by the bromination of cycloöctatetraene,[16] and converted to the monoxide[17] with peracetic acid. The solid isomer of the monoepoxide was isolated and purified by repeated crystallization from hexane to a constant melting point of 85.0–86.2° (lit.[17] m.p. 88°).

***exo*-Bicyclo[4.2.0]oct-7-en-2-ol (VI) from Cycloöctatetraene Dibromide Monoepoxide.**—A solution of 5.65 g. of cycloöctatetraene dibromide monoepoxide in 50 ml. of ether was treated with 0.9 g. of lithium aluminum hydride according to the procedure described previously[4] except that a saturated solution of ammonium sulfate instead of 20% sulfuric acid was used to dissolve the precipitated salts. The viscous colorless oil obtained weighed 5.09 g. (90%).

A solution of 4.29 g. of crude bicyclo[4.2.0]oct-3-en-2-ol 6,7-dibromide in 25 ml. of absolute ethanol was hydrogenated at room temperature and atmospheric pressure with 225 mg. of prereduced platinum oxide until uptake of hydrogen ceased (128% of the theoretical amount for one double bond). Another 0.8 g. of the unsaturated alcohol was reduced similarly. The filtered solutions from these two reductions were combined and the ethanol was removed at room temperature under reduced pressure. Some low-boiling materials were removed from the product by heating at 70–75° (0.5–1 mm.) for 1 hr. The residual oil was washed with pentane. The crude saturated product so obtained (4.45 g., 87%) was dissolved in 20 ml. of absolute ethanol and treated with 3 g. of zinc–copper couple[8] at reflux temperature with stirring for 3 hr. and then at room temperature overnight. The solution was filtered and concentrated and then 35 ml. of water and enough ammonium hydroxide to dissolve the zinc salt were added. The solution was extracted with five 30-ml. portions of ether and the combined extracts were washed twice with water and dried over magnesium sulfate. Distillation through a semi-micro column afforded 1.65 g. (85%) of *exo*-bicyclo[4.2.0]oct-7-en-2-ol, b.p. 93.5–94° (9 mm.), 95% pure by gas chromatography (silicone oil, 130°). Gas chromatography on a TCEP column (130°) showed that it was free from the *endo* isomer. Comparison of retention times and infrared spectra showed that this alcohol was identical with the *exo*-bicyclo[4.2.0]oct-7-en-2-ol obtained previously by photolysis. An analytical sample was collected by gas chromatography on a silicone grease column (130°); $n^{25}D$ 1.5035.

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.30; H, 9.86.

The alcohol could also be purified by chromatography on activity III alumina (eluted with 7% ether in pentane). The first few fractions were pure *exo*-bicyclo[4.2.0]oct-7-en-2-ol. A mixture of 125 mg. of VI and 171 mg. of phenyl isocyanate was heated at 100° for about 40 min. in a closed vial and then allowed to stand at room temperature for 5 hr. The crude phenylurethan was dissolved in 40 ml. of petroleum ether, filtered to remove diphenylurea and crystallized from aqueous methanol to give 203 mg. (81%), m.p. 63.5–65.0°. Three recrystallizations from aqueous ethanol afforded an analytical sample, m.p. 68.0–69.4°.

Anal. Calcd. for $C_{15}H_{17}O_2N$: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.80; H, 7.02; N, 5.82.

***cis*-3-Acetoxy-4-cyclohexene-*cis*-1,2-dicarboxylic anhydride** was prepared in 90% yield by the Diels–Alder reaction of maleic anhydride and 1,3-butadien-1-yl acetate according to the procedure of Flaig[27]; m.p. 58.4–59.5° (lit.[22,28] m.p. 58°).

