

constants are concerned, it is evident that the fulvenes are better treated as dienes than as aromatic systems.

The C^{13} -H spin coupling results are informative regarding the molecular orbital predictions that the exocyclic carbon-6 in the fulvene structure should bear a positive charge. Juan and Gutowsky¹⁸ have derived relationships between J_{CH} , the s-character of the hybrid orbitals of the C-H bond (a_H^2), and a term Δ_X which measures the "affinity" of a substituent X for the carbon 2s-character. They have shown that the value of Δ_X increases with the electronegativity of the substituent and that the effects of multiple substituents on a_H^2 are additive. Using their relationships and the value of the J_{CH} for the methyl group in dimethylfulvene one calculates a value of Δ_X of 0.0168 for the fulvene residue. Using their additivity relationship and their value for a phenyl group gives a calculated value for the methylene group in dibenzylfulvene of a_H^2 of

0.257 which agrees well with the experimental value of 0.256.

A similar set of calculations was carried out using J_{CH} for the methyl group in isobutylene (126 c.p.s.)²⁷ and our values for allylbenzene. The value of Δ_X for the olefin substituent was found to be 0.008. Calculated and observed values for the allylbenzene methylene were a_H^2 0.254 and 0.255, respectively.

The values of Δ_X of 0.0168 for the fulvene residue and 0.008 for the olefin residue point up the greater electronegativity of the former group, a result in keeping with the enhanced positive character of C-6.

Acknowledgment.—We wish to acknowledge the generous financial aid of the Robert A. Welch Foundation in support of this work. The helpful suggestions of Dr. K. B. Wiberg, Dr. Wallace Brey, Jr., and Dr. J. N. Shoolery are also gratefully acknowledged.

(27) N. Muller and D. E. Pritchard, *J. Am. Chem. Soc.*, **83**, 1471 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO, BOULDER, COLO.]

Bridged Polycyclic Compounds. XXVI. The Solvolysis of Some 4-Chlorodibenzobicyclo[3.2.1]octadienes¹

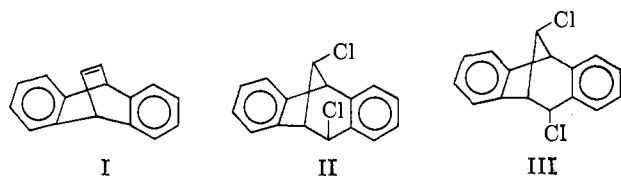
BY STANLEY J. CRISTOL AND DENNIS D. TANNER

RECEIVED FEBRUARY 24, 1964

The solvolyses of *exo*- (II) and *endo*-4-*syn*-8-dichlorodibenzobicyclo[3.2.1]octadiene (III) and of *exo*-4-chlorodibenzobicyclo[3.2.1]octadiene (V) have been studied. Acetolysis of III and V proceeds with good first-order kinetics to give the *exo*-acetate IV and its dichloro analog, respectively. The acetolysis of II to IV is accompanied by epimerization to III, involving ion-pair intermediates. Solvolysis of II in pivalic acid gives the *endo*-pivalate. Various carbonium ions are considered as intermediates, and it is concluded that a classical benzylic carbonium ion can accommodate the results.

Introduction

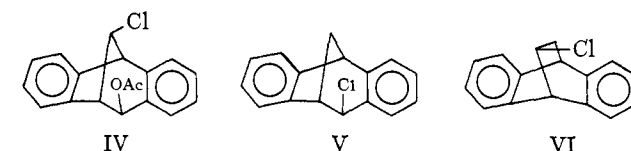
In a recent study² of the ionic chlorination of 9,10-dihydro-9,10-ethenoanthracene (I) the sole products of the reaction were found to be *exo*- and *endo*-4-*syn*-8-dichlorodibenzobicyclo[3.2.1]octadiene (II and III).



The major isomer, compound II, produced in 88% yield, was shown to be the less stable of the two dichlorides. In view of our interest in such compounds, we have investigated the rates and products of solvolysis of the two isomers.

