For accurate dihedral angle measurements one must rely on methods more accurate than n.m.r.

The causes responsible for making V more stable than IVa, even when R is isopropyl, are not well understood. Although the more favorable dipole–dipole interactions in V over IVa and the possibility of hydrogen bonding in V are plausible explanations, they cannot be the sole factors responsible for the greater stability of V, as witnessed by the case of phenylacetaldehyde. Very likely here are good examples of two interacting groups whose distance is in the attractive portion of the van der Waals curve.

Experimental

Except for *t*-butylacetaldehyde, di-*t*-butylacetaldehyde, cyclopropyl-, cyclobutyl-, and cyclopentylcarboxaldehydes, all aldehydes used were freshly distilled samples of commercially available materials.

Di-*t*-butylacetaldehyde was prepared from di-*t*-butyl ketone.[28] Cyclopropylcarboxaldehyde was prepared from cyclopropylnitrile.[29] *t*-Butylacetaldehyde, cyclobutylcarboxaldehyde, and cyclopentylcarboxaldehyde were prepared from the corresponding acids.[30]

N.m.r. spectra were determined at 60 Mc. on a Model A-60 spectrometer.

(28) M. S. Newman, A. Arkell, and T. Fukunaga, *J. Am. Chem. Soc.*, **82**, 2498 (1960).
(29) H. C. Brown and C. P. Garg, *ibid.*, **86**, 1085 (1964).
(30) H. C. Brown and A. Tsukamoto, *ibid.*, **86**, 1089 (1964).

Bridged Polycyclic Compounds. XXIX. Some Rearrangements of Dibenzobicyclo[2.2.2]octadienes to Dibenzobicyclo[3.2.1]octadienes[1]

Stanley J. Cristol, Farn Pwu Parungo, and Donald E. Plorde

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado. Received February 19, 1965

Addition of bromine in acetic acid and of iodine and silver acetate to dibenzobicyclo[2.2.2]octatriene (I) led to syn-8-bromo- (II) and syn-8-iododibenzobicyclo-[3.2.1]octadien-exo-2-ol acetate (III), respectively. Solvolysis of three 7-dibenzobicyclo[2.2.2]octyl pairs (dichlorides V and VI, chloro p-toluenesulfonates X and XI, and chloro acetates XII and XIII) gave rearranged [3.2.1] derivatives with a high degree of stereoselectivity. These results are discussed in light of various carbonium ion intermediates and seem best to be interpreted by classical benzylic cationic intermediates.

Previous work on Wagner–Meerwein rearrangements of dibenzobicyclo[2.2.2]octadienes to dibenzobicyclo-[3.2.1]octadienes has indicated the high degree of stereospecificity of bond migration in rearrangements accompanying both addition and solvolysis.[2–4] It was desirable to test the generality of these findings further in order to elucidate the mechanistic details involved. Examination of both addition rearrangement and solvolysis rearrangement reactions was undertaken.

Addition of the elements of acetyl hypobromite to dibenzobicyclo[2.2.2]octatriene (I) via bromine in acetic acid led to only one product, *syn*-8-bromodi-

benzobicyclo[3.2.1]octadien-*exo*-2-ol acetate (II). In an analogous manner, the product of the treatment of I with iodine and silver acetate was exclusively the *syn-exo* iodo acetate III. When the Prévost reaction was carried out in acetic acid rather than in benzene and with excess silver acetate, the known[3] *exo-syn* diacetate IV was formed.
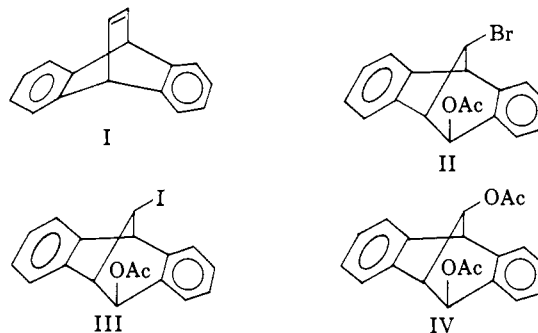
Solvolysis rearrangements of three epimeric pairs of disubstituted dibenzobicyclo[2.2.2]octadienes were also investigated. The *cis-* V and *trans*-dichloride VI reported earlier[5] were solvolyzed in acetic acid assisted by silver acetate. Acetolysis of V led to two known[4,6] products: *syn-exo* chloro acetate VII and *syn-endo* chloro acetate VIII. The relative proportions of VII and VIII changed with reaction time, VIII increasing with longer times. The acid-catalyzed rearrangement of VII to VIII has been reported earlier.[6]

(1) Previous paper in series: S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **30**, 1956 (1965). This work was reported at the 19th National Organic Symposium of the American Chemical Society, Columbus, Ohio, June 1963.
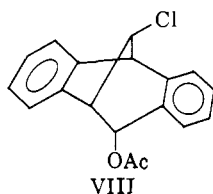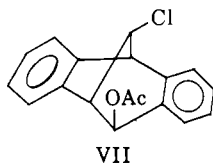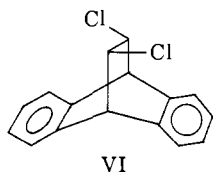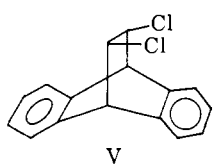(2) W. R. Vaughan and A. C. Schoenthaler, *J. Am. Chem. Soc.*, **80**, 1956 (1958).
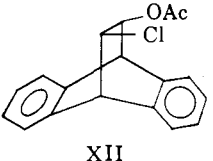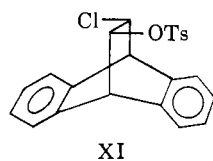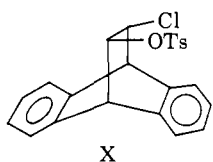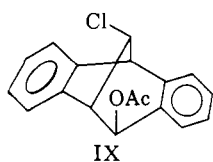(3) S. J. Cristol and R. K. Bly, *ibid.*, **82**, 6155 (1960).
(4) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, **28**, 1374 (1963).

(5) S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, **74**, 2193 (1952).
(6) S. J. Cristol and D. D. Tanner, *ibid.*, **86**, 3122 (1964).

V

VI

VII

VIII

Acetolysis of *trans*-dichloride VI led to the exclusive formation of *anti*-8-chlorodibenzobicyclo[3.2.1]octadien-*exo*-2-ol acetate (IX).

IX

X

XI

XII

Solvolyses of the *cis*- and *trans*-chloro *p*-toluenesulfonates X and XI were also conducted. Acetolysis of X gave only VII, and that of XI gave only IX. These results rule out any special significance to a solid phase in the silver ion assisted solvolyses of V and VI.

The silver ion assisted acetolyses of *cis*- (XII) and *trans*-chloro acetate XIII were also studied. XII produced the known *syn-exo* diacetate IV, while XIII gave the *anti-exo* diacetate XIV.

XIII

XIV

XV

XVI
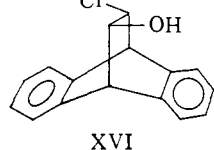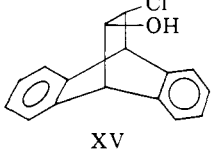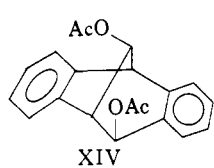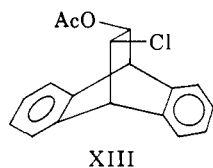
The synthesis of the *cis*- XV and *trans*-chlorohydrin XVI, from which the esters were prepared, involved an interesting reaction which may be of general synthetic utility. Addition of diborane to the chloroolefin XVII[5] followed by a nonaqueous oxidation of the intermediate by peroxybenzoic acid led to the desired *trans*-chlorohydrin XVI (*cis* addition assumed on the basis of earlier work[7]). However when the usual aqueous oxidation with ice-cold alkaline hydrogen peroxide was attempted, the olefin I was obtained. Under the aqueous conditions the diborane–chloroolefin addition compound was attacked by water to

eliminate the elements of boron chloride. Other investigators[8-10] working with chloroolefins have observed that the intermediate addition products decomposed spontaneously to olefin during the period of the diborane addition, so that nonhalogenated alcohol, resulting from further addition of diborane to the olefin, was the final product. In our case the intermediate was stable in ethereal solution or in chloroform, and did not decompose until ice was added. Similar results (isolation of *cis*- and *trans*-stilbene) were observed on treatment of bromo-*cis*-stilbene with diborane, followed by treatment with alkaline hydrogen peroxide. Perhaps conditions could be found, possibly low temperatures for addition and/or rapid treatment, where other intermediate β-haloorganoboranes could be oxidized before elimination could occur.