(27) W. Flaig, *Ann.*, **568**, 1 (1950).

cis-3-Acetoxycyclohexane-*cis*-1,2-dicarboxylic Anhydride (VII).—Catalytic hydrogenation of *cis*-3-acetoxy-4-cyclohexene-*cis*-1,2-dicarboxylic anhydride in the presence of palladium-on-charcoal afforded the saturated anhydride VII in 67% yield, m.p. 70.8–72.2° (lit.[22] m.p. 72°).

cis-3-Hydroxy-*cis*-1,2-cyclohexanedimethanol (Xa).—A solution of 1.59 g. of the anhydride VII in 35 ml. of anhydrous ether was added dropwise to 1.14 g. of lithium aluminum hydride in 25 ml. of ether at such a rate that the solution refluxed gently. The mixture was heated under reflux for 5 hr. after addition was completed, then cooled and decomposed with 65 ml. of saturated ammonium chloride solution. The mixture was continuously extracted with ether for 18 hr., yielding 0.692 g. of a viscous colorless gum. Further extraction for 36 hr. afforded an additional 0.255 g. The crude triol Xa (0.957 g., 79%) was characterized by its triacetate and tris-*p*-nitrobenzoate.

cis-3-Hydroxy-*cis*-1,2-cyclohexanedimethanol Triacetate (Xb).—The triacetate (230 mg., 77%) was prepared from 167 mg. of Xa by the acetic anhydride–pyridine method. Gas chromatography (silicone grease, 230°) showed that the triacetate was homogeneous. A portion was distilled in a short-path still at 0.2–0.5 mm. to give an analytical sample, $n^{25}D$ 1.4629.

Anal. Calcd. for $C_{14}H_{22}O_6$: C, 58.73; H, 7.75. Found: C, 58.71; H, 7.62.

cis-3-Hydroxy-*cis*-1,2-cyclohexanedimethanol Tris-*p*-nitrobenzoate (Xc).—The tris-*p*-nitrobenzoate, prepared from 122 mg. of Xa and 805 mg. of *p*-nitrobenzoyl chloride in 5.5 ml. of dry pyridine and recrystallized from an ethanol–acetone mixture, weighed 325 mg. (70%), m.p. 134.5–137.5°. A portion (141 mg.) was recrystallized from a mixture of acetonitrile and aqueous ethanol (charcoal); m.p. 137.0–139.3°. Two additional recrystallizations from ethyl acetate–hexane afforded an analytical sample, m.p. 137.2–138.5°.

Anal. Calcd. for $C_{29}H_{25}O_{12}N_3$: C, 57.33; H, 4.15; N, 6.92. Found: C, 57.10; H, 4.18; N, 7.18.

cis-3-Hydroxycyclohexane-*cis*-1,2-dicarboxylic Acid γ-Lactone (IX).—A mixture of 713 mg. of the anhydride VII and 6 ml. of water was heated on a steam-bath until the solution became homogeneous and was then allowed to stand at room temperature for 2 hr. A solution of 0.8 ml. of concd. hydrochloric acid in 3.2 ml. of water was added and the mixture was heated at 65–70° for 2 hr. The water was then removed at room temperature under reduced pressure. The lactone IX was obtained in 73% yield (420 mg.) after recrystallization from ether; m.p. 115.5–117.5°. Further recrystallization from ether raised the m.p. to 116.5–117.5° (lit.[23] m.p. 114°).

cis-3-Hydroxy-*cis*-1,2-cyclohexanedimethanol Tris-*p*-nitrobenzoate (Xc) from the γ-Lactone IX.—A solution of 203 mg. of IX in 5 ml. of ether was reduced with 286 mg. of lithium aluminum hydride in 5 ml. of ether to give 154 mg. (80%) of the crude triol.

Treatment of the crude triol with 752 mg. of *p*-nitrobenzoyl chloride in pyridine gave 347 mg. (58%) of the tris-*p*-nitrobenzoate, m.p. 137.2–139.7°, after recrystallization from ethyl acetate–hexane. Two recrystallizations from a mixture of hexane and ethyl acetate raised the m.p. to 138.8–140.1°, undepressed by a sample obtained from the reduction of the anhydride VII with lithium aluminum hydride followed by treatment with *p*-nitrobenzoyl chloride. The infrared spectra of these two samples of the *p*-nitrobenzoates (Xc) were identical.

trans-3-Hydroxy-*cis*-1,2-cyclohexanedimethanol Tris-*p*-nitrobenzoate (XIIc) from the Ozonolysis of *exo*-Bicyclo[4.2.0]oct-7-en-2-yl Acetate (II).—Treatment of a cold solution of 150 mg. of *exo*-bicyclo[4.2.0]oct-7-en-2-ol (VI) in pyridine with 0.26 ml. of acetic anhydride afforded 190 mg. (94%) of crude II.

