dioxane. As the solution was stirred, 2.36 g. (19.0 mmoles) of p-toluenethiol and 0.87 g. (19.0 mmoles) of ethanol in 60 ml. of pure dioxane was slowly added. The solution was refluxed for 14 hr. and then worked up in the previously described manner to give 5.59 g. (86.0%) of *trans*-2-p-tolylmercapto-1-p-tolylsulfonyl-cyclopentane and 0.28 g. (6.8%) of recovered olefin.

Modified Addition of p-Toluenethiol to 1-p-Tolylsulfonylcyclopentene. (a) One Hour.—The same reaction as previously described was repeated except that it was only allowed to reflux for 1 hr. At the end of this time no reaction had occurred.

(b) Four Hours.—In this case the reaction mixture was refluxed for 4 hr. Reaction had occurred to an extent almost equal to that after 14 hr. but only starting material and *trans* adduct were found.

(c) Fifty Hours at Room Temperature.—The reaction was stirred for 50 hr. at room temperature. At the end of this period it was shown that no reaction had occurred.

Tetracyclic Dienes. II. Acid-catalyzed Rearrangement of 1,4,4a,5,8,8a-Hexahydro-*exo-endo*-1,4,5,8-dimethanonaphthalene (I)[1]

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The addition of formic acid to I produces, through a series of bridged ion intermediates, the bird-cage hydrocarbon IV, both a saturated and unsaturated monoformate fraction, and a saturated diformate fraction. The saturated monoformate portion contains the formate esters of the half-cage alcohol II—OH and the bridged alcohol V—OH. Neither of the formates III—OCOH or VI—OCOH were produced, although these isomers might be predicted to result from the postulated bridged ion intermediates. Two unsaturated alcohols, VII—OH and XIV—OH, were obtained from the unsaturated formate fraction. The saturated diformate fraction possesses the *exo-exo* carbon skeleton (XXII) as a result of the addition of formic acid to VII or XIV—OCOH.

The synthesis of 1,4,4a,5,8,8a-hexahydro-*exo-endo*-1,4,5,8-dimethanonaphthalene (I)[2] afforded an unusual diene system which reacted readily with ionic reagents to produce rearranged products. Titration of I with bromine showed that only 1.1 moles of bromine was absorbed, yet 80% of the product was saturated dibromide.[3] The addition of formic acid to I with boron fluoride catalysis was a rapid, exothermic reaction which proceeded smoothly in the absence of a solvent to yield both saturated and unsaturated monoformate esters and a saturated diformate ester.

The addition of formic acid was chosen to illustrate the complex rearrangement pattern of I because protonation of the double bond could lead to the bridged carbonium ions shown in Figure 1. These carbonium ion intermediates have been postulated to explain the products formed from the solvolysis of compounds containing this ring system.[4] In addition, saponification of the formate esters should yield the alcohols reported in connection with these solvolysis experiments.

Discussion

When a threefold excess of formic acid was added to I, the monoformate ester fraction, 35–50% of the total yield of product, consisted of 55–75% saturated monoformate and 45–20% unsaturated monoformate. The remainder of the reaction product consisted of a diformate ester (40–55%) and a saturated hydrocarbon (2%).

When a formic acid to olefin molar ratio of 4:3 was employed, the monoformate portion 70–80% was formed at the expense of diformate (15%). The unsaturated monoformates were separated from the saturated monoformates by using silver nitrate to complex the unsaturated portion.[5]

Protonation of Bond *a*.—Because of the dissymmetry of the molecule, attack of the proton at either bond would not lead to equivalent carbonium ion species, and two different sets of products would be formed. Attack of the proton to the *exo* side of bond *a* will produce a bridged ion. Shift of electrons toward the positive site generated causes further delocalization of the charge to produce the bridged carbonium ion A. Simple Wagner-Meerwein shifts can produce bridged ion B which shows the interaction possible between the *pi* electrons of the double bond *b* with the positive charge generated by the added proton. Bond *b* entering the carbonium ion scheme then opens the way for formation of the unusual bridged ring systems encountered in the reaction mixture.

Ion B can then produce a series of nonclassical ions. Further rearrangement can occur to produce ions C, D, or E, or attack by the formate anion can produce either the half-cage ester, II—OCOH, or the skewed-cage ester, III—OCOH. Loss of a proton from ion C affords the bird-cage hydrocarbon (IV) which was isolated in small yields (2%) from the reaction mixture.