XVII

XVIII

XIX

XX
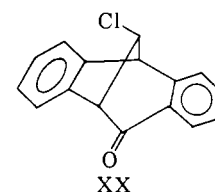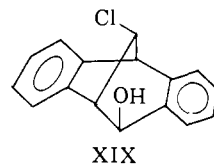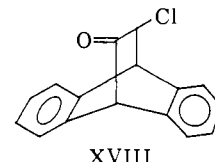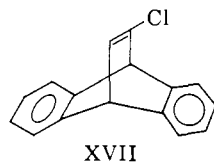
Chromium trioxide oxidation of XVI led to the chloro ketone XVIII. When XVIII was reduced by sodium borohydride in methanol, a mixture of chlorohydrins containing 87% *cis* (XV) and 13% *trans* (XVI) was obtained. XV could be reconverted to XVIII by chromium trioxide oxidation, showing that it was the epimer of XVI.

The structure of the *anti-exo* chloro acetate IX was assigned as follows. Evidence for the *anti*-chloro group rests in the conversion of IX by lithium aluminum hydride reduction to the chlorohydrin XIX followed by chromium trioxide oxidation to the *anti*-chloro ketone XX. XX was different from the *syn*-chloro ketone XXI prepared earlier.[4] Clemmensen reduction of XX led to the *anti*-chloride XXII which again differed from the previously prepared *syn* chloride XXIII.[4] IX could be directly converted to XXII by hydrogenolysis over palladium on charcoal. The ease of hydrogenolysis of IX and the ultraviolet absorp-

XXI

XXII

XXIII

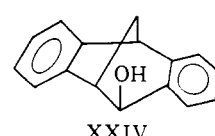XXIV

(7) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 123.
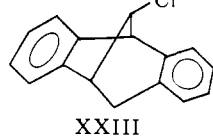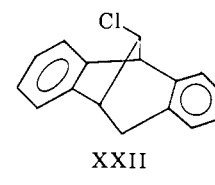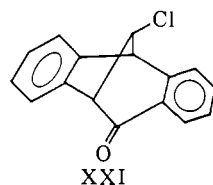
(8) M. F. Hawthorne and J. A. Dupont, *J. Am. Chem. Soc.*, **80**, 5830 (1958).
(9) (a) P. Binger and R. Koster, *Tetrahedron Letters*, No. 4, 156, (1961); (b) H. C. Brown and O. J. Cope, *J. Am. Chem. Soc.*, **86**, 1801 (1964).
(10) J. G. Sharefkin and S. H. Pohl, *J. Org. Chem.*, **29**, 2050 (1964).

tion of XX confirmed the location of the oxygen function at the benzyl position. The ultraviolet spectrum of XX in concentrated sulfuric acid showed a bathochromic shift of 300–600 Å. with a band appearing at 2990 Å. (ϵ 17,000). This and the absence of the normal conjugated carbonyl band at approximately 2400 Å. when the spectrum was taken in absolute ethanol are in good agreement with the results obtained for XXI and other similar ketones.[11] Reduction of both IX and VII[6] by sodium biphenyl in glyme (ethylene glycol dimethyl ether) produced dibenzo-bicyclo[3.2.1]octadien-exo-2-ol (XXIV). XXIV is also formed by deamination of XXV, by solvolysis of XXVI,[12] or by solvolysis of XXVII.[6]

XXV   XXVI
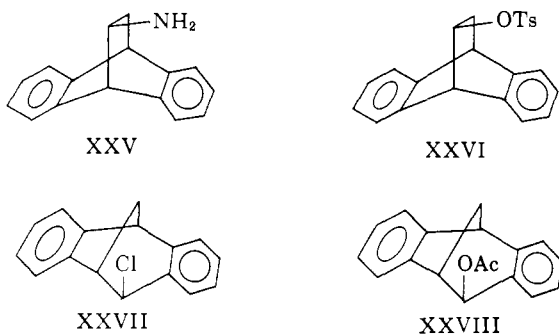
XXVII   XXVIII

The syn-exo iodo acetate III was reduced by hydrogen over Raney nickel or zinc in acetic acid to the exo acetate XXVIII and then to the exo alcohol XXIV by lithium aluminum hydride. Alternatively III could be reduced by lithium aluminum hydride to the iodohydrin XXIX and then to XXIV by hydrogen over Raney nickel. Oxidation of XXIX gave the syn-iodo ketone XXX which had an ultraviolet absorption maximum in sulfuric acid at 2970 Å. (ϵ 7600).


XXIX   XXX

XXXI   XXXII
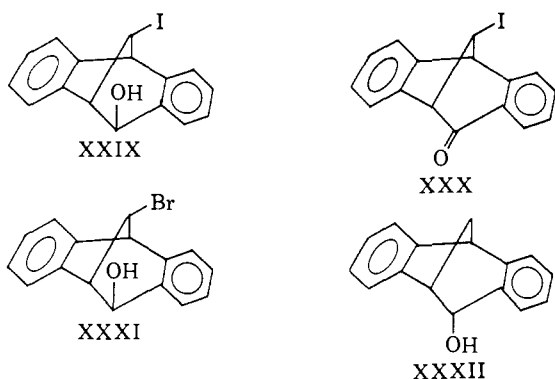
The syn-exo bromo acetate II could be reduced by lithium aluminum hydride to give the syn-exo bromohydrin XXXI. Both II and XXXI have been independently synthesized.[13] Reduction of II with sodium biphenyl in glyme gave XXIV.

Proof was needed that, in reduction of the syn-exo bromo and chloro acetates (II and VII) and anti-exo chloro acetate IX to the exo alcohol XXIV, no epimerization about the benzyl position took place. This was demonstrated by the reduction of the syn-endo chloro acetate VIII by sodium biphenyl in glyme to the endo alcohol XXXII. If this reduction had led to

(11) See ref. 4, and references therein.
(12) J. R. Mohrig, Ph.D. Thesis, University of Colorado, 1963.
(13) I. G. Dinulescu, M. Avram, G. D. Mateescu, and C. D. Nenitzescu, Chem. Ind. (London), 2023 (1964).

the hydroxyl in the most stable configuration, epimeric acetates would have all given one alcohol; this was not observed.

XXXII has also been obtained along with XXIV in the solvolysis of the exo chloride XXVII in aqueous dioxane in the absence of an acid acceptor.[14] XXXII and XXIV were shown to be epimeric by oxidation to the same ketone XXXIII. XXXIII in sulfuric acid had an ultraviolet absorption maximum at 3000 Å. (ϵ 13,000). Reduction of XXXIII with lithium aluminum hydride or with sodium in ethanol gave only the presumably more stable endo alcohol XXXII. Clemmensen reduction of XXXIII gave the hydrocarbon XXXIV which had been prepared earlier by the hydrogenolysis of the exo chloride XXVII.[14]

XXXIII   XXXIV
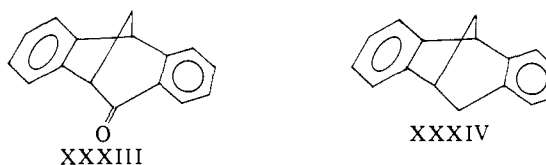
The chemical evidence presented for the structures as given for [3.2.1] derivatives has been substantiated by proton magnetic resonance studies.[1] Equivalent evidence is available for the [2.2.2] derivatives discussed here.[12,15]

The solvolysis rearrangement reactions detailed above are clearly ionic. In the following discussion only the cationic intermediates are considered. In all of the examples of solvolysis rearrangement listed above, the stereochemical outcome corresponds to the migration of the bond anti to the leaving group.

