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 concentrated 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]

Acknowledgments. The authors are indebted to the National Science Foundation for support of this work. We are further indebted to Mr. Charles Leeper for improvements in the Prévost procedures reported.

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

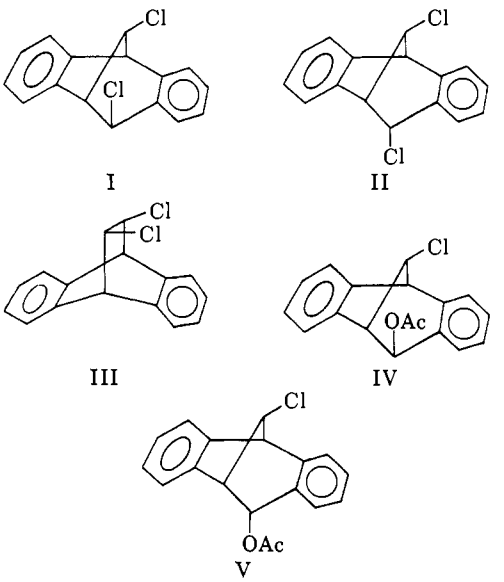
Stanley J. Cristol, Farn Pwu Parungo, Donald E. Plorde, and Kurt Schwarzenbach

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-dichlorodibenzobicyclo[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]



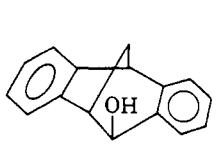
(1) Previous paper in series: S. J. Cristol, F. P. Parungo, and D. E. Plorde, *J. Am. Chem. Soc.*, 87, 2870 (1965). This work was reported at the 19th National Organic Symposium of the American Chemical Society, Columbus, Ohio, June 1963.

(2) W. R. Vaughan and A. C. Schoenthaler, *J. Am. Chem. Soc.*, 80, 1956 (1958).

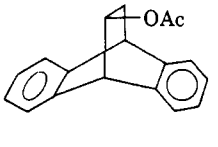
(3) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, 28, 1374 (1963).

(4) S. J. Cristol and D. D. Tanner, *J. Am. Chem. Soc.*, **86**, 3122 (1964).

The first indication of the thermodynamic stability of the [3.2.1] system relative to that of the [2.2.2] system came with the complete transformation of dibenzobicyclo[3.2.1]octadien-*exo*-2-ol (VI) to dibenzobicyclo[2.2.2]octadien-2-ol acetate (VII) by use of perchloric acid in acetic acid.[5]

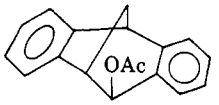


VI

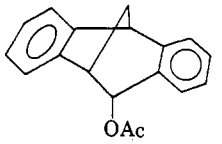


VII

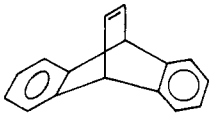
When the *exo* acetate VIII[6] was warmed with 1 *M* anhydrous perchloric acid in acetic acid only the [2.2.2] acetate VII was isolated. Similarly the *endo*-2-acetate IX rearranged completely to VII. Addition of acetic



VIII



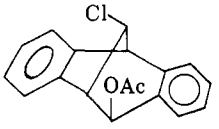
IX



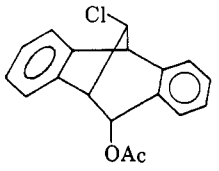
X

acid to dibenzobicyclo[2.2.2]octatriene (X)[1] under equilibrating conditions gave only acetate VII plus an unidentified high molecular weight material.[7]

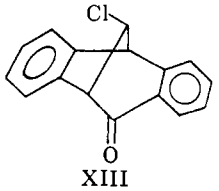
Treatment of the *anti-exo* chloro acetate XI in acetic acid at 160° led to a gradual epimerization to the *anti-endo* chloro acetate XII. XII was shown to be epimeric with XI by reduction with lithium aluminum hydride followed by chromium trioxide oxidation to the *anti* chloro ketone XIII prepared earlier from XIV.[1]



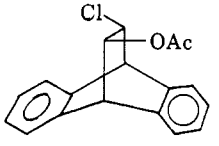
XI



XII

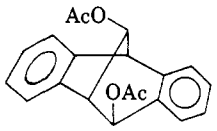


XIII

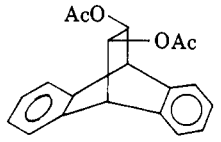


XIV

The n.m.r. spectrum of XII confirmed the assigned structure.[8] When XI was equilibrated using anhydrous perchloric acid in acetic acid at 70° for 25 hr., a mixture of XI, XII, and the previously reported *trans*-3-chlorodibenzobicyclo[2.2.2]octadien-2-ol acetate (XIV)[1] was obtained. When the equilibration time was increased to 90 hr., only XIV was found. Prolonged treatment of XIV (45 days) under similar conditions caused no other rearrangements or equilibrations. In a similar manner, the *anti-exo* diacetate XV[1] was equilibrated in anhydrous perchloric acid in acetic acid for 5 days at 70° to give exclusively the *trans*-dibenzobicyclo-[2.2.2]octadiene-2,3-diol diacetate (XVI) prepared earlier.[9]

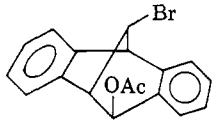


XV

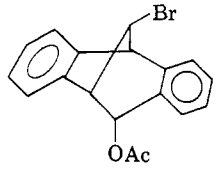


XVI

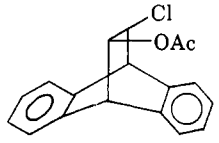
Epimerization of *syn*-8-*exo*-2 compounds to their *endo* epimers was seen above. Similarly the *syn-exo* bromo acetate XVII[1] could be heated in acetic acid to effect epimerization to its *endo* epimer (XVIII).