Rearrangement of ion B to ion D and attack by formate ion produces V—OCOH. Basic hydrolysis of the formate ester afforded an alcohol with properties identical to those of alcohol V of known structure.[4,6]

It is clear that ion D and III—OH are related because of the similar skewed arrangement of the bridges; how-

(1) (a) This research was supported by a grant (NSF G10472) from the National Science Foundation, whose assistance is gratefully acknowledged. (b) This paper taken in part from the Ph.D. thesis of P.R.K., University of Iowa, June, 1962.

(2) First paper in this series: J. K. Stille and D. A. Frey, *J. Am. Chem. Soc.*, **81**, 4273 (1959).

(3) Further work on these bromides was discontinued in view of the potential health hazard.

(4) (a) L. deVries and S. Winstein, *J. Am. Chem. Soc.*, **82**, 5363 (1960). (b) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.*, 405, 590 (1960). (c) S. Winstein, *Experientia Suppl.*, **II**, 137 (1955).

(5) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938).

(6) We wish to thank Professor S. Winstein for supplying us with samples of II—OH and V—OH.
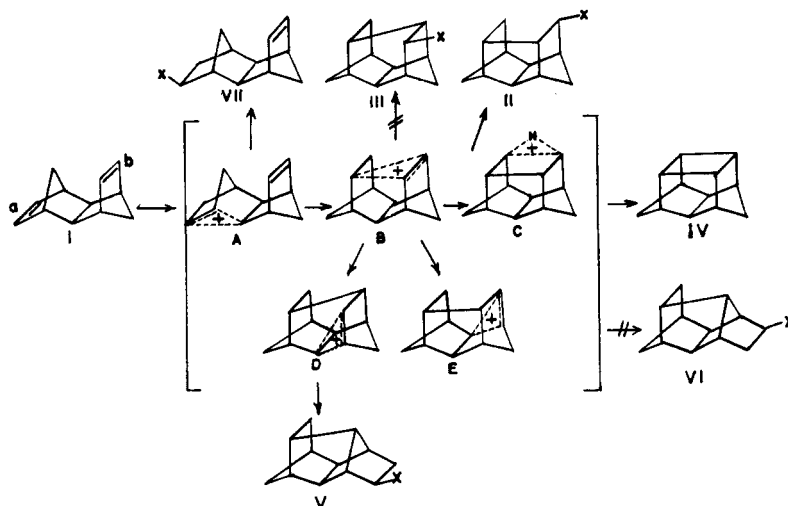
Figure 1

ever, no detectable amount of alcohol III was obtained from the reaction mixture. This fact is not totally unexpected, because it has been observed that this skewed alcohol was not obtained directly from acetolysis of the exo-bromobenzenesulfonate which generates ion A.[4a] It is suggested that rearrangement of ion B to ion D and thus production of isomer V is either more rapid than the direct addition of the formate anion to give III—OCOH, or V is produced at the expense of III to give the thermodynamically controlled product. Compound V achieves the more desirable exo-endo fusion rather than the endo-endo configuration.[7]

On the other hand, after saponification no material with structure VI—OH was isolated while a good yield of II—OH was obtained. Because it has been demonstrated that under similar conditions the conversion of ion B to E is not reversible,[4a] it is unlikely that any products are formed from ion E through the solvolysis of VI (OCOH). The identity of isomer II—OH was established by comparison with authentic sample.[4a,6]

In addition, it should be noted that small amounts of isomers III—OH and VI—OH could have been present in the saponified sirups which remained uncrystallizable even after several chromatographic purifications, but these sirups were a minor portion of the total reaction product and could not be purified.

The unsaturated alcohol VII—OH was obtained from the unsaturated monoformate portion of the reaction mixture. Unlike the unsaturated monoformate XIV—OCOH, VII—OCOH did not afford a precipitated silver nitrate complex, but remained soluble in the aqueous silver nitrate solution and could thus be separated from XVI.