One may consider the two classical cationic structures XXXV and XXXVI as possible intermediates in the reactions being discussed or as resonance forms contributing to a nonclassical cationic intermediate. The stereochemical evidence presented above implies that the [2.2.2] carbonium ion XXXV cannot be an intermediate either in the addition rearrangements or in the solvolysis rearrangements. If it were, such an intermediate would give similar mixtures of syn and anti products in addition rearrangements and in solvolysis of both cis and trans isomers. As this is not observed, migration does not follow ionization (or addition of the cationic fragment) but must accompany it.

XXXV

XXXVI   XXXVII
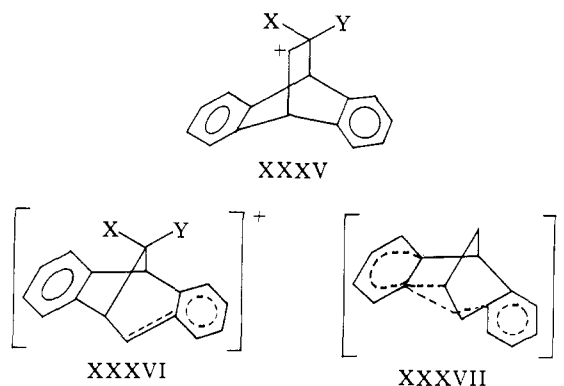
If the migration occurs at the time of ionization, the cationic intermediate can be envisaged as either a

(14) D. D. Tanner, Ph.D. Thesis, University of Colorado, 1961.
(15) D. E. Plorde, Ph.D. Thesis, University of Colorado, 1963.

"classical" benzylic ion XXXVI with only ordinary delocalization into the vicinal aromatic ring, or as the "nonclassical" intermediate XXXVII. Species such as XXXVII have been discussed in connection with similar problems already,[6] and will be considered again in detail in the following paper.[16]

The formation of the *syn-exo* diacetate IV from the Prévost reaction or by the reaction of silver acetate with the *syn*-iodo *exo*-acetate III is an interesting example of replacement with retention. As discussed briefly earlier,[17] this appears to be a reaction involving a cationic intermediate where stereochemistry is protected by participation of the π-electrons of an aromatic ring.

Experimental

The Preparation of Dibenzobicyclo[2.2.2]octatriene (I). The procedure used was a modification of the reported method.[5] To a 500-ml., round-bottom flask, equipped with a reflux condenser protected by a drying tube, was added 18 g. of the *trans*-dichloride VI (or the *cis*-dichloride V) (65 mmoles) and 300 ml. of diglyme (diethylene glycol dimethyl ether) which had been distilled from lithium aluminum hydride and stored under nitrogen. The solution was heated to reflux and 3.4 g. of metallic sodium (0.15 g.-atom) was added in small pieces over a 5-min. period. The solution immediately turned dark and the surface of the unreacted sodium was violet. The entire reaction mixture assumed a violet color and white precipitate was evident after 1 hr. After an additional 12 hr. of heating at reflux, the reaction mixture was cooled and methanol was added to destroy the excess sodium (the violet color was discharged after addition of 30 ml. of methanol). The solvent was removed by evaporation with a warm stream of dry air. The residue was then triturated with 300 ml. of water and the resulting suspension was extracted twice with 250-ml. portions of benzene. The benzene layer was washed with dilute hydrochloric acid, twice with water, and finally dried over anhydrous magnesium sulfate. The solvent was evaporated with a warm jet of dry air and the residue of 16.8 g. was dissolved in ethanol. The ethanol solution was treated with activated charcoal, the filtered solution was concentrated, and the product was crystallized from solution. The first crop gave 10.0 g., m.p. 119.5–120°, and showed no mixture melting point depression with a genuine sample of I.[5] Further crops gave 1.3 g. of I, m.p. 116–118°. The total yield was 11.3 g. or 85%.

Treatment of I with Bromine and Acetic Acid. I (2.14 g., 10.5 mmoles) and 859 mg. of anhydrous sodium acetate (10.5 mmoles) were dissolved in 75 ml. of glacial acetic acid. A solution of 1.67 g. of bromine (10.4 mmoles) in 50 ml. of glacial acetic acid was added slowly with stirring. After standing for 10 hr. in the dark, the reaction mixture was heated at reflux for 12 hr. The reaction mixture was cooled and the solvent was removed by rotary evaporation. The residue was dissolved in 200 ml. of ether and this solution was washed with dilute sodium bicarbonate solution and then dried over anhydrous magnesium sulfate.

(16) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Am. Chem. Soc.*, 87, 2879 (1965).
(17) S. J. Cristol, J. R. Mohrig, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, 85, 2675 (1963).

The ether was removed by rotary evaporation leaving 3.58 g. of a light yellow solid. The product was dissolved in ethanol and the resulting solution was decolorized with activated charcoal before crystallization of the product by concentration of the solution. A total of 3.09 g. (86%) of *syn*-8-bromodibenzobicyclo-[3.2.1]octadien-*exo*-2-ol acetate (II), m.p. 152.5–153°, was obtained.

Anal. Calcd. for $C_{18}H_{15}BrO_2$: C, 62.99; H, 4.41. Found: C, 63.18; H, 4.47.

An infrared spectrum of the product in carbon disulfide solution showed a strong acetoxy absorption at 5.75 and 8.15 μ.

The Preparation of syn-8-Iododibenzobicyclo[3.2.1]-octadien-exo-2-ol Acetate (III) by the Prévost Method. A mixture of 3.05 g. (0.015 mole) of I, 5.0 g. (0.030 mole) of silver acetate, 3.81 g. (0.015 mole) of iodine, and 140 ml. of benzene was heated at reflux for 26 hr. The yellow solid formed was filtered from the hot solution and the solvent was evaporated with a warm jet of air leaving 5.5 g. of an oily residue. Trituration with petroleum ether (b.p. 60–70°) gave a white solid, m.p. 125–140°. The product was chromatographed on alumina. Three fractions were isolated. The first fraction was 0.56 g. (18%) of starting material (I), m.p. 118–120°. The second fraction gave 4.7 g. (77%) of material melting at 130–140°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) gave 3.2 g. of *syn*-8-iododibenzobicyclo-[3.2.1]octadien-*exo*-2-ol acetate (III), m.p. 141–142°.

Anal. Calcd. for $C_{18}H_{15}IO_2$: C, 55.42; H, 3.92; I, 32.44. Found: C, 55.52; H, 4.08; I, 32.21.

The third fraction gave 45 mg. (4%) of a brown oil whose infrared absorption was the same as that of the *exo-syn* diacetate IV.[3]

The Preparation of Dibenzobicyclo[3.2.1]octadiene-exo-2-syn-8-diol Diacetate (IV) by the Prévost Method. Dibenzobicyclo[2.2.2]octatriene (35 g., 0.171 mole) and 56.94 g. (0.3430 mole) of silver acetate were dissolved in 3 l. of glacial acetic acid. Then 43.56 g. (0.1715 mole) of sublimed, powdered iodine was added. This mixture was stirred at room temperature overnight and then heated at reflux with stirring for 30 hr. While the solution was still hot, the solid was filtered. Distillation of the solvent from the filtrate left 68 g. of residue. This was purified by crystallization from petroleum ether (b.p. 60–70°)–benzene mixture and by chromatography over neutral alumina. The resulting IV, 39.6 g. (72%), melted at 168–169°. The infrared spectrum was the same as that of the known *exo-syn* diacetate IV,[3] and a mixture melting point with genuine IV was not depressed.