XVII



XVIII



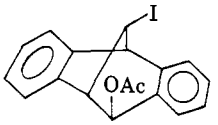
XIX

As described above, the 2-acetates of the [3.2.1] system readily underwent acid-catalyzed Wagner–Meerwein rearrangements to their [2.2.2] isomers, when there was no substituent at C-8 (VIII and IX to VII), and stereospecifically (with the normal *anti* migration[10]) when an *anti* substituent was present at C-8 to give the corresponding *trans* [2.2.2] product (XI and XII to XIV, and XV to XVI). On the other hand, when the *syn*-chloro *exo*-acetate IV was heated with perchloric acid in acetic acid for 48 days, only the *endo* epimer V was formed. Neither the anticipated *cis* [2.2.2] chloro acetate XIX nor the *trans* isomer XIV was produced, although the conditions were those where the corresponding *anti* 8-chloro acetates XI and XII rearrange completely to the [2.2.2] isomer XIV in 90 hr. That this is a kinetic phenomenon and not necessarily a thermodynamic one was shown by an experiment in which the *cis*-chloro acetate XIX was subjected to perchloric acid for 20 days and was recovered unchanged.

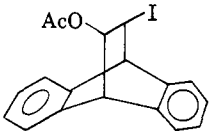
If a *syn*-8-substituted [3.2.1] compound did rearrange to the [2.2.2] system, a *cis* [2.2.2] acetate would be anticipated by *anti* migration rules.[10] In fact, however, the *syn*-8-iodo *exo*-2-acetate XX[1] rearranged rapidly, but to the *trans*-iodo acetate XXI, rather than to the

(5) D. D. Tanner, Ph.D. Thesis, University of Colorado, 1961.
(6) J. R. Mohrig, Ph.D. Thesis, University of Colorado, 1963.
(7) Details of the rearrangements of VII, VIII, and IX are now under investigation in our Laboratory (with A. E. Johnson and R. Kellman) and will be reported later. This work indicates that the rearrangements of VIII to IX and *vice versa* are somewhat faster than the rearrangements of each of these to the [2.2.2] isomer VII. Additions to X are also under study.
(8) S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **30**, 1956 (1965).
(9) F. Pwu, Ph.D. Thesis, University of Colorado, 1961.
(10) For a discussion of this, see D. J. Cram in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 5.

cis isomer. The structure of XXI was determined from its n.m.r. spectrum and by its silver ion assisted acetolysis to the *anti-exo* diacetate XV.

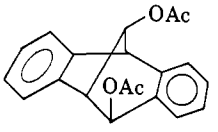


XX

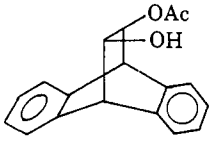


XXI

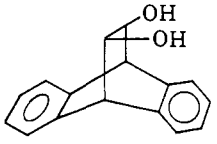
While the *anti*-8-chloro and *anti*-8-acetoxy 2-acetates had similar rates of rearrangement to the *trans* compounds (approximately 50 hr. at 70° being required), the *syn*-8-*exo*-2-diacetate XXII,[11] in remarkable contrast to the nonreactive *syn*-8-chloro compound, rearranged completely to the [2.2.2] system in 2 days at room temperature. The product, however, of either perchloric acid or sulfuric acid catalyzed reaction in acetic acid, followed by treatment with water, was not a diacetate but was the *cis*-diol monoacetate XXIII. The structure of XXIII was adduced by spectral evidence, analysis, and by conversion to the known *cis*-diol XXIV[11] or by *base*-catalyzed acetylation to the *cis*-diacetate XXV.[11] When anhydrous conditions were used in the work-up, diacetate XXV was produced. XXV was transformed to diol monoacetate XXIII by treatment with acetic acid containing sulfuric acid or perchloric acid, followed by aqueous work-up.



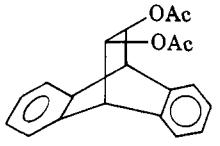
XXII



XXIII



XXIV



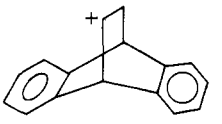
XXV

Discussion of Results

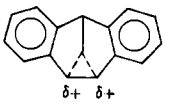
In this paper and in earlier related ones[1,3,4,11] we have observed a number of Wagner–Meerwein rearrangements, where cationic species were formed either by addition or by solvolysis, and where 2-dibenzobicyclo[2.2.2]octadienyl derivatives have been transformed to 2-dibenzobicyclo[3.2.1]octadienyl derivatives or the reverse. Enough data are now in hand to warrant some speculations regarding the intermediate or intermediates involved in these rearrangements, although many experimental details are still lacking and certain of these are presently under scrutiny in our laboratory.

First, in all systems in which we have been able to reach equilibrium, the dibenzobicyclo[2.2.2]octadienyl isomers have been considerably more stable than the corresponding [3.2.1] isomers. Thus it is clear that the driving force for the [2.2.2] to [3.2.1] rearrangement (accompanying electrophilic addition or cation-intermediate displacement) is not the formation of the thermodynamically stable product. Instead, in analogy to the classical Wagner–Meerwein case (camphene-hydro, isobornyl, and bornyl),[12] kinetic control of products leads to the least stable [3.2.1]-*exo*-2-ol derivatives, which are then transformed to the [3.2.1]-*endo*-2-ol derivatives, which are of intermediate stability. Finally the most stable [2.2.2]-2-ol derivatives are formed.