The unsaturated alcohol VII—OH is obtained by the hydrolysis of the Diels–Alder adduct of vinyl acetate with two moles of cyclopentadiene.[4a] Its structure was verified by hydrogenation to the saturated alcohol XII—OH, which was independently synthesized (Figure 2). Hydrogenation and subsequent dehalogenation of the adduct VIII,[2,8] afforded pure monoölefin X.[2] Epoxidation[9] of norbornene and exo-dihydrocyclopentadiene with perbenzoic acid and subsequent reduction with lithium aluminum hydride[9,10] has been shown to
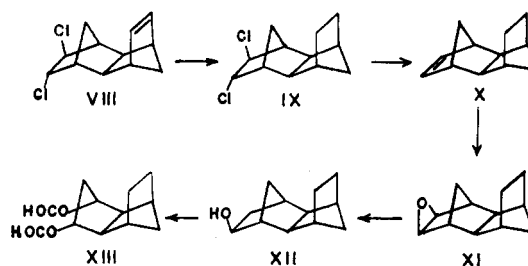

Figure 2

proceed without rearrangement. Epoxidation of X followed by hydrogenolysis with a Raney nickel catalyst, afforded a sample of XII which was identical to the material obtained by the hydrogenation of VII. The fact that the structure of XII is as shown and that no rearrangement had occurred during the independent synthesis was established by its oxidation to the known α-diacid (XIII).[11]

Protonation of Bond b.—The carbonium ion possible from initial attack of the proton on the double bond b is illustrated in Figure 3. Ion species F is the only one formed since interaction with bond a is impossible. Attack of the formate ion can take place either without rearrangement to give unsaturated isomer XXI—OCOH or the endo to exo rearrangement can take place to give XIV—OCOH.

The fact that the rearrangement did take place and the unsaturated isomer isolated was indeed XIV was demonstrated by relating it to XVI—OH, a known alcohol.[11] Hydrogenation of XIV—OH afforded XVI—OH of known exo-exo structure, as demonstrated by the hydration of XV.[11] This identity was established by superimposable infrared spectra and by undepressed mixed melting point. This isomer, XVI—OH, was also related to the γ-diacid[11] by potassium permanganate oxidation. Of the unsaturated monoformates formed in the reaction, the ratio of XIV to VII was 8:1.

The preparation of a sample of XIX—OH for comparison with XVI—OH and with other alcohols isolated from reactions in this series was carried out by epoxida-

(7) P. D. Bartlett and A. Schneider, J. Am. Chem. Soc., 68, 6 (1946).
(8) K. Alder and H. Rickert, Ann., 543, 1 (1939).
(9) S. B. Soloway and S. J. Cristol, J. Org. Chem., 25, 327 (1960).

(10) H. M. Walborsky and D. F. Loncrini, J. Am. Chem. Soc., 76, 5396 (1954).
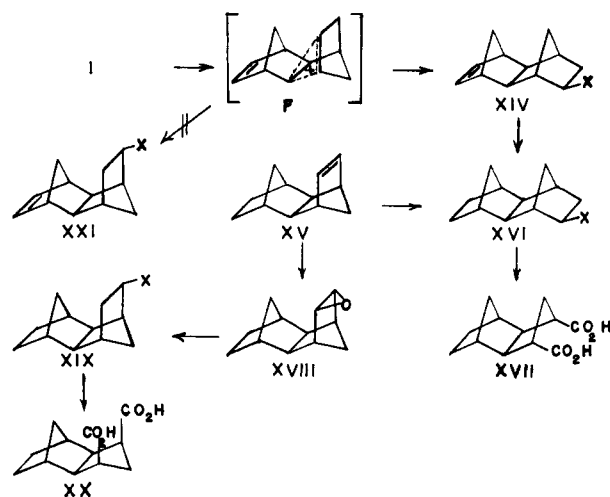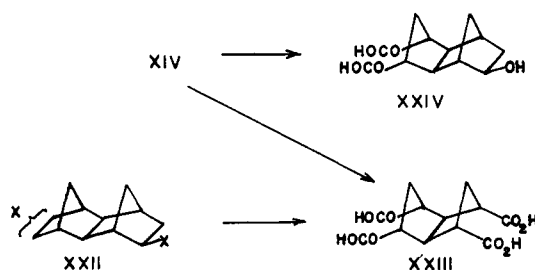(11) S. B. Soloway, ibid., 74, 1027 (1952).