Results

Solvolysis rates were followed in dry acetic acid, with added potassium acetate. A plot of the experimental data for the acetolysis of the *endo* isomer III at 74.74° gave a constant first-order rate which showed no observable trends. Only one product was obtained from solvolysis of III; this product was identified as *syn*-8-chlorodibenzobicyclo[3.2.1]octadien-*exo*-2-yl ace-



tate (IV).² The specific rate constant obtained graphically was $1.68 \times 10^{-6} \text{ sec}^{-1}$. An average of three kinetic runs was used to obtain this value.

When the *exo* isomer II was solvolyzed, a first-order plot of the experimental data showed a considerable downward drift. The steadily decreasing rate was shown to be caused by the concomitant isomerization of the *exo* to the *endo* isomer during the course of the solvolysis. Thus, when a sample of the *exo* isomer was allowed to react to about 50% completion, the remaining (46%) dichloride which was recovered was the *endo* isomer III. The acetolysis product appeared to be entirely *syn*-8-chlorodibenzobicyclo[3.2.1]octadien-*exo*-2-yl acetate (IV), the same product obtained from the solvolysis of III.

This behavior is analogous to that observed in the acetolysis of α, α -dimethylallyl chloride,³ and the same kinetic procedure was used in this work to calculate the specific rate of solvolysis for II and the rate of isomerization of II to III, except that an analytical procedure, rather than a graphical one, was used to calculate the specific reaction rate constants.⁴

(3) W. G. Young, S. Winstein, and H. L. Goering, *J. Am. Chem. Soc.*, **73**, 1958 (1951).

(4) Details of this procedure are given in the Ph.D. Thesis of D. D. Tanner, University of Colorado, 1961.

(1) Previous paper in series: S. J. Cristol and D. I. Davies, *J. Org. Chem.*, **29**, 1282 (1964). This work was reported at the 18th National Organic Symposium of the American Chemical Society, Columbus, Ohio, June, 1963.

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

TABLE I

RATE OF SOLVOLYSIS OF *exo*-4-*syn*-8-DICHLORODIBENZOBICYCLO[3.2.1]OCTADIENE AT $74.74 \pm 0.05^\circ$ IN GLACIAL ACETIC ACIDSample data for a typical kinetic run^a

Time, sec.	[RCl] ₀ - [RCl] _t , moles/l.	Instantaneous rate constant at <i>t</i> , 10 ⁶ <i>k</i> _t , sec. ⁻¹
	Obsd. Calcd. ^b	
0	0	15.7
4920	0.00168	14.4
7860	.00217	13.6
11400	.00294	12.6
16200	.00387	11.2
19500	.00468	10.3
22900	.00549	9.36
27700	.00591	8.11
36000	.00650	6.29
44300	.00715	4.97
55200	.00806	4.02
87100	.00934	3.35

^a Initial concentration: 0.0207 *M* II, 0.0342 *M* KOAc. ^b Alkyl halide consumed, as computed by the analytical procedure; standard error of estimate = 0.00019.

rearrangement and/or return prior to titrimetrically measurable dissociation.^{3,5-7}

The acetolysis rate of *exo*-4-chlorodibenzobicyclo[3.2.1]octadiene (V) was also investigated; V showed steady first-order kinetics, $k = 58 \times 10^{-6}$ sec.⁻¹, when the initial concentration of the alkyl chloride samples was corrected for solvolytically active chloride, calculated from its infinity titer.⁸

The acetolysis of both II and III yields as the sole isolable reaction product *syn*-8-chlorodibenzobicyclo[3.2.1]octadien-*exo*-2-yl acetate (IV). The stereochemistry of IV was assigned for the following reasons. Acetolysis of II and III gives the same chloroacetate IV as was obtained by the ionic addition of *t*-butyl hypochlorite in acetic acid to I; since the structure of IV had been established as either *syn*-8-chlorodibenzobicyclo[3.2.1]octadien-*exo*- or *endo*-2-yl acetate, only the configuration of the acetoxy group at the 2-position remained to be established.^{2,4}

Evidence suggesting a strong diaxial interaction has been found for the *syn-exo*-dichloride II.² If it is as-

TABLE II
COMPARISON OF RATE OF SOLVOLYSIS OF *exo*-4-*syn*-8-DICHLORODIBENZO[3.2.1]OCTADIENE WITH AND WITHOUT ADDED CHLORIDE ION IN ACETIC ACID AT 74.74°