The Acetolysis of cis-7,8-Dichlorodibenzobicyclo-[2.2.2]octadiene (V). The *cis*-dichloride[5] (2.00 g., 7.29 mmoles) and 1.21 g. of silver acetate (7.26 mmoles) were placed in 150 ml. of glacial acetic acid and the resulting reaction mixture was heated at reflux for 116 hr. After cooling, the reaction mixture was filtered and the acetic acid was removed by rotary evaporation. The residue was treated with 150 ml. of hot benzene and the unreacted silver acetate was filtered. The benzene solution was washed with sodium carbonate solution and dried over anhydrous magnesium sulfate. The benzene was removed by rotary evaporation leaving 2.1 g. of colorless oil which

slowly crystallized. The product was dissolved in carbon tetrachloride and chromatographed on 125 g. of Fisher neutral alumina packed in carbon tetrachloride. The column was eluted with carbon tetrachloride, 10% chloroform in carbon tetrachloride, 100% chloroform, and 100% ethyl acetate. The carbon tetrachloride fractions gave 300 mg. of material melting at 202–203°. A mixture melting point with starting material (V) was not depressed. The fractions eluted with 10% chloroform in carbon tetrachloride gave 624 mg. of material melting at 153.5–155.5°. Recrystallization from ethanol gave material melting at 155–156°. A mixture melting point with genuine *syn-exo* chloro acetate VII was not depressed. The infrared spectrum of the product taken in carbon disulfide solution was identical with that of VII.

The fractions eluted with 100% ethyl acetate gave 232 mg. of a white solid, m.p. 120–127°. The infrared spectrum taken in carbon disulfide solution showed no acetoxy absorption but showed an hydroxy absorption at 2.77 μ. The infrared spectrum also indicated that this alcohol was a mixture of the *syn-endo* chlorohydrin XXXVIII and the *syn-exo* chlorohydrin XXXIX.[6] The fractions eluted with 100% chloroform gave 428 mg. of material melting at 113–130°. Recrystallization from ethanol gave material melting at 145–146°.

Anal. Calcd. for $C_{18}H_{15}ClO_2$: C, 72.36; H, 5.06. Found: C, 72.32; H, 5.02.

A mixture melting point with genuine *syn-endo* chloro acetate (VIII) (m.p. 135–136.7°)[6] melted in between the two values (138.5–141.5°). After solidification, a remelting point of the mixture gave a value of 135–136.7°. The infrared spectra of the two materials, which apparently were homomorphs, although differing somewhat when taken in potassium bromide pellets were identical when taken in carbon disulfide solution.

To determine the ratio of *exo* to *endo* acetates formed, the acetolysis reaction was carried out for differing lengths of time. The infrared spectra of the crude reaction mixtures were compared to known mixtures of the *exo* and *endo* acetates. The *exo* isomer has an absorption peak at 12.45 μ which is not present in the *endo* isomer. Likewise, the *endo* isomer has an absorption peak at 12.10 μ not present in the *exo* isomer. The technique of differential quantitative infrared analysis[18] was used in determining the proportions of *exo* and *endo* formed. After a reaction time of 113.5 hr., the product contained 23 ± 2% *endo;* and after a reaction time of 141 hr., the amount of *endo* product formed increased to 27 ± 2%.

The Acetolysis of trans-7,8-Dichlorodibenzobicyclo-[2.2.2]octadiene (VI). The *trans*-dichloride[5] (5.09 g., 18.5 mmoles) and 3.16 g. of silver acetate (18.9 mmoles) were added to 300 ml. of glacial acetic acid and the resulting reaction mixture was heated at reflux for 54 hr. The reaction mixture was cooled and filtered, and the solvent was removed by rotary evaporation. The residue was dissolved in 250 ml. of hot benzene. This solution was filtered, washed with aqueous sodium bicarbonate and with water, and then dried over anhydrous magnesium sulfate. The solvent was removed

(18) I. M. Kolthoff and E. S. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., The Macmillan Co., New York, N. Y., 1952, p. 632.

by rotary evaporation leaving 6.57 g. of a yellow oil which slowly crystallized upon standing. The product was dissolved in ethanol and the resulting solution was decolorized with activated charcoal before crystallization of the product by concentration of the solution. The first crop consisted of 1.81 g., m.p. 143.7–144.7°. Succeeding crops gave a total yield of 5.02 g. (99%) of *anti-exo* chloro acetate IX. Recrystallization gave material melting at 144.5–145.5°. The infrared spectrum of the product taken in carbon disulfide solution showed the characteristic acetoxy absorption at 5.77 and 8.10 μ.

Anal. Calcd. for $C_{18}H_{15}ClO_2$: C, 72.36; H, 5.06. Found: C, 72.20; H, 5.08.

The Preparation of trans-3-Chlorodibenzobicyclo-[2.2.2]octadien-2-ol (XVI). The chloroolefin[5] XVII (5.3 g., 22.2 mmoles) was dissolved in 300 ml. of dry ethyl ether (distilled from lithium aluminum hydride) and treated with an excess of diborane at 0° under an atmosphere of nitrogen. The diborane was generated from 3.2 g. of boron fluoride etherate and 6.32 g. of sodium borohydride in 250 ml. of dry diglyme. The reaction mixture was allowed to stand, with stirring, under nitrogen for 4 hr. The excess diborane and ether were then carefully distilled off under nitrogen. The colorless oil remaining was dissolved in 100 ml. of dry chloroform.

To this chloroform solution was added slowly, with stirring and cooling, a solution of 9.36 g. of peroxybenzoic acid in 180 ml. of chloroform. The reaction mixture was kept under nitrogen in order to exclude moisture. After 36 hr., the reaction mixture was extracted five times with 100-ml. portions of a 5% solution of ferrous ammonium sulfate (acidified with a few drops of concentrated sulfuric acid). The chloroform layer was then washed twice with aqueous sodium bicarbonate, with water, and then dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation leaving a yellow oil. This oil was dissolved in 200 ml. of carbon tetrachloride and chromatographed on 225 g. of Merck acid-washed alumina packed in carbon tetrachloride. The column was eluted with carbon tetrachloride, chloroform, 10% ethyl acetate in chloroform, and 100% ethyl acetate. The fractions eluted with 10% ethyl acetate in chloroform contained 3.23 g. of a light yellow solid, m.p. 72.5–76.5°. Recrystallization from ethanol gave a total yield of 3.21 g. (56%) of the *trans*-chlorohydrin XVI, m.p. 91–93°. The infrared spectrum of the product in carbon disulfide solution showed an hydroxyl absorption at 2.77 and the absence of an olefinic peak at 6.25 μ.

Anal. Calcd. for $C_{16}H_{13}ClO$: C, 74.85; H, 5.10. Found: C, 74.71; H, 5.09.

The chloroolefin XVII (450 mg.) dissolved in 15 ml. of dry ether was treated with excess diborane, and the excess diborane was decomposed with ice and water. Addition of 3 ml. of 3 M sodium hydroxide solution and 2 ml. of 30% hydrogen peroxide, followed by the usual work-up,[7] gave, after recrystallization from ethanol, 332 mg. (86%) of olefin I, m.p. and m.m.p. 118–119°. A similar result was obtained when the alkali and hydrogen peroxide were omitted.