A solution of 175 mg. of crude II in 20 ml. of petroleum ether (b.p. 30–60°) was ozonized at −45° to −40° until uptake of ozone ceased, and then was immediately added with stirring to a solution of 310 mg. of lithium aluminum hydride in 25 ml. of dry ether (cooled to −35°). The mixture was allowed to come to room temperature, heated under reflux for 4 hr., then cooled and decomposed with 40 ml. of nearly saturated ammonium sulfate solution. Continuous extraction of the mixture with ether for 36 hr. afforded 92 mg. of crude triol XIIa which was treated with 400 mg. of *p*-nitrobenzoyl chloride in pyridine. The crude *p*-nitrobenzoate (XIIc) was dissolved in 15 ml. of benzene and passed through a column of 15 g. of activity III alumina in benzene. Recrystallization from ethyl acetate–hexane gave 166 mg., m.p. 96.5–100.5°. Three recrystallizations from ethyl acetate–hexane and one final recrystallization from ethyl acetate–ethanol afforded an analytical sample, m.p. 100.6–102.0°.

Anal. Calcd. for $C_{29}H_{25}O_{12}N_3$: C, 57.33; H, 4.15; N, 6.92. Found: C, 57.36; H, 4.26; N, 6.69.

The mixed melting point of XIIc and Xc was 96–120°; their infrared spectra were very similar but not identical.

endo-Bicyclo[4.2.0]oct-7-en-2-yl Acetate on a Preparative Scale.—To a solution of 2.25 g. of a mixture of *endo*- and *exo*-bicyclo[4.2.0]oct-7-en-2-ol in 25 ml. of acetone, 4.8 ml. (*ca.* 6% excess) of a chromium trioxide solution prepared from 267 g. of chromic anhydride, 230 ml. of concd. sulfuric acid and 400 ml. of water was added dropwise with stirring at 10–15° over a period of 0.5 hr. The mixture was then diluted with 75 ml. of water, and extracted with five 25-ml. portions of ether. The combined ether extracts were washed successively with water, saturated sodium carbonate solution, water, saturated sodium chloride solution, and dried over magnesium sulfate. The solvent was removed under reduced pressure, giving 1.70 g. of bicyclo[4.2.0]oct-7-en-2-one, which was reduced with sodium borohydride to 1.51 g. of a mixture of the isomeric bicyclo[4.2.0]oct-7-en-2-ols. These alcohols were converted to the acetates by treatment with acetic anhydride in pyridine at room temperature. The mixture of acetates was shown to contain 80% of *endo*- and 20% of *exo*-bicyclo[4.2.0]oct-7-en-2-yl acetate by gas chromatography on TCEP at 140°, and by comparison of their infrared spectra with the spectra of samples previously prepared by photoisomerization of 2,4-cycloöctadien-1-yl acetate. *endo*-Bicyclo[4.2.0]oct-7-en-2-yl acetate was separated by preparative gas chromatography on TCEP at 140° and GE XF-1150 at 150°.

Ozonization of *endo*-Bicyclo[4.2.0]oct-7-en-2-yl Acetate.—Ozonization of 300 mg. of *endo*-bicyclo[4.2.0]oct-7-en-2-yl acetate followed by treatment with lithium aluminum hydride as described for the *exo*-acetate afforded 230 mg. (80%) of crude *cis*-3-hydroxy-*cis*-1,2-cyclohexanedimethanol. One-quarter of the crude triol XIa was converted to the corresponding triacetate by treatment with acetic anhydride in pyridine at room temperature (79% yield). This triacetate XIb was shown to be identical with authentic *cis*-3-hydroxy-*cis*-1,2-cyclohexanedimethanol triacetate (Xb) prepared from the Diels–Alder reaction product by comparison of retention times on gas chromatography (silicone grease, 205°) and infrared spectra.

The remaining three-quarters of the crude triol was converted to the tris-*p*-nitrobenzoate XIc, 460 mg. (70%). Four recrystallizations from an ethyl acetate–*n*-hexane mixture afforded the pure tris-*p*-nitrobenzoate, m.p. 138.5–139.5°. A mixed melting point of XIc with Xc was not depressed.