Time, sec.	Reaction, %		Reaction, %	
	[KOAc] ₀ = 0.034 <i>M</i> [RX] ₀ = 0.020 <i>M</i>	[KOAc] ₀ = 0.034 <i>M</i> [RX] ₀ = 0.020 <i>M</i>	[KCl] ₀ = 0.0091 <i>M</i> [KOAc] ₀ = 0.025 <i>M</i> [RX] ₀ = 0.020 <i>M</i>	[KCl] ₀ = 0.0168 <i>M</i> [KOAc] ₀ = 0.017 <i>M</i> [RX] ₀ = 0.0164 <i>M</i>
3000	5	5	5	5
6800	10	10	10	9
11500	15	15	14	14
16100	20	20	18	17
22500	25	25	23	21
39500	33	35	34	30
69000	42	45	44	39

Table I gives the data for a sample kinetic run for II. The calculated values of the instantaneous rate constants for solvolysis evaluated from the slope of the synthesized curve decrease from 16×10^{-6} to about 3.3×10^{-6} sec.⁻¹ (approaching the rate of the solvolysis for the *endo* isomer) by the time the reaction is approximately 45% complete. The specific reaction rate constant for isomerization was found to be approximately 24×10^{-6} sec.⁻¹.

The solvolysis of the *exo*-chloride II was examined for its dependence on added chloride ion at constant ionic strength. An accurate value for the rate of solvolysis with added chloride could not be readily obtained owing to the interference of appreciable concentrations of chloride ion with the observation of the titrimetric end point.³ However, comparison of the values for per cent reaction *vs.* time, shown in Table II, indicates that the rates of solvolysis and ionization are quite insensitive to initially added chloride ion within the limits of experimental error. Thus, there is no detectable evidence of either bimolecular isomerization of *exo*-chloride or reaction of a carbonium ion with external chloride ion. The reaction then clearly represents another example of an internal epimerization of a type previously reported by S. Winstein and co-workers, where *p*-chlorobenzhydryl chloride undergoes intramolecular racemization in conjunction with its solvolysis in glacial acetic acid.⁵ Numerous studies have established the occurrence of ion-pair

sumed that chloroacetate IV is the *syn*-chloro-*exo*-acetate and arises from attack of acetic acid or acetate anion from the *exo* side, then a very large anion, larger than chloride or acetate, might attack the benzyl position from the *endo* side of the carbonium ion and result in a product related to the epimeric alcohol.

When II was treated with silver pivalate in pivalic acid and the resulting ester was hydrolyzed, a chlorohydrin, VII, epimeric to the one derived from the acetolysis product, was obtained. In the case of II and III, the *endo* isomer III was shown to be the thermodynamically more stable product; likewise, when the chloroacetate IV was treated with perchloric acid in acetic acid, the isomeric chloroacetate VIII, derived also from VII, was obtained. When VII was subjected to permanganate oxidation, the chloro-ketone, IX, that was isolated from the oxidation of *syn*-8-chlorodibenzobicyclo[3.2.1]octadien-*exo*-2-ol (X),² was produced. For these reasons, X has been designated as the *syn*-8-*exo*-2-chlorohydrin and VII as the *syn*-8-*endo*-2-chlorohydrin.

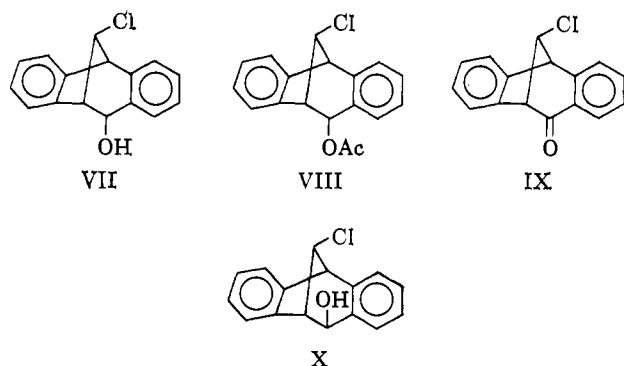
(6) S. Winstein, *et al.*, *ibid.*, **76**, 2597 (1954); **78**, 328, 2763, 2767, 2784 (1956); **80**, 169, 459 (1958); *Chem. Ind. (London)*, 664 (1954); *Helv. Chim. Acta*, **41**, 807 (1958).