The Preparation of trans-3-Chlorodibenzobicyclo-[2.2.2]octadien-2-ol p-Toluenesulfonate (XI). The *trans*-

chlorohydrin XVI (657 mg., 2.56 mmoles) and 541 mg. of p-toluenesulfonyl chloride (2.84 mmoles) were dissolved in 10 ml. of pyridine and the resulting reaction was allowed to stand, with stirring, at room temperature for 3 days. The reaction mixture was poured into 350 ml. of water to precipitate the product. The product was extracted with three 150-ml. portions of ether. The ethereal solution was washed with dilute hydrochloric acid and aqueous sodium carbonate, and finally dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation leaving 886 mg. of a colorless oil which slowly crystallized. The product was recrystallized from petroleum ether (b.p. 60–70°). The first crop gave 218 mg. of white crystalline *trans*-chloro p-toluenesulfonate XI, m.p. 160–161°. Further crops gave 598 mg. of material melting at 141.0–141.5°. The infrared spectra of both materials in carbon disulfide solution were identical and showed the absence of hydroxy absorption at 2.77, and the presence of characteristic sulfonate absorptions at 7.30 and 8.50 μ. The total yield of XI was 816 mg., 78%.

Anal. Calcd. for $C_{23}H_{19}ClO_3S$: C, 67.23; H, 4.66. Found: C, 67.45; H, 4.55.

The Preparation of *trans*-3-Chlorodibenzobicyclo-[2.2.2]octadien-2-ol Acetate (XIII). The *trans*-chlorohydrin XVI (200 mg., 0.78 mmole) was dissolved in 30 ml. of acetic anhydride containing 1 ml. of pyridine. The reaction mixture was heated at reflux for 2 hr. and then after cooling was poured into 300 ml. of water and stirred until the product precipitated. This suspension was extracted four times with 50-ml. portions of ether. The ethereal solution was washed with aqueous sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation and the resulting oil was dissolved in ethanol. This solution was decolorized with activated charcoal. The product was then crystallized by concentration of the solution. Material melting at 111–114° was obtained. Recrystallization from ethanol gave 230 mg. (99%) of the *trans*-chloro acetate XIII, m.p. 116–118°. An infrared spectrum of the product taken in carbon disulfide solution showed acetoxy absorptions at 5.73 and 8.20, and no hydroxy absorption at 2.77 μ.

Anal. Calcd. for $C_{18}H_{15}ClO_2$: C, 72.36; H, 5.06. Found: C, 72.52; H, 5.26.

The Preparation of 3-Chlorodibenzobicyclo[2.2.2]-octadien-2-one (XVIII). The *trans*-chlorohydrin XVI (8.29 g., 0.032 mole) was dissolved in 500 ml. of acetone (distilled from potassium permanganate), and 78 ml. of a solution of chromium trioxide in aqueous sulfuric acid was added. The chromium trioxide solution was made up by dissolving 13.4 g. of chromium trioxide in 115 ml. of concentrated sulfuric acid and 200 ml. of water, and then diluting to 500 ml. total volume with water. The reaction mixture was stirred for 15 min. at which time the reaction mixture had turned from brown to green. The reaction mixture was then poured into 1.3 l. of water giving a fine, white precipitate. The product was extracted three times with 300-ml. portions of ether after saturating the aqueous solution with sodium chloride. The ethereal solution was washed with aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. The ether

was removed by rotary evaporation leaving a yellow oil which slowly crystallized. The product was dissolved in ethanol and this solution was decolorized with activated charcoal. The product was then crystallized out by concentration of the solution. The total yield of the crystalline chloro ketone XVIII was 7.38 g. (91%), m.p. 132.5–135°. An infrared spectrum of the product taken in carbon disulfide solution showed the absence of an hydroxyl absorption at 2.77, but showed the presence of a strong carbonyl absorption at 5.72 μ.

Anal. Calcd. for $C_{16}H_{11}ClO$: C, 75.45; H, 4.35. Found: C, 75.22; H, 4.50.

The position of the carbonyl absorption for XVIII is about 0.08 μ lower than the carbonyl absorption of dibenzobicyclo[2.2.2]octadien-1-one, which absorbs at 5.80 μ.[19] This is consistent with the observed shift found with α-halogenated ketones.[20]

The Sodium Borohydride Reduction of 3-Chlorodibenzobicyclo[2.2.2]octadien-2-one (XVIII). The chloro ketone XVIII (7.38 g., 29 mmoles) was dissolved in 300 ml. of absolute methanol and a large excess of sodium borohydride (5 g.) was added in two portions with stirring. After all hydrogen evolution had ceased, the solvent was removed by rotary evaporation and the residue was treated with 600 ml. of water. The product was then extracted with three 150-ml. portions of ether. The ethereal solution was dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation leaving 6.15 g. of a white solid. An infrared spectrum of this material taken in carbon disulfide solution showed an hydroxyl absorption at 2.77 μ. The spectrum was substantially different from that of the *trans*-chlorohydrin XVI. However, small absorptions at 7.25 and 9.55 μ corresponded to strong absorptions of XVI.

The product was dissolved in 200 ml. of carbon tetrachloride and chromatographed on 200 g. of Merck neutral alumina packed in carbon tetrachloride. The column was eluted with carbon tetrachloride, 50% chloroform in carbon tetrachloride, and 100% chloroform. The 50% chloroform in carbon tetrachloride fractions gave 3.95 g. of light yellow solid. The infrared spectrum of this material taken in carbon disulfide solution showed the material to be essentially the *cis*-chlorohydrin XV, with a small trace of XVI. The 100% chloroform fractions gave 598 mg. of a yellow oil whose infrared spectrum in carbon disulfide solution indicated that the main component was XVI with only a trace of the *cis*-chlorohydrin XV present. The yield of chlorohydrin mixture was 4.55 g. (66%), of which 87% was the *cis*-chlorohydrin XV.

The crude *cis*-chlorohydrin XV was dissolved in ethanol and the resulting solution was decolorized with activated charcoal before crystallization of the product by concentration of the solution. The first two crops gave 1.39 g. of product melting at 175–177°.

Anal. Calcd. for $C_{16}H_{13}ClO$: C, 74.85; H, 5.10. Found: C, 74.62; H, 5.05.

The Chromium Trioxide Oxidation of cis-3-Chlorodibenzobicyclo[2.2.2]octadien-2-ol (XV). Oxidation of the *cis*-chlorohydrin XV (100 mg., 0.39 mmole), sub-

(19) K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939).
(20) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 139.

stantially as described above for the *trans* isomer, gave, after recrystallization from ethanol, 89 mg. (90%) of XVIII, m.p. 128.5–131.5°. A mixture melting point with genuine XVIII was not depressed, and the infrared spectra were identical.

The Preparation of cis-3-Chlorodibenzobicyclo[2.2.2]-octadien-2-ol p-Toluenesulfonate (X). Treatment of the *cis*-chlorohydrin XV (1.16 g., 4.5 mmoles) and an excess of *p*-toluenesulfonyl chloride (1.42 g., 7.4 mmoles) dissolved in 50 ml. of dry pyridine, substantially as described above for the *trans* isomer, gave, after recrystallization from petroleum ether (b.p. 60–70°), 822 mg. (44%) of white, crystalline *cis*-chloro *p*-toluenesulfonate X, m.p. 153–163° (with decomposition). Recrystallization from absolute ethanol gave X melting at 168–172° (with decomposition). Characteristic sulfonate absorptions in the infrared were observed at 7.00 and 8.50 μ.

Anal. Calcd. for $C_{23}H_{19}ClO_3S$: C, 67.23; H, 4.66. Found: C, 67.39; H, 4.68.

The Preparation of cis-3-Chlorodibenzobicyclo[2.2.2]-octadien-2-ol Acetate (XII). Treatment of the *cis*-chlorohydrin XV (311 mg., 1.21 mmoles) with 1 ml. of pyridine in 50 ml. of acetic anhydride substantially as described above for the *trans* isomer gave 288 mg. (79%) of *cis*-chloro acetate XII, m.p. 156–157°. Its acetoxy absorptions were at 5.75, 8.10, and 8.26 μ.

Anal. Calcd. for $C_{18}H_{15}ClO_2$: C, 72.36; H, 5.06. Found: C, 72.60; H, 4.83.