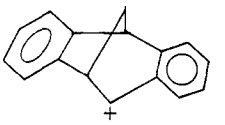
Stereochemical results (*anti*-8 ⇄ *trans*, *syn*-8 ⇄ *cis*) reported here and previously on both addition reactions and solvolyses preclude the participation of the [2.2.2] classical ion XXVI as an intermediate in either the rearrangement of the [2.2.2] system to the [3.2.1] system or in the reverse reaction, as has been pointed out previously.[1,2,3,4,11,13]



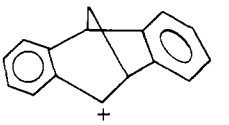
XXVI



XXVII



XXVIII



XXIX

These same facts (stereospecific rearrangements from [3.2.1] to [2.2.2] systems in which *endo*-[3.2.1] isomers intervene) also make it clear that nonclassical intermediates such as XXVII or rapid and reversible equilibria between classical ions XXVIII and XXIX are also not observed in the systems under study. Analogous cations have been proposed for reactions involving *endo*-2-bicyclo[3.2.1]octyl and *endo*-2-bicyclo-[3.2.1]octenyl systems in their transformations among each other or with their [2.2.2] analogs.[14,15]

With ions XXVI and XXVII (or their equivalents) ruled out as possible intermediates in our reactions, we may now consider the classical [3.2.1] benzylic cation XXX and the nonclassical bridged ion XXXI (or variants of the latter) as possible intermediates. The bridged ion XXXI immediately suggests itself as

(11) S. J. Cristol and R. K. Bly, *J. Am. Chem. Soc.*, **82**, 6155 (1960).

(12) (a) This system has been reviewed recently in considerable detail by J. A. Berson in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3. (b) See also P. Beltramé, C. A. Bunton, A. Dunlop, and D. Whittaker, *J. Chem. Soc.*, 658 (1964).

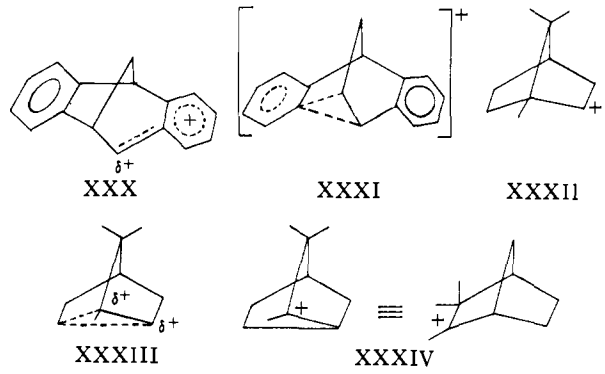
(13) A referee has pointed out that our comments regarding the relative stabilities of the [2.2.2] and [3.2.1] systems and the probable non-involvement of [2.2.2] ions such as XXVI should be qualified by statements that there will be special cases where these comments will not be valid. For example, he points out that special substituents in the molecules may cause interactions which will make the [3.2.1] system more stable and that resonance stabilization of XXVI by appropriate substitution should make such ions apparent.

(14) (a) H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1397 (1961); (b) H. L. Goering, private communication.

(15) Professor Goering has suggested that nonparticipation of ions such as XXVII (and we would assume as well, lack of the XXVIII ⇄ XXIX equilibration, where XXVII would be a transition state) is to be ascribed to the additional strain associated with the differences in angles in the dibenzo system as contrasted with the saturated system. This appears very reasonable to us. This idea finds support in the fact that acetolysis of 4-cycloheptenylcarbinyl *p*-bromobenzenesulfonate gives large amounts of *endo*-2-bicyclooctyl acetate,[16] while it may be assumed that corresponding 2,3,6,7-dibenzo-2,4,6-cycloheptatrienylcarbinyl compounds solvolyze without ring closure to bicyclooctadienes.[17]

(16) G. LeNy, *Compt. rend.*, **251**, 1526 (1960).

(17) (a) E. D. Bergmann and M. Rabinovitz, *Bull. Res. Council Israel*, **8a**, 172 (1959); *Chem. Abstr.*, **55**, 3536*a* (1961); (b) P. Tardieu, *Ann. Chim.* (Paris), [13] **6**, 1445 (1961); (c) E. Ciorănescu, A. Bucur, M. Elian, M. Bianciu, V. Voicu, and C. D. Nenitzescu, *Tetrahedron Letters*, 3835 (1964).



XXX XXXI XXXII

XXXIII XXXIV

an intermediate to explain the predominant *exo* nature of the kinetically controlled products. However, as discussed earlier[4] and in a similar case (bicyclooctenyl system) by Goering and Towns,[18a] these data (and solvolysis rate data) can be accommodated by an open cation with stereoelectronic favoring of formation and of cleavage of quasi-*axial* over quasi-*equatorial* bonds. Our system differs significantly from the classical Wagner–Meerwein system (camphenehydro, isobornyl, and bornyl) in that the other system[12] requires at least two intermediates. One of these is formed from bornyl systems and is presumably the classical bornyl ion XXXII (stereochemical requirements do not permit the formation of the nonclassical ion XXXIII or the camphenehydro cation XXXIV directly from bornyl systems), and at least one other is formed from camphenehydro or isobornyl systems. This may be either XXXIII or XXXIV (*vide supra*).