(7) G. Kohnstam and B. Shillaker, *J. Chem. Soc.*, 1915 (1959).

(8) The sample of V utilized for the rate determination was prepared by the reaction of 11-dibenzobicyclo[2.2.2]octadienol with thionyl chloride and had an infinity titer of 68% of solvolytically active chloride. Later attempts to reproduce this preparation were unsuccessful, leading to VI instead,³ so it appears likely that the inactive material present in the sample used for reaction rate measurements was VI. When V was prepared by another synthesis, it had an infinity titer of 100% and gave the *exo*-acetate related to X as product.⁹

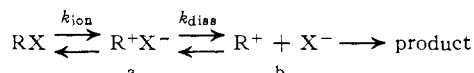
(9) D. E. Florie, Ph.D. Thesis, University of Colorado, 1963.

(5) S. Winstein, J. S. Gall, M. Hojo, and S. Smith, *J. Am. Chem. Soc.*, **82**, 1010 (1960); the transformation of *exo* to *endo* isomer, in our system, is stereochemically similar to racemization in their case.



Discussion

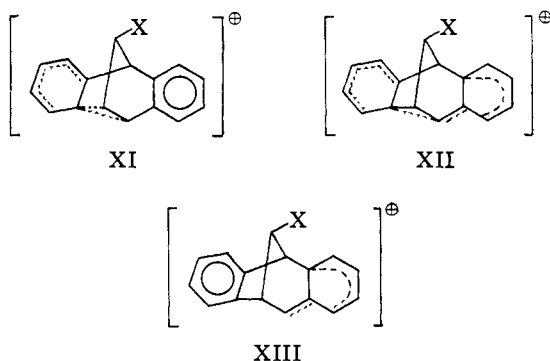
The acetolysis of an alkyl halide or sulfonate has been depicted as proceeding through various stages of solvent separation.^{5,10-12}



For the purposes of our discussion, only ion-pair intermediates, a, and dissociated ions, b, need be considered. The characteristics of a are that rearrangement and ion-pair return are probable occurrences and that chloride ion is not produced for titration. Species b, on the other hand, leads to products, with little possibility of ion return, and provides free titratable chloride ion.^{5,11,12}

As discussed above, the epimerization of II to III, which accompanied the acetolysis of II, undoubtedly occurs at one of the undissociated ion-pair stages.

The isomerization and solvolysis rate data provide information regarding the nature of the carbonium ions present in both stages of the reaction. Considering only R^{\oplus} and not the counter ion or counter dipolar molecule, three cationic structures present themselves for consideration. These three include two in which substantial electron delocalization of the so-called



"nonclassical" type is involved (XI and XII) and a third, the classical cation XIII, in which only benzylic electron delocalization is important. Both cations XI and XII would be expected to maintain *exo* structure at C-2, but differ in that in XI a substantial amount of positive charge would leak onto C-1. This would not be true of XII.

Some information regarding electron distribution in the transition state for ionization may be inferred from

(10) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Am. Chem. Soc.*, **78**, 328 (1956).

(11) S. Winstein, A. Ledwith, and M. Hojo, *Tetrahedron Letters*, **No. 10**, 341 (1961).

(12) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 148, 167.

the solvolysis rate data for II, III, and V (see Table III). For this purpose, consideration of the inductive retardation to solvolysis of a second chlorine atom in the molecule seems useful. The magnitude of the inductive effect should be proportional to the distance of the added chlorine atoms from the incipient positive charge in the transition state, and, for this purpose, it is instructive to consider analogous cases described in the literature.