Figure 3

Figure 4

tion of XV followed by hydrogenolysis of the epoxide. Although lithium aluminum hydride is generally the reagent of choice in these reductions and seldom fails to reduce the cyclic ether,[9,10] in this case the steric environment of the epoxide function predicts a slow, difficult reaction. Epoxide reductions involve the nucleophilic attack by the bulky aluminohydride ion (AlH_4^-) at the electron deficient carbon atom.[12] The back face of the carbon atoms bearing the epoxide function in molecule XVIII is so hindered by the neighboring methano group that refluxing the epoxide with lithium aluminum hydride in tetrahydrofuran for 28 days failed to produce XIX—OH and starting material was quantitatively recovered. Reduction of XVIII was achieved by hydrogenolysis. That no rearrangement took place during the reaction series was demonstrated by conversion of XIX—OH to the β-diacid.[11]

Structure of the Saturated Diol.—Saponification of the diformate fraction afforded a saturated diol. In light of the rearrangement sequence shown to occur at each side of I, the original exo-endo configuration would no t be expected to remain intact. Since diformate is recovered in different amounts at the expense of the monoformate fraction, depending on the olefin to formic acid ratio, it is evidently obtained from the addition of formic acid to VII or XIV—OCOH. Addition of a proton to XIV—OCOH would generate a carbonium ion capable of exo to endo rearrangement. Such rearrangements, however, are not realized from ions in this series since the acetolysis of both 2-exo- and endo-bromobenzenesulfonates of decahydro-endo-exo-1,4,5,8-dimethanonaphthalene affords unrearranged acetates.[4a] Addition of a proton to VII—OCOH would give an ion capable of

endo to exo rearrangement, a rearrangement which does take place on addition of a proton to bond b of I. Addition of formic acid then to either VII or XIV—OCOH would be expected to give a diformate with the same exo-exo carbon skeleton.

Oxidation of the diol, XXII—OH, produced a new tetracarboxylic acid (XXIII) which was not the tetracarboxylic acid obtained from the oxidation of an exo-endo skeleton.[2] The structure of XXIII and thus the exo-exo skeleton of XXII was established by the oxidation of XIV to cis-bicyclo[3.3.0]- trans,trans,trans,trans-2,4,6,8-tetracarboxylic acid. In addition, the hydroxy diacid (XXIV) was obtained from this oxidation.

Infrared Spectra.—The unusually high C—H stretching frequencies observed for compounds with certain half cage structures and exo-exo as well as endo-exo structures has been attributed to steric crowding of the opposed methylene hydrogen atoms.[13,14] A similar effect apparently causes an anomalously high =C—H out of plane deformation frequency in compounds in which the hydrogen atoms attached to olefin carbons are opposed by the methanol hydrogen atoms. Unhindered C—H out of plane frequencies for X and XIV —OH are 678 and 695 cm.$^{-1}$, respectively, while those for the hindered structures XV (717 cm.$^{-1}$), VII—OH (734 cm.$^{-1}$), and VIII (739 cm.$^{-1}$) are higher. Compound I, which contains both hindered and unhindered vinylic hydrogens shows both maxima at 679 cm.$^{-1}$ (bond a) and 713 cm.$^{-1}$ (bond b).

Experimental[15]

Addition of Bromine to I.—Titration of I with bromine at room temperature showed an absorption of 1.1 moles to yield a dibromide (70–80%), b.p. 116°/0.3 mm.

Anal. Calcd. for $C_{12}H_{14}Br_2$: C, 45.31; H, 4.44; Br, 50.25. Found: C, 45.10; H, 4.49; Br, 49.71.

The infrared spectrum showed no unsaturation as evidenced by the absence of absorption in the 650–750-cm.$^{-1}$ region. The remainder of the product from bromine addition was tetrabromide (10%), m.p. 208–210°.

Anal. Calcd. for $C_{12}H_{14}Br_4$: C, 30.16; H, 2.97; Br, 66.87. Found: C, 29.93; H, 3.28; Br, 67.42.

Addition of Formic Acid to 1,4,4a,5,8,8a-Hexahydro-1,4,5,8-exo-endo-dimethanonaphthalene (I).—To 63.6 g. (0.403 mole) of freshly distilled I[2] in an ice bath was added with stirring a mixture of 55.2 g. (46 ml., 1.20 moles) of formic acid containing 5 ml. of boron fluoride etherate. The temperature did not rise above 4° during the 2.5-hr. period of addition. The mixture was then allowed to warm slowly to room temperature during which time a deep red homogeneous solution was formed.

The deep red solution was extracted with water and then with ether. The yellow ether solution was washed with sodium bicarbonate followed by water and dried. The ether was removed to afford 90.5 g. of a thick yellow oil which was subjected to fractional distillation under reduced pressure to yield the following fractions:

Fraction	B.p., °C.	Wt., g.	Yield, %[a]
1. Recovered I	65–82°/0.32 mm.	8.1	—
2. Monoformate	85–89°/0.32 mm.	24.3	34
3. Diformate	90–100°/0.01 mm.	48.2	55

[a] Based on I consumed.