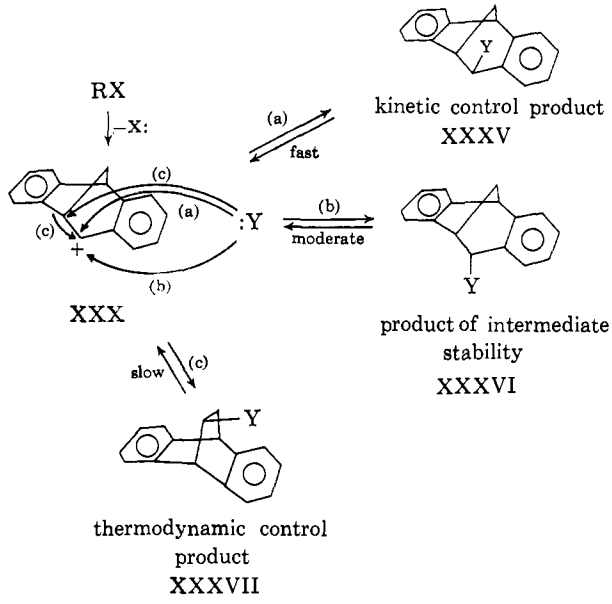


Figure 1. Pictorial representation of [2.2.2] ⇄ [3.2.1] rearrangement.

In the dibenzobicyclooctadienyl system, however, *only one cationic intermediate is required* by the data, and the fact that *exo–endo* isomerism occurs rapidly compared with [3.2.1] → [2.2.2] isomerization excludes the *nonclassical* ion XXXI as that single intermediate. If ion XXXI is in fact an intermediate, it must be rapidly and reversibly converted to the classical ion XXX, an equilibration that is not observed to a large extent in the analogous saturated system.[14] The classical ion XXX, stabilized by benzylic resonance, so as to lower the importance of homobenzylic interaction,[19] on the other hand, can be the sole intermediate in all the rearrangements studied. As shown in Figure 1, it is assumed that no [2.2.2] cation intervenes in the reaction in either direction of rearrangement. Instead, as described above, the [3.2.1] cation XXX may be assumed to react from the *exo* (quasi-*axial*) side reversibly most rapidly to give (generally) the *exo* product XXXV as that of kinetic control (path a Figure 1). Reaction on the *endo* side (path b, Figure 1) of XXX (formation and cleavage) may be assumed to go with moderate ease to give the *endo* product XXXVI as that with intermediate stability. The third reaction path involves, in the [3.2.1] to [2.2.2] rearrangement, attack by the nucleophile at the bridgehead carbon atom vicinal to the cationic carbon atom with attendant displacement of the carbon–carbon bond as shown as path c of Figure 1. While such a process[20] may seem contrived, the reverse of this process, [2.2.2] to [3.2.1], *e.g.*, XXXVII to XXX, which involves migration of a carbon–carbon bond coincident with and *anti* to departure of a leaving group, has been accepted for a considerable time.[21] The principle of microscopic reversibility ensures that an acceptable path for the forward reaction is, of course, also acceptable for the reverse.[22]

The unreactivity of the *syn*-8-chloro [3.2.1] 2-acetates IV and V toward rearrangement to the [2.2.2] system as compared to the ready transformation of the *anti*-8-

(18) (a) H. L. Goering and D. L. Towns, *J. Am. Chem. Soc.*, **85**, 2295 (1963). (b) For other cases where stereochemical preferences are observed in bicyclo[3.2.1]octenyl and bicyclo[3.2.1]octadienyl systems see: W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963); R. C. DeSelms and C. M. Combs, *ibid.*, **28**, 2206 (1963); E. Bergman, *ibid.*, **28**, 2210 (1963).

(19) For a comparable acyclic case, see S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952).

(20) If it is felt essential to coin a word describing the attack of a reagent at the atom neighboring the cationic center with coincident migration of the *anti* bond to the cationic center, we are willing to propose the one suggested by Mrs. Joy King, from time to time a member of the Department of Classics of the University of Colorado. The adjectival term is geitonodesmic, from the words γειτων (Greek, neighbor) and δεσμός (Greek, bond). This seems better than either *ciremihcna* (anchimeric spelled backward) or *citetranys* (synartetic spelled backward) to describe the reverse of these displacements.

(21) See, for example, P. D. Bartlett and I. Pöckel, *J. Am. Chem. Soc.*, **59**, 820 (1937). See also ref. 10, and Y. Pocker in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 1.

(22) Similar ideas were suggested for the camphene hydrochloride to isobornyl chloride rearrangement, and the reverse reaction, by Hughes and Ingold and their co-workers,[23,24] where only the camphenehydro cation XXXIV may lead to and from both camphenehydro derivatives and isobornyl derivatives, and are equally well applicable to the pinenehydro–bornyl–fenchyl system[25] where the pinenehydro cation may lead directly to and from pinenehydro derivatives and directly to (but not from) bornyl and fenchyl derivatives by synartetic and/or geitonodesmic substitution. These ideas were apparently abandoned in favor of nonclassical ions because of reactivity arguments.[10,12,24,26,27] These arguments have recently been questioned.[28]

(23) L. C. Bateman, K. A. Cooper, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 925 (1940).

(24) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 511 ff.

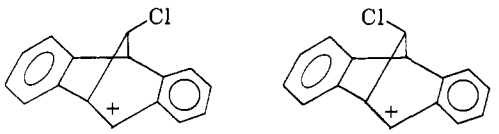
(25) G. Wagner, *J. Russ. Phys. Chem. Soc.*, **31**, 680 (1899); G. Wagner and W. Brickner, *Ber.*, **32**, 2302 (1899); H. Meerwein and K. van Emster, *ibid.*, **53**, 1815 (1920); **55**, 2500 (1922). But see W. D. Burrows and R. H. Eastman, *J. Am. Chem. Soc.*, **81**, 245 (1959).

(26) F. Brown, E. D. Hughes, C. K. Ingold, and J. F. Smith, *Nature*, **168**, 65 (1951).

(27) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1127 (1952).