TABLE III

SUMMARY OF RATE DATA FOR SOLVOLYSIS OF HALIDES IN GLACIAL ACETIC ACID AT 74.74°

Alkyl halide	[RX], M	[KOAc], M	10 ⁶ k, sec. ⁻¹	10 ⁶ k _{av.} , sec. ⁻¹
II	0.021	0.0342	15.7	16.0
	.020	.0342	16.4	
III	.021	.0342	1.62	1.68
	.020	.0342	1.73	
	.020	.0342	1.68	
V	.018	.0342		58

The solvolysis of 7-*anti*-norbornenyl chloride and *exo*-2-norbornyl tosylate have been assumed to proceed through the transition states XIV^{13,14} and XV,¹⁵ respectively. When the hydrogen in the 5-position of 7-*anti*-norbornenyl chloride was substituted with a chlorine atom, the rate of solvolysis of the 7-chloride was retarded to one-twentieth that of the nonsubsti-



tuted case.^{13,14} Substitution of a chlorine atom in the 7-position of *exo*-2-norbornyl tosylate retarded the rate of acetolysis by a factor of 400.^{13,15} The solvolysis of II *via* the intermediate XI would place a chlorine atom one carbon atom away from a partial positive charge. This should result in a retardation to the solvolysis of II compared with that for V of about 400 times, analogous to the case of norbornyl tosylate and its *syn*-7-chlorine derivative. As the retardation observed in the dibenzobicyclo[3.2.1] system was less than 4, XI does not appear to represent very well the structure of the intermediate formed in the rate-determining step.

The homobenzylic cation XII, on the other hand, may be compatible with the inductive argument based on its analogy to 7-*anti*-norbornenyl chloride and its substituted analog. The classical intermediate XIII is also acceptable as the solvolytic intermediate to explain the magnitude of the inductive effect. However, if the homobenzylic cation XII is involved, it must be rapidly and reversibly transformed to the classical ion XIII to explain the observed rapid epimerization of II to III during solvolysis, the formation of IV by solvolysis of both II and III, and the formation of the *endo*-pivalate related to VII by treatment of II with silver pivalate, as well as the formation

(13) W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5653 (1956).

(14) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

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

of both II and III by addition of chlorine to I. Such ready transformations are not usually observed.¹⁶

The data appear to be well (and perhaps best) accommodated by the assumption that only classical ions of type XIII are involved in all of these reactions,¹⁷ if it is assumed that there is a small stereoelectronic preference¹⁸ for reaction of XIII (X = Cl) with nucleophiles from the *exo* (axial) side than from the *endo* (equatorial) side. This assumes that there is less loss of benzylic resonance ($p-\pi$ overlap) in the transition state for *exo* attack than for *endo* attack. This electronic preference may be balanced or overcome by steric interaction between the nucleophile and the *syn*-chlorine atom. Thus, with acetic acid, the amount of *endo*-acetate VIII was too small for us to observe; with chloride, the *exo-endo* ratio was 88:12²; and with pivalic acid, the *endo* ester was produced.

Experimental

Materials.—The mixture of isomeric compounds *endo*-4-*syn*-8-dichlorodibenzobicyclo[3.2.1]octadiene (III) and *exo*-4-*syn*-8-dichlorodibenzobicyclo[3.2.1]octadiene (II) was prepared by the chlorination of dihydroethenoanthracene.² The mixture of isomers was subjected to rapid fractional recrystallization from ethanol, and the *exo* isomer II crystallized and was recrystallized to a constant melting point, 126–127°. Isomer II was isomerized to the *endo* isomer in liquid sulfur dioxide and *o*-cresol,² and the crude reaction product, dissolved in petroleum ether (b.p. 60–70°), was subjected to column chromatography on an alumina column and eluted with carbon tetrachloride. The *endo* isomer was recrystallized to a constant melting point, 122–123.5°.

The monochlorinated isomer *exo*-4-chlorodibenzobicyclo[3.2.1]octadiene (V) was prepared by the treatment of 9,10-dihydro-9,10-ethanoanthracen-11-ol with thionyl chloride.^{4,8} The product was recrystallized from absolute ethanol to a constant melting point, 113–114°.

The solvent used for the kinetic runs, without initially added chloride ion, was found to have 0.23% water present, as determined by Karl Fisher titration. The solvent used in the kinetic runs, with initially added chloride ion, was shown to be anhydrous by Karl Fisher determination.