Fraction 2. *Anal.* Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.30; H, 7.90.

(12) W. G. Brown, *Org. Reactions*, 469 (1951).

(13) D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, *J. Am. Chem. Soc.*, **83**, 2938 (1961).

(14) L. deVries and P. R. Ryason, *J. Org. Chem.*, **26**, 621 (1961).

(15) Infrared spectra were run as 1% solutions in carbon disulfide on both Perkin-Elmer Model 21 and 421 infrared spectrophotometers. . For a discussion of the spectra of structures of this type, see ref. 13 and 14.

Fraction 3. *Anal.* Calcd. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.35; H, 7.23.

In another trial under apparently the same reaction conditions, a 53% yield of monoformate ester and a 38% yield of diformate ester were obtained. When 46.0 g. (38 ml., 1.0 mole) of formic acid was added to 118.7 g. (0.75 mole) of I, 49.9 g. of unchanged olefin, 77.2 g. (80%) of monoformate ester and 16.8 g. (14%) of diformate ester were obtained. Attempts to run this reaction without external cooling resulted only in total charring, and no organic materials were isolated.

Separation of Saturated Monoformate Ester from Unsaturated Monoformate Ester.—The monoformate ester, fraction 2 (65.0 g.), was shaken with 200 ml. of aqueous saturated silver nitrate solution. The reaction mixture consisted of an oily layer of unaltered starting material, a solid silver nitrate complex, and an aqueous layer of the complexed unsaturated ester. The precipitated complex was removed and both the precipitate and the aqueous layer were extracted with ether to remove the uncomplexed oil. This saturated oil in two different runs represented 53.3 to 76.4% of the monoformate fraction. In two different runs, when the mole ratio of formic acid to I was 4:3, an average of 50% of saturated monoformate ester was obtained. The infrared spectrum showed no bands characteristic of unsaturation but did have a formate ester maximum at 1170 cm.$^{-1}$.

To the aqueous layer and to the solid complex was added 300 ml. each of concentrated ammonium hydroxide, and the mixtures were allowed to reflux for 3 hr. The regenerated olefins were extracted with ether to afford solutions of the respective unsaturated alcohols. From the ether extract of the decomposition mixture of the solid complex was obtained 19.1 g. (34.0%) of solid unsaturated alcohol and from the extract of the decomposition mixture of the aqueous soluble complex was obtained 2.4 g. (4.3%) of solid unsaturated alcohol. This represents 46.7% of the total monoformate ester fraction recovered from the silver nitrate treatment. Similar treatment of the monoformate fraction from a separate reaction revealed that only 19.3% of the monoformate fraction was unsaturated. In reactions in which the ratio of formic acid to I was 4:3, an average of 50% of the monoformate fraction was unsaturated.

The infrared spectra of the unsaturated alcohols showed maxima in the OH stretching region and no maxima in the ester carbonyl region, indicating that the formate esters had been hydrolyzed under the basic conditions of the complex decomposition.

Purification of Saturated Alcohol Isomers.—A saturated ester fraction, 17.35 g., was allowed to react with 60 ml. of 10% potassium hydroxide in ethanol with stirring for 5 hr. A moderate amount of heat evolved and a white precipitate was formed which dissolved on addition of more ethanol. Addition of water to the ethanol solution caused a heavy yellow oil to separate which was taken up into ether. The ether solution was washed with water, dried, and the ether was removed to yield 14.29 g. (94.5%) of a mixture of crude alcohols. The sample was chromatographed on 315 g. of alumina as follows:

Fractions	Eluent	Wt., g.
1–4	100% pentane	. . .
5–7	20–50% ether	. . .
9–12 (II—OH)	100% ether	6.148
13–15 (II—OH and V—OH)	50–100% ethyl acetate	4.489
16–17 (V—OH)	100% ethyl acetate	2.751

4-Hydroxypentacyclo[6.2.1.1.^{3,6}.0^{2,7}0.^{5,9}]dodecane (II—OH).—Fractions 9–12 were recrystallized from hexane to yield colorless rhombic clusters, m.p. 129–130° (reported[4] 130–131°). The melting point of a mixture of this alcohol and an authentic sample of II[4a,6] was not depressed. Identical infrared spectra of the two samples were obtained, showing maxima at 3615 cm.$^{-1}$ (OH str.), 3490 cm.$^{-1}$ (OH str., bonded), and 3040 cm.$^{-1}$ (CH, hindered).[13,14]

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.79; H, 9.15. Found: C, 81.90; H, 8.95.