The Acetolysis of cis-3-Chlorodibenzobicyclo[2.2.2]-octadien-2-ol p-Toluenesulfonate (X). The *cis*-chloro *p*-toluenesulfonate X (136 mg., 0.33 mmole) and 27 mg. of anhydrous sodium acetate (0.33 mmole) were dissolved in 30 ml. of dry acetic acid (distilled from boron triacetate) and the resulting solution was heated at reflux for 51 hr. After cooling, the reaction mixture was poured onto 20 g. of ice and diluted with 500 ml. of water to give a fine white precipitate. The product was extracted with three 100-ml. portions of ether. The ethereal solution was washed with aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation leaving a colorless oil which crystallized upon standing. The infrared spectrum of the product in carbon disulfide solution was identical with that of the known *syn-exo* chloro acetate VII.[6] The yield of VII was 95 mg. (97%).

The Acetolysis of trans-3-Chlorodibenzobicyclo[2.2.2]-octadien-2-ol p-Toluenesulfonate (XI). The *trans*-chloro *p*-toluenesulfonate (229 mg., 0.56 mmole) and 50 mg. of anhydrous sodium acetate (0.60 mmole) were dissolved in 25 ml. of dry acetic acid (distilled from boron triacetate) and the resulting solution was heated at reflux for 75 hr. After cooling, the reaction mixture was poured into 500 ml. of water to give a fine white precipitate. Work-up as described in the previous paragraph gave a colorless oil which slowly crystallized. Recrystallization of the product from ethanol gave 136 mg. (82%) of colorless crystals, m.p. 144.5–145.5°. The infrared spectrum of the product taken in carbon disulfide solution was identical with that of the *anti-exo* chloro acetate IX. A mixture melting point with genuine IX gave no depression.

The Acetolysis of cis-3-Chlorodibenzobicyclo[2.2.2]-octadien-2-ol Acetate (XII). The *cis*-chloro acetate XII (204 mg., 0.68 mmole) and 118 mg. of silver acetate (0.71 mmole) were placed in 50 ml. of glacial acetic acid. The resulting reaction mixture was heated at reflux for 96 hr. The reaction mixture was cooled and the solid silver chloride was filtered. The solvent was removed by rotary evaporation and the residue was treated with 100 ml. of hot benzene. The unreacted silver acetate was filtered, and the benzene solution was washed with aqueous sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The benzene was removed by rotary evaporation leaving 196 mg. (61%) of a colorless oil. An infrared spectrum of the oil taken in carbon disulfide solution was identical with that of the known *exo-syn* diacetate IV. Crystallization of the product from ethanol gave 102 mg. of white crystalline IV, m.p. 167–168°. A mixture melting point with genuine IV[3] was not depressed.

The Acetolysis of trans-3-Chlorodibenzobicyclo[2.2.2]-octadien-2-ol Acetate (XIII). The *trans*-chloro acetate XIII (622 mg., 2.08 mmoles) and 350 mg. of silver acetate (2.10 mmoles) were placed in 125 ml. of glacial acetic acid and the resulting reaction mixture was heated at reflux for 120 hr. After being cooled, the reaction mixture was filtered and the solvent was removed by rotary evaporation leaving a solid residue. This was extracted with 150 ml. of hot benzene. This solution was filtered, washed with aqueous sodium bicarbonate, and dried over anhydrous magnesium sulfate. The benzene was removed by rotary evaporation leaving a light yellow oil. The product was dissolved in ethanol and crystallized by concentration of the solution. The total yield of the *anti-exo* diacetate XIV, m.p. 193–193.5°, was 588 mg. (88%). The infrared spectrum of XIV taken in carbon disulfide differed significantly from that of the *syn-exo* diacetate IV and the starting material XIII. The spectrum showed strong acetoxy absorptions at 5.75 and 8.20 μ.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.67; H, 5.68.

The Lithium Aluminum Hydride Reduction of anti-8-Chlorodibenzobicyclo[3.2.1]octadien-exo-2-ol Acetate (IX). The *anti-exo* chloro acetate IX (856 mg., 2.86 mmoles) was dissolved in 60 ml. of ether and slowly added to a suspension of 380 mg. of lithium aluminum hydride in 50 ml. of ether, with stirring. The reaction mixture was allowed to stir for an additional 10 hr. before destruction of the excess lithium aluminum hydride by careful addition of water. The residual hydrated aluminum oxide was filtered and thoroughly washed with ether. The ethereal solution was dried over anhydrous magnesium sulfate and the ether was removed by rotary evaporation leaving 855 mg. of a yellow oil. The oil was dissolved in ethanol and, after decolorization of the solution with activated charcoal, the product was crystallized by concentration of the solution. The first crop gave 300 mg. of the *anti-exo* chlorohydrin XIX, m.p. 140–141°. Succeeding crops gave a total yield of 725 mg. (99%). An infrared spectrum of the product taken in carbon disulfide solution showed a strong hydroxyl absorption at 2.77 and the absence of acetoxy absorption at 5.75 or 8.10 μ.

Anal. Calcd. for C₁₆H₁₃ClO: C, 74.85; H, 5.10. Found: C, 74.72; H, 4.99.

The Chromium Trioxide Oxidation of anti-8-Chloro-dibenzobicyclo[3.2.1]octadien-exo-2-ol (XIX). The *anti-exo* chlorohydrin XIX (779 mg., 3.03 mmoles) was dissolved in 150 ml. of glacial acetic acid and to this solution was added dropwise a solution of 205 mg. of chromium trioxide (2.05 mmoles) in 50 ml. of 75% aqueous acetic acid. The reaction mixture slowly turned from the orange color of chromium trioxide solution to a deep green after 12 hr. of stirring. All but a few milliliters of solvent was removed by rotary evaporation and the residue was poured into 300 ml. of water to give a white precipitate. The product was extracted into three 100-ml. portions of ether. The ethereal solution was washed with aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation leaving 693 mg. of a yellow oil which crystallized upon standing. The product was recrystallized from ethanol after decolorization of the ethanol solution with activated charcoal. The first crop gave 25 mg. of the *anti* chloro ketone XX as colorless needles, m.p. 138–139°. Succeeding crops gave a total yield of XX of 693 mg. (90%).

Anal. Calcd. for C₁₆H₁₁ClO: C, 75.45; H, 4.35. Found: C, 75.36; H, 4.49.

An infrared spectrum of XX taken in carbon disulfide solution showed no hydroxyl absorption at 2.77, but showed a strong carbonyl absorption at 5.88 μ. The product was different from the *syn* chloro ketone XXI[4] in melting point, mixture melting point, and infrared spectrum. The ultraviolet spectrum of XX in absolute ethanol did not show the usual conjugated aromatic ketone band at 2400–2450 Å. However, when the ultraviolet spectrum was taken in concentrated sulfuric acid, a strong band, characteristic of conjugated aromatic ketones,[11] appeared at 2990 Å. (ε 17,000).

The Clemmensen Reduction of anti-8-Chlorodibenzo-bicyclo[3.2.1]octadien-2-one (XX). A mixture of 120 mg. of the *anti* chloro ketone XX (0.47 mmole), 4.8 g. of amalgamated zinc, 5 ml. of toluene, 5 ml. of glacial acetic acid, and 6 ml. of concentrated hydrochloric acid was heated at reflux for 38 hr. During this time, five 4-ml. portions of concentrated hydrochloric acid were added. The reaction mixture was cooled and extracted three times with 40-ml. portions of benzene. The benzene extracts were washed with aqueous sodium bicarbonate and water, and then dried over anhydrous magnesium sulfate. The benzene was removed by rotary evaporation leaving a colorless oil which was dissolved in 15 ml. of 30% carbon tetrachloride in petroleum ether (b.p. 60–70°) and chromatographed on 30 g. of Merck acid-washed alumina packed in petroleum ether (b.p. 60–70°). The column was eluted with 30% carbon tetrachloride in petroleum ether and with carbon tetrachloride. The fractions eluted with 30% carbon tetrachloride in petroleum ether contained 75 mg. (62%) of white crystalline *anti*-8-chlorodibenzobicyclo[3.2.1]octadiene (XXII), m.p. 110–116°. Recrystallization from ethanol gave XXII melting at 121.5–122.5°.