Rate Measurements.—The procedure for the measurement of acetolysis rates in anhydrous acetic acid, using the sealed ampoule technique, was the same as described by Young, Winstein, and Goering,³ and all solvent solutions and analytical reagents used were prepared by this method.

The concentration of all solutions are given at room temperature. All the kinetic data reported were obtained at 74.74 ± 0.05°.

Throughout the course of each kinetic run, about twelve analyses were made. Owing to the nature of the mathematical treatment of the data, the majority of the analyses were carried out before 30% of the acetolysis reaction was completed.

Time was counted from the time the first ampoule was removed from the temperature bath.

Titrations.—The progress of the solvolysis reaction was followed by neutralizing the excess acetate ion present in the reaction mixture with excess standard *p*-toluenesulfonic acid in glacial acetic acid, and back titration with standard sodium acetate solution to the bromphenol blue end point.³

Solvolysis of II in Glacial Acetic Acid.—*exo*-4-*syn*-8-Dichlorodibenzobicyclo[3.2.1]octadiene (II) (800 mg., 0.00291 mole) was dissolved in 100 ml. of the kinetic solvent of glacial acetic acid which was 0.03424 *M* in potassium acetate. The reaction mixture was placed in a constant temperature bath at 74.74° for 31.5 hr. At the end of this period, the solvent was removed by rotary evaporation at 80° in 15 min. The solid residue

remaining in the reaction vessel was dissolved in carbon tetrachloride and placed on a chromatography column, packed with 100 g. of Merck Co. acid-washed alumina in petroleum ether (b.p. 60–70°). It has been demonstrated that the *exo* isomer could undergo the chromatographic treatment without any observable rearrangement taking place.²

The alumina column was eluted with solvents in the following sequence: carbon tetrachloride, 5% chloroform in carbon tetrachloride, and 100% chloroform. From the carbon tetrachloride fractions was isolated 368 mg. (46%) of the *endo* isomer III. The identity of this compound was determined by comparison of its melting point and mixture melting point with an authentic sample of III. The melting point of this compound was 102.5–103.5°. The chloroform fractions contained 406 mg. of product, from which was obtained 363 mg. of *syn*-8-chlorodibenzobicyclo[3.2.1]octadien-*exo*-2-yl acetate. This was demonstrated to be IV by comparison of its melting point with that of a known sample,² and by the observation that the mixture melting point was not depressed. The isolated *exo*-chloroacetate melted over the range 154–156.5° for 289 mg. and 146–152° for 74 mg. of the isolated compound. The 74-mg. fraction was isolated after recrystallization from ethanol. When the mother liquors from this recrystallization were concentrated and all of the ethyl alcohol evaporated by reduced pressure distillation, an infrared spectrum of the residual oil showed an hydroxyl band at 2.9 μ . The spectrum indicated that the impurities present in the reaction mixture most probably were the chlorohydrin, *syn*-8-chlorodibenzobicyclo[3.2.1]octadien-*exo*-2-ol.

Solvolysis of III in Glacial Acetic Acid.—Several unused ampoules from each kinetic run, without initially added chloride ion, of compound III were combined, and the reaction mixture was placed in a water bath at 94° for several weeks. The solution was evaporated to dryness by rotary evaporation. The residue, a mixture of potassium acetate and the product from the acetolysis of the *endo* isomer, was leached several times with hot petroleum ether (b.p. 60–70°) and placed on a chromatographic column containing approximately 100 g. of Merck Co. acid-washed alumina. The column was eluted with petroleum ether (b.p. 60–70°), carbon tetrachloride, 5% chloroform in carbon tetrachloride, and pure chloroform, in that order. The 5% chloroform fractions contained 351 mg. of a white compound melting over the range 152–158°. A mixture melting point with a sample of IV showed no depression. The fractions from elution with pure chloroform contained 187 mg. of a mixture, melting point 124–146°. When these fractions were recrystallized from absolute ethanol, 115 mg. of IV, m.p. and mixture m.p. 153–156°, was obtained. Thus III gives the *exo*-acetate IV on acetolysis.