4-Hydroxypentacyclo[6.2.1.1^{1,8}.0^{2,7}.0^{9,11}]dodecane (V—OH).—Fraction 17 was the most crystalline material obtained from this chromatography. Sublimation yielded a white crystalline solid m.p. 68–69°. Recrystallization from hexane produced fine white needles with the melting point of 74–75° (reported[4] 76–77°), which was undepressed on admixture of a sample of authentic skewed alcohol V—OH.[4a,6] The infrared spectra of the two sam-

ples were identical, showing maxima at 3615 cm.$^{-1}$ (OH str.) and 3495 cm.$^{-1}$ (OH str., bonded) and no maximum due to a hindered C—H str.[13,14]

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.79; H, 9.15. Found: C, 81.91; H, 9.79.

Hexacyclo[6.2.1.^{3,6}.0^{2,7}.0^{4,10}.0^{5,9}]dodecane (IV).—A chromatography column was packed with 250 g. alumina and 7.98 g. of the ester distillate forecut (fraction 1, b.p. 65–82°/0.32 mm.) was introduced with minimum amount of pentane. Washing the column with 500 ml. of pentane produced 0.492 g. (2%) of an oily white solid. Two sublimations at 55°/20 mm. yielded white crystalline flakes, m.p. 161–163° (reported,[4a] 165–167°). Comparison of the infrared spectrum of the bird-cage hydrocarbon to the published spectrum[4a] revealed the same maxima.

1,2,3,4,4a,5,8,8a-Octahydro-1,4,5,8-*endo-exo*-dimethano-*exo*-2-naphthol (VII—OH).—The unsaturated alcohol residue, 2.4 g., obtained from the decomposition of the aqueous solution of the silver nitrate complex was chromatographed on 200 g. of alumina. No compounds were removed from the column with pentane or ether. The white crystalline material which was obtained on elution with ethyl acetate was recrystallized three times from hexane to afford 1.6 g. of pure product, m.p. 98–99° (reported[4a] 101–102°). The infrared spectrum of VII—OH showed maxima at 3610 cm.$^{-1}$ (OH str.), 3495 cm.$^{-1}$ (OH str., bonded), 3057 and 3045 cm.$^{-1}$ (CH str.), 751 cm.$^{-1}$ and 734 cm.$^{-1}$. (=CH def.).

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.79; H, 9.15. Found: C, 81.62; H, 9.10.

***trans*-2,3-Dichlorodecahydro-1,4,5,8-*endo-exo*-dimethanonaphthalene (IX).**—A solution of 22.0 g. (0.096 mole) of *trans*-2,3-dichloro-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-*endo-exo*-dimethanonaphthalene (VIII)[2,8] in 200 ml. of ethyl acetate containing 0.2 g. of platinum oxide catalyst was hydrogenated at 25° under 32 lb. of pressure. The reduction was complete in 1 hr. and the catalyst was removed. The solvent was removed under reduced pressure to afford 14.0 g. (63%) of IX, b.p. 85–88°/1.0 mm. The infrared spectrum showed no unsaturation.

1,2,3,4,4a,5,8,8a-Octahydro-1,4,5,8-*endo-exo*-dimethanonaphthalene (X).—To 3.32 g. (0.013 mole) of iodine and 7.95 g. (0.322 g.-atom) of magnesium in 200 ml. of ether was slowly added a solution of 50.0 g. (0.216 mole) of IX in 50 ml. of ether to maintain a gentle reflux.[2] The mixture was heated with stirring at the reflux temperature for an additional 15 hr. The reaction mixture was decomposed on ice containing 1 ml. of 6 N sulfuric acid. The ether layer was washed with sodium bicarbonate and water, and dried. The ether was removed and the residue was distilled under reduced pressure to give 20.3 g. (58.5%) of X, b.p. 96–97°/11 mm., n^{25}D 1.5272. Vapor fractometry showed pure olefin. The infrared spectrum showed a maximum at 678 cm.$^{-1}$ (=CH def.).

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.36; H, 10.52.