Anal. Calcd. for C₁₆H₁₃Cl: C, 79.83; H, 5.44. Found: C, 79.98; H, 5.59.

The infrared spectrum of the product taken in carbon disulfide solution showed no carbonyl absorption at 5.88 μ. A mixture melting point with the epimeric *syn* chloride XXIII[4] was depressed and infrared spectra of the two epimeric chlorides in carbon disulfide solution were significantly different.

The Hydrogenolysis of anti-8-Chlorodibenzobicyclo-[3.2.1]octadien-exo-2-ol Acetate (IX). The *anti-exo* chloro acetate IX (1.02 g., 3.4 mmoles) was dissolved in 100 ml. of absolute ethanol and 210 mg. of 10% palladium-on-charcoal catalyst was added. The reaction mixture was shaken under 1 atm. of hydrogen at room temperature for 3 days. The catalyst was filtered off and the solution was concentrated by rotary evaporation, upon which the product crystallized from solution. The first two crops gave 637 mg. (79%) of the *anti* chloride XXII, m.p. 122–123.5°. This was identical with the XXII described in the previous paragraph.

The Sodium Reduction of anti-8-Chlorodibenzobicyclo-[3.2.1]octadien-exo-2-ol Acetate (IX). The *anti-exo* chloro acetate IX (491 mg., 1.65 mmoles) was dissolved in 50 ml. of benzene and placed in a separatory funnel. "Organic halogen reagent"[21] (a mixture of sodium biphenyl,[22] in excess biphenyl and glyme) was added until the blue-green color persisted (1 vial) and then the reaction mixture was shaken vigorously. The excess reagent was destroyed by addition of 2 ml. of ethanol. The benzene layer was washed three times with 25-ml. portions of 3 *M* nitric acid, with aqueous sodium bicarbonate, and then dried over anhydrous magnesium sulfate. The benzene was removed by rotary evaporation and the residue was dissolved in 100 ml. of carbon tetrachloride and chromatographed on 120 g. of Merck acid-washed alumina packed in carbon tetrachloride. The column was eluted with carbon tetrachloride, chloroform, and ethyl acetate. The carbon tetrachloride fractions gave 3.3 g. of biphenyl. The ethyl acetate fraction gave 318 mg. of a yellow oil. The oil was dissolved in ethanol and the resulting solution was decolorized with activated charcoal before crystallization of the product by concentration of the solution. Recrystallization of the product gave a yield of 151 mg. (41%) of dibenzobicyclo[3.2.1]octadien-*exo*-2-ol (XXIV), m.p. 116–117°. A mixture melting point with genuine XXIV,[12] m.p. 117–118°, was not depressed. Infrared spectra of the two samples of XXIV in carbon disulfide solution were identical.

The Sodium Reduction of syn-8-Chlorodibenzobicyclo-[3.2.1]octadien-exo-2-ol Acetate (VII). The *syn-exo* chloro acetate VII (442 mg., 1.48 mmoles) was treated in a similar fashion with sodium biphenyl to give, after appropriate work-up, 248 mg. (75%) of the *exo* alcohol XXIV.[12]

The Reduction of syn-8-Iododibenzobicyclo[3.2.1]-octadien-exo-2-ol Acetate (III) to Dibenzobicyclo-[3.2.1]octadien-exo-2-ol Acetate (XXVIII). With Hydrogen and Raney Nickel. A mixture of 0.50 g. of the *syn-exo* iodo acetate III and a teaspoonful of W2 Raney nickel was placed in 50 ml. of absolute ethanol and hydrogenated under 1 atm. of hydrogen at room

(21) Product of DistAnal Inc., Baton Rouge, La.
(22) One vial contains *ca.* 460 mg. of sodium (0.02 g.-atom).

temperature for 20 hr. The catalyst was filtered and the solvent was evaporated leaving 0.34 g. of an oily residue which was purified by chromatography over alumina. The fractions eluted with benzene gave 0.31 g. of white solid, m.p. 60–74°. Recrystallization from 90% aqueous methanol gave pure *exo* acetate XXVIII, m.p. 72–74°. A mixture melting point with a genuine sample of XXVIII[12] was not depressed.

With Zinc in Acetic Acid. To 20 ml. of glacial acetic acid was added 800 mg. of III and 2 g. of zinc dust. The reaction mixture was heated at reflux for 24 hr., and, after cooling, the zinc was removed by filtration. The acid was neutralized using aqueous potassium hydroxide. The precipitated product was extracted with ether, and the ethereal solution was washed with dilute hydrochloric acid and dried over anhydrous sodium sulfate. The ether was removed by rotary evaporation giving 0.45 g. of an oily residue which was dissolved in petroleum ether (b.p. 60–70°) and chromatographed over alumina. The fractions eluted with benzene gave about 400 mg. of material melting at 64–72°. Recrystallization from 90% aqueous methanol gave the pure *exo* acetate XXVIII,[12] m.p. 74–75°.

The Lithium Aluminum Hydride Reduction of Dibenzobicyclo[3.2.1]octadien-exo-2-ol Acetate (XXVIII). The *exo* acetate (75 mg.) was reduced with 0.3 g. of lithium aluminum hydride substantially as described for the chloro acetate IX above, giving the *exo* alcohol XXIV, m.p. 109–114°. After several recrystallizations from petroleum ether (b.p. 60–70°) XXIV melting at 118–119° was obtained. A mixture melting point with genuine XXIV[12] was not depressed.

The Lithium Aluminum Hydride Reduction of syn-8-Iododibenzobicyclo[3.2.1]octadien-exo-2-ol Acetate (III). A similar reduction gave the *syn*-8-iodo-*exo*-2-ol in 90% yield. Recrystallization gave pure XXIX, m.p. 135–136°.

Anal. Calcd. for $C_{16}H_{13}IO$: C, 55.18; H, 3.76; I, 36.45. Found: C, 55.29; H, 3.64, I, 36.36.

The alcohol gave a benzoate, m.p. 166–166.5°.

Anal. Calcd. for $C_{23}H_{17}IO_2$: C, 61.07; H, 3.78; I, 28.14. Found: C, 60.69; H, 3.76; I, 28.28.

Reduction of syn-8-Iododibenzobicyclo[3.2.1]octadien-exo-2-ol (XXIX) with Hydrogen and Raney Nickel. The *syn-exo* iodohydrin XXIX (100 mg.) was dissolved in 15 ml. of absolute ethanol and one teaspoonful of W2 Raney nickel was added. The resulting mixture was hydrogenated under 1 atm. of hydrogen at room temperature for 4 hr. The catalyst was removed by filtration and the solvent was removed by rotary evaporation leaving 68 mg. of crude product. After recrystallization from petroleum ether (b.p. 60–70°), 50 mg. (78%) of pure *exo* alcohol XXIV,[12] m.p. 117–118°, was obtained.

The Potassium Permanganate Oxidation of syn-8-Iododibenzobicyclo[3.2.1]octadien-exo-2-ol (XXIX). The iodohydrin XXIX (300 mg.) and 0.5 g. of potassium permanganate were dissolved in 20 ml. of water and 10 ml. of pyridine, and the resulting reaction mixture was heated at reflux for 4 hr. The excess permanganate was destroyed by adding an aqueous solution of sodium bisulfite until the purple color was discharged. The hot solution was filtered and cooled to crystallize the product. A quantitative yield of the white crystalline

iodo ketone XXX, m.p. 152–154°, resulted. A qualitative test for iodine was positive. An ultraviolet spectrum of XXX in concentrated sulfuric acid had a strong band at 2970 Å. (ϵ 7600).