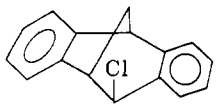
(28) H. C. Brown and F. J. Chloupek, *ibid.*, **85**, 2322 (1963).

chloro [3.2.1] 2-acetates XI and XII to the *trans*-chloro acetate XIV may now be rationalized as involving steric hindrance to geitonodesmic attack on the *syn* ion XXXVIII compared with that on the *anti* ion XXXIX.[29]



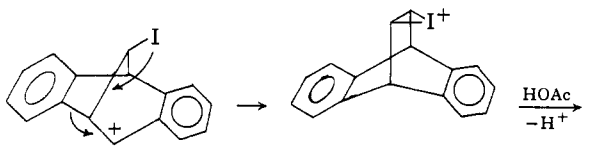
XXXVIII

XXXIX

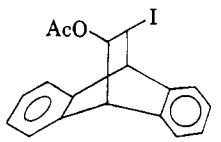


XL

While the *syn* chloro compounds IV and V do not isomerize readily to the [2.2.2] system, the *syn*-8-iodo [3.2.1] 2-acetate rearranged rapidly, but not *via* the normal path to the *cis* isomer, but rather to the *trans*-iodo[2.2.2] acetate XXI. This can be envisaged by assuming that the [3.2.1] cation XLI rearranged with participation by neighboring iodine to the iodinium ion XLII which then opens by inversion. This process accommodates the lack of rearrangement of the corresponding chloro analog XXXVIII on the fact that chlorine is much poorer in neighboring group participation than iodine.[30]

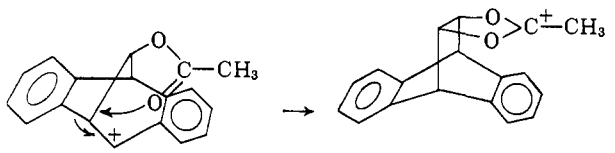


XLI XLII



XXI

The effect of neighboring group participation is seen again in the rearrangement of the *syn*-8- and *anti*-8 [3.2.1] 2-diacetates. Here the *anti*-8 epimer XV rearranges to the *trans* [2.2.2] diacetate XVI at about the same rate as the *anti*-8-chloro [3.2.1] acetates (XI and XII) rearrange, while the *syn* compound XXII rearranges with much greater speed. Plausible intermediates include XLIII and XLIV. Analogy to



XLIII XLIV

similar intermediates in the cyclohexane system[31] rationalize the production of *cis*-diol monoacetate XXIII under conditions of aqueous work-up and *cis*-diacetate XXV under anhydrous work-up.

Experimental

Rearrangement of Dibenzobicyclo[3.2.1]octadien-exo-2-ol Acetate (VIII) in Perchloric Acid and Acetic Acid. The *exo* acetate VIII (515 mg.) was dissolved in 50 ml. of anhydrous 1 *M* perchloric acid in acetic acid (see below for this preparation), and stirred for 1 hr. at room temperature. The reaction mixture was poured onto 20 g. of ice and diluted with 500 ml. of water to precipitate the product. The product was extracted with three 100-ml. portions of ether. The ethereal solution was washed with sodium carbonate solution and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation leaving 515 mg. of a colorless oil. An infrared spectrum of the product taken in carbon disulfide solution was identical with that of the known dibenzobicyclo[2.2.2]octadien-2-ol acetate (VII).[32] Crystallization of the oil from ethanol solution gave 515 mg. (100%) of VII, m.p. and m.m.p. 99–100°.

Preparation of Anhydrous 1 M Perchloric Acid in Acetic Acid. To 100 ml. of dry acetic acid (distilled from boron triacetate) was added 22.0 ml. of 70% perchloric acid (1.165 g. $HClO_4$/ml.). Acetic anhydride (66.3 g., 0.65 mole) was added to the perchloric acid in acetic acid with cooling and stirring. This solution was then diluted to 250 ml. total volume with dry acetic acid. The solution contains a small excess of acetic anhydride in order to maintain the anhydrous character of the solution.

Acetylation of Dibenzobicyclo[3.2.1]octadien-endo-2-ol. The *endo* alcohol[1] (50 mg.) was dissolved in 2 ml. of acetic anhydride and 50 mg. of sodium acetate was added. The reaction mixture was heated on a steam bath for 2 hr. and was then poured into 20 ml. of ice–water. The white precipitate which formed was filtered. A total of 48 mg. (81%) of the *endo* acetate IX, m.p. 120–125°, was obtained. Recrystallization from ethanol gave material melting at 131–132°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.54; H, 6.05.

Rearrangement of Dibenzobicyclo[3.2.1]octadien-endo-2-ol Acetate (IX) in Perchloric Acid in Acetic Acid. The *endo* acetate IX (93 mg.) was dissolved in 15 ml. of anhydrous 1 *M* perchloric acid in acetic acid. The reaction mixture was allowed to stand, with stirring, at room temperature for 21 hr. The reaction mixture was then poured onto 10 g. of ice and diluted with 500 ml. of water to give a white precipitate. The product was extracted with three 75-ml. portions of ether. The ethereal solution was washed with sodium carbonate solution and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation leaving 60 mg. (65%) of a colorless oil. The infrared spectrum of the product taken in carbon disulfide solution was identical with that of the known [2.2.2] acetate VII.

Addition of Acetic Acid to Dibenzobicyclo[2.2.2]-octatriene (X) under Equilibrium Conditions. The

(29) The possibility that the *syn* compound does not give the carbonium ion at a rate comparable to that of the *anti* compound is an alternative explanation. It seems an unlikely one for a number of reasons, including the facts that *exo-endo* isomerization occurs readily and that I, II, and XL acetolyze at rates differing by factors of less than 40.[4] Precise data on several systems for all of the rate constants (or relative rate constants) amenable to experimental study in paths a, b, and c of Figure 1 are being gathered in this laboratory.

(30) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948).

(31) S. Winstein and R. E. Buckles, *ibid.*, **64**, 2787 (1942); S. Winstein, H. V. Hess, and R. E. Buckles, *ibid.*, **64**, 2796 (1942).