2,3-Epoxyoctahydro-1,4,5,8-*endo-exo*-dimethanonaphthalene (XI).—To a solution of 20.0 g. (0.14 mole) of perbenzoic acid in 300 ml. of chloroform at 0° was added 10.0 g. (0.0625 mole) of X. The reaction mixture was allowed to remain at 0° for 5 hr., after which time it was washed with sodium bicarbonate and water, and dried. The chloroform was removed under reduced pressure. The residue was dissolved in hexane, and washed with sodium hydroxide to remove residual benzoic acid. The solution was dried, the hexane was removed under reduced pressure, and the residue was sublimed at 55°/0.05 mm. to give 7.8 g. 71% of XI, m.p. 66–68°. The infrared spectrum showed maxima at 3063, 1002, 900, and 948 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.79; H, 9.15. Found: 81.25; H, 9.02.

Decahydro-1,4,5,8-*endo-exo*-dimethano-*exo*-2-naphthol (XII).—A solution of 1.6 g. (9.1 mmoles) of XI in 100 ml. of ethyl acetate was hydrogenated with a Raney nickel catalyst at 60° under 1500 lb. for 12 hr. The catalyst was removed, the solvent removed under reduced pressure, and the residue recrystallized twice from hexane to give 1.5 g. (93%) of XII, m.p. 126–127.5 (reported[4a] 123–124°). The infrared spectrum of XII showed maxima at 3605 cm.$^{-1}$ (OH str.) and 3495 cm.$^{-1}$ (OH str., bonded), and 3047 cm.$^{-1}$ (CH str., hindered).[13,14]

XII was also obtained by the hydrogenation of VII. A solution of 0.352 g. (2 mmoles) of VII in 20 ml. of absolute ethanol was hydrogenated with a platinum catalyst at 25°/1 atm. to yield 0.34 g. (96%) of XII, m.p. 122–123°.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.65; H, 10.52.

A mixture of this sample and the sample prepared by the hydrogenolysis of the epoxide melted at 122–124°.

Oxidation of XII with potassium permanganate produced the α-diacid, m.p. 217–218° (reported[11] 216–217°).

1,2,3,4,4a,5,8,8a-Octahydro-1,4,5,8-*exo-exo*-dimethano-*exo*-2-naphthol (XIV—OH).—A solution of 9 g. of the unsaturated alcohol obtained from the precipitated silver nitrate complex in pentane was chromatographed on 200 g. of alumina. No compounds were removed from the column with pentane or ether. The alcohol which was eluted with ethyl acetate was recrystallized four times from hexane to produce white needles, m.p. 84.5–85.5°. The infrared spectrum showed maxima at 3610 cm.⁻¹ (OH str.), 3500 cm.⁻¹ (OH—str., bonded), 3045 cm.⁻¹ (CH str., hindered), 710 cm.⁻¹ and 695 cm.⁻¹ (=CH wag).

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.79; H, 9.15. Found: C, 81.49; H, 9.45.

Decahydro-1,4,5,8-dimethano-*exo-exo-exo*-2-naphthol (XVI-OH).—A solution of 1.01 g. (5.74 mmoles) of XIV—OH in 50 ml. of absolute ethanol was hydrogenated at room temperature under 1 atm. of hydrogen with 0.15 g. of a platinum oxide catalyst. After 3 hr. the theoretical amount of hydrogen had been absorbed and no more hydrogen was consumed. The catalyst was removed by filtration and the ethanol was removed to afford 1.02 g. (100%) of the saturated alcohol.

One recrystallization from hexane yielded 0.9 g. of fine white needles, m.p. 78–79°. The infrared spectrum showed no absorption in the 710–690-cm.⁻¹ region, but maxima at 3608 cm.⁻¹ (OH str.), 3490 cm.⁻¹ (OH str., bonded), and 3045 cm.⁻¹ (CH str., hindered).[13,14]

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.04; H, 11.05.

An authentic sample of XVI—OH was prepared by hydration of XV in the manner described by Soloway[11] with the exception that formic acid with a boron fluoride catalyst was employed rather than the acetic-sulfuric acid mixture described.

The formate ester was saponified in alcoholic potassium hydroxide, and recrystallization of the alcohol from hexane yielded a white crystalline product, m.p. 77–78° (reported[11] 76–78°), whose infrared spectrum was superimposable on that of the alcohol obtained from the hydrogenation of XIV. A mixture of the two samples melted at 78–79°. Oxidation of both alcohol samples with potassium permanganate yielded the γ-diacid, m.p. 245–247°. The melting point of a mixture of these acids was undepressed.

2,3-Epoxyoctahydro-1,4,5,8-*exo-exo*-dimethanonaphthalene (XVIII).—To 200 ml. (212 mequiv.) of a perbenzoic acid solution in chloroform at room temperature was added 18.4 g. (115 mequiv.) of X. Sufficient heat was evolved to cause the chloroform to reflux. Immediate titration indicated 211 mequiv. of acid had been consumed and an additional 100 ml. of the reagent was added to ensure the completion of the reaction.