Anal. Calcd. for $C_{16}H_{11}IO$: C, 55.55; H, 3.24. Found: C, 55.78; H, 3.08.

The Lithium Aluminum Hydride Reduction of syn-8-Bromodibenzobicyclo[3.2.1]octadien-exo-2-ol Acetate (II). The *syn-exo* bromo acetate II (1.29 g., 3.76 mmoles) was dissolved in 60 ml. of ether and slowly added, with stirring, to a suspension of 268 mg. of lithium aluminum hydride in 20 ml. of ether. Work-up as described above for similar preparations gave 640 mg. (50%) of white crystalline *syn-exo* bromohydrin XXXI, m.p. 102–103°.

Anal. Calcd. for $C_{16}H_{13}BrO$: C, 63.80; H, 4.35. Found: C, 63.73; H, 4.38.

The Sodium Reduction of syn-8-Bromodibenzobicyclo-[3.2.1]octadien-exo-2-ol Acetate (II). Treatment of II (314 mg., 0.91 mmole) with sodium biphenyl as described above for similar dehalogenations gave 143 mg. (70%) of the *exo* alcohol XXIV.

The Sodium Reduction of syn-8-Chlorodibenzobicyclo-[3.2.1]octadien-endo-2-ol Acetate (VIII). The *syn-exo* chloro acetate VIII (512 mg., 1.71 mmoles) was treated with sodium biphenyl solution as described above for similar reactions to give 308 mg. of a colorless oil which slowly crystallized. The product was crystallized from petroleum ether (b.p. 60–70°) to give 263 mg. (69%) of white crystalline *endo* alcohol XXXII, m.p. 110–114°. The infrared spectrum of the product taken in carbon disulfide solution was identical with that of the known *endo* alcohol XXXII,[14] and the spectrum also showed the absence of the characteristic absorption for *exo* alcohol XXIV at 9.88 μ.

The Potassium Permanganate Oxidation of Dibenzobicyclo[3.2.1]octadien-exo-2-ol (XXIV). The *exo* alcohol XXIV (0.11 g., 0.5 mmole) was dissolved in 30 ml. of acetone and 5 ml. of water. To this was added 0.2 g. of potassium permanganate, and the resulting reaction mixture was heated at reflux for 1 hr. on a steam bath. The excess oxidizing agent was destroyed by addition of aqueous sodium bisulfite. The solids were filtered and water was added to precipitate the product. The total yield of white crystalline ketone XXXIII, m.p. 114.5–115°, was 100 mg. (90%). No mixture melting point depression was observed when mixed with a genuine sample of XXXIII.[12] The ultraviolet spectrum of XXXIII in concentrated sulfuric acid gave a band at 3000 Å. (ϵ 13,000).

The Potassium Permanganate Oxidation of Dibenzobicyclo[3.2.1]octadien-endo-2-ol (XXXII). Similar treatment of 100 mg. of the *endo* alcohol XXXII gave 93 mg. of the ketone XXXIII, m.p. 114–115°.

The Reduction of Dibenzobicyclo[3.2.1]octadien-2-one (XXXIII). With Lithium Aluminum Hydride. The ketone XXXIII (50 mg.) was dissolved in 20 ml. of ether and 400 mg. of lithium aluminum hydride was added. The reaction mixture was stirred at room temperature for 3 hr. before destruction of the excess lithium aluminum hydride by addition of water. The ethereal solution was dried over anhydrous sodium sulfate and the ether was removed by rotary evapora-

tion, leaving 46 mg. of solid *endo* alcohol XXXII, m.p. 139–143°.

With Sodium in Alcohol. To a solution of 50 mg. of the ketone XXXIII in 10 ml. of absolute ethanol was added 0.5 g. of metallic sodium. The resulting reaction mixture was heated at reflux for 30 min. and the solvent then was removed by rotary evaporation. The product was extracted with ether. The ethereal solution was washed twice with water and dried over anhydrous sodium sulfate. Removal of the ether by rotary evaporation gave 36 mg. of the *endo* alcohol XXXII, m.p. 142–143°.

The Clemmensen Reduction of Dibenzobicyclo[3.2.1]-octadien-2-one (XXXIII). To a solution of 0.2 g. of the ketone XXXIII in 10 ml. of ethanol was added 2 g. of freshly amalgamated zinc and 10 ml. of concen-

trated hydrochloric acid. The reaction mixture was heated at reflux for 24 hr. during which time an additional 10 ml. of concentrated hydrochloric acid was added. The ethanol was distilled off and the residue was extracted with ether. The ethereal solution was washed with aqueous sodium bicarbonate and dried over anhydrous sodium sulfate. The ether was removed by rotary evaporation leaving 168 mg. of an oily residue. Sublimation of the material gave pure dibenzobicyclo[3.2.1]octadiene (XXXIV), m.p. 36–37°. An infrared spectrum of the product was identical with that of XXXIV prepared earlier.[14]

Bridged Polycyclic Compounds. XXX. Equilibration Studies of Some Substituted Dibenzobicyclo[3.2.1]octadienes and Dibenzobicyclo[2.2.2]octadienes[1]

Stanley J. Cristol, Farn Pwu Parungo, Donald E. Plorde, and Kurt Schwarzenbach

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado. Received February 19, 1965

It was found that the endo-2 isomers of various substituted dibenzobicyclo[3.2.1]octadiene derivatives were more stable than the exo epimers and that acid-catalyzed epimerizations were readily carried out. In addition, more severe conditions led, in many cases, to rearrangements from dibenzobicyclo[3.2.1]octadienes to [2.2.2] isomers. These results are discussed in light of possible mechanisms and possible carbonium ion intermediates involved.

In the course of the study of solvolysis rearrangement or addition rearrangement of dibenzobicyclo[2.2.2]-octadienes to dibenzobicyclo[3.2.1]octadienes,[1] it became desirable to investigate the thermodynamic stabilities of various substituted *endo-* and *exo-*2-dibenzobicyclo[3.2.1]octadienyl compounds relative to each other and to their [2.2.2] analogs. It was conceivable that the driving force for the rearrangement of the [2.2.2] system to the [3.2.1] system is due to a greater thermodynamic stability of the [3.2.1] system, as suggested earlier.[2]

Earlier work had shown that in the [3.2.1] system with a *syn*-8-chlorine, the *endo*-2-substituted compound was thermodynamically more stable than its *exo*-2 epimer.[3,4] Thus *syn*-8-*exo*-4-dichlorodibenzo-

bicyclo[3.2.1]octadiene (I) epimerized completely to its *endo*-4 epimer II in liquid sulfur dioxide and cresol.[3] In the acetolysis of the *cis*-dichloride III assisted by silver acetate, both the *syn-exo* (IV) and *syn-endo* (V) chloro acetates were formed with the relative amount of V increasing with increasing reaction times.[1] It has also been shown that IV rearranges completely to V when treated with perchloric acid in acetic acid.[4]
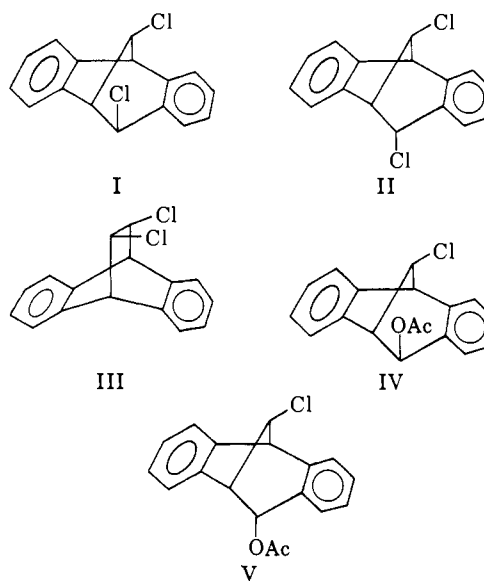
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