(32) K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939).

olefin X (500 mg.) was dissolved in a mixture of 5 ml. of acetic acid and 5 ml. of concentrated sulfuric acid, and the resulting solution was heated at reflux for 5 hr. The reaction mixture was then cooled and poured into 50 ml. of ice–water, and the precipitated product was extracted with benzene. The benzene solution was washed with aqueous sodium carbonate, with water and then dried over anhydrous sodium sulfate. The benzene was removed by rotary evaporation, leaving 520 mg. of a gray solid. The product was treated with 20 ml. of methanol and filtered. The methanol solution was concentrated and 65 mg. (11%) of the [2.2.2] acetate VII crystallized from solution. A better procedure for the addition will be described later.[7] The insoluble solid from above (350 mg.) was purified by column chromatography over alumina using benzene as an eluent. Material melting at 240–255° was obtained. The infrared spectrum of the material in a potassium bromide pellet showed no hydroxy, acetoxy, or olefinic absorptions. Recrystallization from petroleum ether (b.p. 60–70°) gave material melting at 256–263°.

Anal. Found: C, 89.55; H, 5.29.

A molecular weight of 914 was determined for the compound by melting point depression of a camphor mixture. No further identification of this material was undertaken.

Epimerization of anti-8-Chlorodibenzobicyclo[3.2.1]-octadien-exo-2-ol Acetate (XI) to Its endo Epimer. The *anti-exo* chloro acetate XI (1.01 g., 3.39 mmoles), 590 mg. of silver acetate (3.53 mmoles), and 100 ml. of glacial acetic acid were sealed in a Carius combustion tube and heated at 170° for 48 hr. The tube was cooled and opened and the contents filtered. The solvent was evaporated from the filtrate with a warm jet of dry air and the residue was dissolved in 100 ml. of hot benzene. The benzene solution was washed with sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The benzene solution was then decolorized with activated charcoal and the benzene was removed by rotary evaporation leaving a deep red oil. The oil was dissolved in 100 ml. of carbon tetrachloride and chromatographed over 50 g. of Fisher neutral alumina packed in carbon tetrachloride. The column was eluted with carbon tetrachloride and with chloroform. The carbon tetrachloride fractions gave 112 mg. of an orange oil which 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 110 mg. (11%) of starting material (XI), m.p. 145–146°, was obtained. The chloroform fractions gave 231 (23%) mg. of a red oil which was dissolved in ethanol and the resulting solution decolorized with activated charcoal before crystallization of the product by concentration of the solution. The first crop gave 50 mg. of colorless crystalline *anti-endo* chloro acetate XII, m.p. 137–143°. Recrystallization from ethanol gave XII melting at 146.5–147°. A mixture melting point with starting material XI was depressed and an infrared spectrum of the product taken in carbon disulfide solution was different from that of the starting material.

Anal. Calcd. for $C_{18}H_{15}ClO_2$: C, 72.36; H, 5.06. Found: C, 72.15; H, 5.22.

This was an experiment in which we had hoped to displace the *anti*-8-chloride by an acetoxy group and did not succeed.[33] However it does represent a successful epimerization at C-2.

The epimerization was repeated in the absence of silver acetate at 160° for 117 hr. The same work-up was used. Infrared analysis of the crude reaction mixture was used to determine the relative proportions of XI and XII. The *exo* isomer XI has peaks at 12.25 and 15.25 μ not present in the *endo* isomer. The *endo* isomer XII has peaks at 12.50 and 14.80 μ not present in the *exo* isomer. The technique of differential quantitative infrared analysis[34] was used in determining the proportions of *exo* and *endo* products. In the above reaction mixture, there was a 50–50 mixture of *exo* and *endo* isomers.

Preparation of anti-8-Chlorodibenzobicyclo[3.2.1]-octadien-2-one (XIII) from anti-8-Chlorodibenzobicyclo-[3.2.1]octadien-endo-2-ol Acetate (XII). The *anti-endo* chloro acetate XII (971 mg., 3.25 mmoles) dissolved in 50 ml. of ether was slowly added, with stirring, to a suspension of 798 mg. of lithium aluminum hydride in 40 ml. of ether. After standing for 3 hr., the reaction mixture was treated with water to destroy the excess lithium aluminum hydride. The ether solution was decanted and the residual hydrated aluminum oxide was washed thoroughly with ether. The ethereal solution was dried over anhydrous magnesium sulfate and the ether was removed by rotary evaporation leaving 900 mg. of a yellow oil. An infrared spectrum of the product taken in carbon disulfide solution showed the presence of an hydroxy absorption but no acetoxy absorption. The total yield of chlorohydrin was 994 mg. (95%).

The oily product from above was dissolved in 20 ml. of glacial acetic acid and to this solution was added slowly, with stirring, a solution of 207 mg. of chromium trioxide (2.07 mmoles) in 50 ml. of 75% aqueous acetic acid. The reaction mixture was allowed to stand for 12 hr. The resulting deep green solution was concentrated to 10 ml. total volume by rotary evaporation, and then poured into 250 ml. of water giving a fine white precipitate. The product was extracted with three 100-ml. portions of ether. The ethereal solution was washed with aqueous sodium carbonate and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation leaving 728 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. The total yield of white crystalline *anti* chloro ketone XIII, m.p. 138–140°, was 146 mg. (18%). An infrared spectrum of the product taken in carbon disulfide solution was identical with that of the known XIII.[1]

Rearrangement of anti-8-Chlorodibenzobicyclo[3.2.1]-octadien-exo-2-ol Acetate (XI) with Perchloric Acid in Acetic Acid. Experiment A. The *anti-exo* chloro acetate XI (250 mg.) was dissolved in 20 ml. of anhydrous 1 *M* perchloric acid in acetic acid and heated at 70° for 25 hr. After cooling, the reaction mixture

(33) S. J. Cristol, J. R. Mohrig, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Am. Chem. Soc.*, 85, 2675 (1963).