The solution was washed with sodium bicarbonate and water. The chloroform layer was dried and the solvent was removed. Distillation of the residue afforded 8.40 g. (41.5%) of liquid (b.p. 100–102°/0.5 mm.) which showed infrared maxima at 1000, 975, 845, and 797 cm.⁻¹. No carbonyl absorption was found. Chromatography of this oil with ether afforded a very waxy white solid which was sublimed to yield a white solid, m.p. 54–56°.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.79; H, 9.15. Found: C, 81.08; H, 9.02.

Decahydro-1,4,5,8-*exo-endo*-dimethano-*exo*-2-naphthol (XIX—OH).—A solution of 7.0 g. (0.038 mole) of XVIII in 200 ml. of ethyl acetate was hydrogenated with a Raney nickel catalyst at 60°/1500 lb. for 24 hr. The catalyst was removed and the solvent was removed under reduced pressure. The solid residue was recrystallized from hexane to yield 5.0 g. (71%) of XIX—OH, m.p. 99.5–100°. The infrared spectrum showed maxima at 3610 cm.⁻¹ (OH str.), 3490 cm.⁻¹ (OH str., bonded), and 3040 cm.⁻¹ (CH str. hindered).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.11; H, 10.11.

Oxidation of a sample of XIX—OH with potassium permanganate afforded the β-diacid (XX) m.p. 254–256° (reported[11] 256°).

Treatment of the epoxide XVIII with lithium aluminum hydride in refluxing tetrahydrofuran for 28 days resulted in a quantitative recovery of starting material.

The Diol (XXII—OH).—To a solution of 10 g. of potassium hydroxide in 150 ml. of a water–ethanol mixture was added 10 g. (0.04 mole) of diformate ester dissolved in ethanol. The mixture was stirred at room temperature for 12 hr., after which 100 ml. of water was added to precipitate an oil. The oil was extracted with ether, the ether was removed, and the residue was recrystallized from chloroform to give 7.1 g. (91%) of XXII. Recrystallization from water and from chloroform afforded pure product, m.p. 201–202°. The infrared spectrum indicated no unsaturation and no ester.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.87; H, 9.51.

***cis*-Bicyclo[3.3.0]-*trans,trans,trans,trans*-2,4,6,8-tetracarboxylic Acid (XXIII).**—A slurry of 3.88 g. (0.02 mole) of XXII—OH in 200 ml. of water was heated to 95° to dissolve as much of XXII—OH as possible. To this hot mixture was added 2.0 g. of potassium hydroxide and 16.85 g. (0.1066 mole) of potassium permanganate. The mixture was heated at 95° with stirring for 10 hr., after which the mixture was allowed to come to room temperature and the manganese dioxide was removed by filtration. The filtrate was carefully acidified with dilute hydrochloric acid and extracted with ether to remove any unchanged starting material. The volume of the filtrate was reduced to 30 ml. to afford 1.2 g. (24%) of XXIII. Recrystallization from water gave pure XXIII, m.p. 267–269°. A mixture of a sample of this acid and a sample of *cis*-bicyclo[3.3.0]octane-*cis,cis,trans,trans*-2,4,6,8-tetracarboxylic acid[2] (m.p. 270–271°) melted at 248–253°.

Anal. Calcd. for $C_{12}H_{14}O_8$: C, 50.35; H, 4.93. Found: C, 49.99; H, 4.66.

A 1.76-g. sample of XIV was oxidized with potassium permanganate under the same conditions. The first crop of crystals obtained from the acidified aqueous filtrate, was *exo*-2,3,3a,4,5,6,-7,7a-octahydro-*exo*-5-hydroxy-4,7-methanoindene-*trans-trans*-1,3-dicarboxylic acid (XXIV), m.p. 250–251° which was recrystallized from water. The infrared spectrum (mull) showed maxima at 3500 cm.⁻¹ (broad, OH str.) in addition to the acid OH str. (broad). No ketone carbonyl was present.

Anal. Calcd. for $C_{12}H_{16}O_5$: C, 60.01; H, 6.72. Found: C, 59.91; H, 6.67.

The second crop of crystals obtained was recrystallized from water to afford XXIII, m.p. 265–269°. A mixture of this sample and one obtained from the oxidation of XXII (m.p. 266–268°) melted at 264–267°.