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

was poured onto 10 g. of ice and diluted with 500 ml. of water, giving a white precipitate. The product was extracted with three 100-ml. portions of ether. The ethereal solution was washed with aqueous sodium carbonate and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation, leaving 223 mg. (89%) of a yellow oil. The infrared spectrum of the product taken in carbon disulfide solution showed characteristic peaks for the *anti-endo* chloro acetate XII at 12.50, the starting material XI at 12.25, and the *trans*-chloro acetate (XIV[1]) at 9.80 μ.

Experiment B. The same procedure was used, only the reaction time was increased to 90 hr. The work-up was the same. Infrared analysis showed that the product was exclusively the *trans*-chloro acetate XIV. The yield of XIV was 79%.

Treatment of trans-3-Chlorodibenzobicyclo[2.2.2]-octadien-2-ol Acetate (XIV) with Perchloric Acid in Acetic Acid. The *trans*-chloro acetate XIV (550 mg.) was dissolved in 50 ml. of anhydrous 1 *M* perchloric acid in acetic acid. The reaction mixture was stirred at room temperature for 45 days. At the end of this time the reaction mixture was poured onto 30 g. of ice and diluted with 500 ml. of water giving a precipitate. The product was extracted with three 150-ml. portions of ether. The ethereal solution was washed with aqueous sodium carbonate and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation leaving 538 mg. (98%) of a light yellow oil. The infrared spectrum of the product taken in carbon disulfide solution was identical with that of the starting material XIV.

Rearrangement of Dibenzobicyclo[3.2.1]octadien-exo-2-anti-8-diol Diacetate (XV) with Perchloric Acid in Acetic Acid. The rearrangement of this diacetate to *trans*-diacetate XVI was carried out in 1 *M* perchloric acid in acetic acid at 80° for 5 days, substantially as described above for XI. The product XVI had an infrared spectrum identical with known XVI,[9] and no trace of *cis*-diol monoacetate XXIII could be noted. XVI was recovered unchanged when treated similarly, but at 25° for 4 days.

Epimerization of syn-8-Bromodibenzobicyclo[3.2.1]-octadien-exo-2-ol Acetate (XVII) to Its endo Epimer XVIII. Treatment of 541 mg. (1.58 mmoles) of XVII with 290 mg. (1.74 mmoles) of silver acetate in 100 ml. of acetic acid in a sealed tube at 155° for 96 hr., followed by a work-up as described above for the analogous chloro compounds, gave 442 mg. of yellow oil, whose infrared spectrum was different from the starting XVII. Recrystallization from ethanol gave XVIII, m.p. 114–116°. Proof of structure was by n.m.r. spectroscopy.[8] This was an experiment devised to replace the bromine by acetoxy which did not succeed.[33]

Treatment of syn-8-Chlorodibenzobicyclo[3.2.1]octadien-exo-2-ol Acetate (IV) with Perchloric Acid in Acetic Acid. The *syn-exo* chloro acetate IV (220 mg.) was dissolved in 30 ml. of anhydrous 1 *M* perchloric acid in acetic acid and heated at 70° for 1150 hr. The reaction mixture was cooled and poured onto 20 g. of ice and diluted with 500 ml. of water to give a precipitate. The product was extracted with three 100-ml. portions of ether. The ethereal solution was washed with sodium carbonate solution and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation leaving 135 mg. (61%) of a colorless oil. The infrared spectrum of the product taken in carbon disulfide solution was identical with that of the *syn-endo* chloro acetate V.[4]

Treatment of cis-3-Chlorodibenzobicyclo[2.2.2]octadien-2-ol Acetate (XIX) with Perchloric Acid in Acetic Acid. The *cis*-chloro acetate XIX[1] (137 mg.) was dissolved in 50 ml. of anhydrous 1 *M* perchloric acid in acetic acid and heated at 75° for 485 hr. Work-up as described for similar reactions gave 132 mg. (96%) of a light yellow oil which slowly crystallized upon standing. The infrared spectrum of the product taken in carbon disulfide solution was identical with that of the starting material (XIX).[1]

Rearrangement of syn-8-Iododibenzobicyclo[3.2.1]-octadien-exo-2-ol Acetate (XX) with Perchloric Acid in Acetic Acid. The *syn-exo* iodo acetate XX[1] (220 mg.) was dissolved in 40 ml. of anhydrous 1 *M* perchloric acid in acetic acid and heated at 70° for 128 hr. Work-up as described for similar reactions gave 188 mg. (85%) of a colorless oil. The infrared spectrum of the product taken in carbon disulfide solution still showed acetoxy absorptions at 5.75 and 8.15 μ, but was very different from that of the starting material. 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 gave 22 mg. of white crystalline *trans*-iodo acetate XXI, m.p. 135–137°. Succeeding crops gave a total of 104 mg. (47%) of XXI. Similar results obtained in a 72-hr. experiment. The infrared spectrum of XXI taken in carbon disulfide solution was almost superimposable on that of the *trans*-chloro acetate XIV,[1] and the n.m.r. spectrum was similar to that of the *trans*-chloro acetate XIV and different from that of the *cis*-chloro acetate XIX. The *cis* protons have a coupling constant of 7.5 c.p.s., while that of the *trans* protons is 3.0 c.p.s.

Anal. Calcd. for $C_{18}H_{15}IO_2$: C, 55.40; H, 3.87. Found: C, 55.60; H, 4.00.

Acetolysis of trans-3-Iododibenzobicyclo[2.2.2]octadien-2-ol Acetate (XXI). A mixture of 155 mg. (0.40 mmole) of XXI, 73 mg. (0.44 mmole) of silver acetate, and 50 ml. of glacial acetic acid was heated at reflux for 8 hr. The mixture was cooled, and the precipitated silver iodide was filtered. The filtrate was evaporated to dryness and extracted with 100 ml. of hot benzene. The benzene solution was washed with aqueous sodium bicarbonate solution until the washings were basic to litmus. The solution was dried over anhydrous magnesium sulfate and the solvent was removed by evaporation, leaving 121 mg. of solid, m.p. 177–186°. Recrystallization from ethanol gave 48 mg. of *anti-8-exo*-2-dibenzobicyclo[3.2.1]octadienediol diacetate (XV),[1] m.p. and m.m.p. 192.5–193.5°.

Acid Treatment of Dibenzobicyclo[3.2.1]octadiene-exo-2-syn-8-diol Diacetate (XXII). With Sulfuric Acid in Acetic Acid. The *syn-exo* diacetate (XXII)[11] (245 mg.) was placed in a cooled mixture of 2 ml. each of glacial acetic acid, acetic anhydride, and concentrated sulfuric acid. The resulting reaction mixture was heated on a steam bath for 4 hr. The reaction mixture was cooled and poured into 100 ml. of ice–water to precipitate the product. The product was extracted

with benzene, and the benzene solution was washed with aqueous sodium bicarbonate and with water and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation leaving 205 mg. (96%) of white crystalline *cis*-diol monoacetate XXIII, m.p. 167–169°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) gave XXIII melting at 169–170°. The infrared spectrum of the compound in a potassium bromide pellet showed a strong hydroxy absorption at 2.83, and acetoxy absorptions at 5.78 and 8.00 μ.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.11; H, 5.75. Found: C, 77.31; H, 5.90.

With Anhydrous Perchloric Acid in Acetic Acid. Treatment of XXII with 1 *M* perchloric acid, substantially as described above for XI, but at room temperature for 2 days, gave quantitative conversion to XXIII, m.p. 167°.

Acetylation of cis-Dibenzobicyclo[2.2.2]octadiene-2,3-diol Monoacetate (XXIII). The *cis*-diol monoacetate XXIII (132 mg.) and 55 mg. of sodium acetate were dissolved in 4 ml. of acetic anhydride. The resulting reaction mixture was heated on a steam bath for 3 hr. The solution was poured into 50 ml. of ice–water to give a white precipitate. The product was extracted with benzene. The benzene solution was washed with aqueous sodium bicarbonate and with water, and finally was dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation, leaving 156 mg. (100%) of white crystalline *cis* diacetate XXV, m.p. 157–159°. A mixture melting point with genuine XXV[11] was not depressed, and an infrared spectrum of the product in a potassium bromide pellet was identical with that of genuine XXV.

Lithium Aluminum Hydride Reduction of cis-Dibenzobicyclo[2.2.2]octadiene-2,3-diol Monoacetate (XXIII). The *cis*-diol monoacetate XXIII (90 mg.) was dissolved in 20 ml. of ether and 500 mg. of lithium aluminum hydride was added. The reaction mixture was stirred at room temperature for 10 hr. Water was then added to destroy the excess lithium aluminum hydride. The ethereal solution was washed with dilute hydrochloric acid and with water, and finally dried over anhydrous sodium sulfate. The ether was removed by rotary evaporation leaving 82 mg. of white crystalline *cis*-diol XXIV, m.p. 198–200°. A mixture melting point with genuine XXIV[9] was not depressed, and an infrared spectrum of the product in a potassium bromide pellet was identical with that of the known XXIV.

Rearrangement of Dibenzobicyclo[3.2.1]octadiene-exo-2-syn-8-diol Diacetate (XXII) Followed by Non-aqueous Work-Up. A mixture of 1 ml. of fuming sulfuric acid (30%) and 2 ml. of glacial acetic acid was made with cooling. The *syn-exo* diacetate XXII (120 mg.) was added, and the resulting reaction mixture was heated on a steam bath for 4 hr. in a flask equipped with reflux condenser protected by a drying tube. The product was cooled and poured into a mixture of 10 ml. of glacial acetic acid, 10 ml. of acetic anhydride, and 4 g. of sodium acetate (dried by fusion). The solvents were removed by rotary evaporation and the residue was treated with benzene to extract the product. The benzene solution was filtered and the product was crystallized by concentration of the solution. The first crop gave 56 mg. (47%) of the *cis*-diacetate XXV. Evaporation of the remaining benzene from the mother liquor gave 45 mg. of an oil whose infrared spectrum indicated the presence of some *cis*-diol monoacetate XXIII.

Equilibration of cis-Dibenzobicyclo[2.2.2]octadiene-2,3-diol Diacetate (XXV). With Sulfuric Acid in Acetic Acid. To a mixture of 2 ml. each of acetic anhydride, concentrated sulfuric acid, and glacial acetic acid was added 100 mg. of the *cis*-diacetate XXV. The resulting reaction mixture was heated on a steam bath for 4 hr. The reaction mixture was allowed to cool and then poured into 30 ml. of ice–water, giving a precipitate. The product was extracted with benzene, and the benzene solution was washed with aqueous sodium bicarbonate and with water, and finally dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation leaving 74 mg. (85%) of the *cis*-diol monoacetate XXIII.

With Anhydrous Perchloric Acid in Acetic Acid. XXV was recovered unchanged after being held in a 1 *M* solution of perchloric acid in acetic acid for 4 days at room temperature. However, heating a similar solution of XXV for 3 days at 70° gave the monoacetate XXIII.

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