***syn*-8-Chlorodibenzobicyclo[3.2.1]octadien-*endo*-2-ol (VII).**—A mixture of 1.010 g. (3.67 mmoles) of the *exo*-dichloride II, 1.00 g. (4.8 mmoles) of silver pivalate,¹⁹ and 60 ml. of pivalic acid was heated at 95° for 24 hr. with continuous stirring. The reaction mixture was distilled under reduced pressure until approximately 10 ml. remained. To the residue was added 20 ml. of benzene, and the solution was washed with an aqueous solution of sodium carbonate. Dilute hydrochloric acid was then slowly added until the silver carbonate precipitate had reacted. The silver chloride precipitate was filtered, and the benzene layer was washed several times with water. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed by rotary evaporation. The residue weighed 4.50 g. and contained residual pivalic acid. The residue was dissolved in ether, and the ethereal solution was added through a dropping funnel into a solution of 2.30 g. of lithium aluminum hydride. The reaction was run at room temperature for approximately 1 hr. Ethyl acetate was added. The supernatant solution was decanted and the solvent removed by rotary evaporation. The residual oil, weighing 1.464 g., was dissolved in hot petroleum ether (b.p. 60–70°) and subjected to chromatography on an alumina column made up from 50 g. of Merck Co. acid-washed alumina, which was packed in petroleum ether (b.p. 60–70°). The column was eluted with petroleum ether, 5% carbon tetrachloride in petroleum ether (b.p. 60–70°), 100% carbon tetrachloride, 10% chloroform in carbon tetrachloride, and 100% chloroform. The chloroform fractions contained 939 mg. of oily product. When these fractions were subjected to recrystallization from absolute methanol, 534 mg. (57%) of VII which melted at 125–126° was obtained. A mixture melting point with the known

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

(17) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952), have pointed out the unimportance of anchimeric assistance in benzylic systems.

(18) For a similar case see H. L. Goering and D. L. Towns, *ibid.*, **85**, 2295 (1963).

(19) R. A. Zingiro, *ibid.*, **71**, 575 (1959).

syn-8-chlorodibenzobicyclo[3.2.1]octadien-*exo*-2-ol (m.p. 137.5–138.5°) (X) was depressed. The infrared solution spectra of the two compounds taken in carbon disulfide showed marked differences.⁴

Anal. Calcd. for C₁₆H₁₃ClO: C, 74.85; H, 5.08. Found: C, 75.02; H, 5.07.

***syn*-8-Chlorodibenzobicyclo[3.2.1]octadien-*endo*-2-yl Acetate (VIII).**—A solution of 263 mg. (1.025 mmoles) of VII in acetic anhydride and several drops of concentrated sulfuric acid was heated on a hot plate for 5 min. The solution was poured slowly into water and extracted with two 50-ml. portions of chloroform. The reaction mixture was dried over anhydrous sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The oily residue was dissolved in carbon tetrachloride and subjected to column chromatography on a column which was packed with 100 g. of Woelm neutral alumina in carbon tetrachloride. The column was eluted with the following solvents: carbon tetrachloride, chloroform, and 10% ethyl acetate in chloroform. The first fraction containing ethyl acetate yielded 253 mg. (83%) of VIII melting at 133.5–138°. Recrystallization from ethanol gave a melting point of 136–137°.

This compound when compared with IV showed different infrared solution spectra in carbon disulfide. A mixture melting point for the two isomers was depressed.

An analysis was obtained in this laboratory⁹ for a compound believed to be the *syn*-chloro-*endo*-acetate, but synthesized in a different manner. This melted at 145–146°. When a mixture melting point was taken of the two, the mixture melted at 138.5–141.5°. A remelting point of the resolidified mixture was 135–136.7°. There was a marked difference between the infrared spectra of the two compounds from 13–25 μ when the spectra were taken in potassium bromide pellets. When the two samples were each dissolved in carbon disulfide, their solution spectra were shown to be identical from 2–25 μ . Crystalline modifications were observed both in the *syn*-chloro-*endo*-alcohols and acetates. Products from the [3.2.1] ring system were always compared in the above manner.

The Permanganate Oxidation of *syn*-8-Chlorodibenzobicyclo[3.2.1]octadien-*endo*-2-ol (VII) to *syn*-8-Chlorodibenzobicyclo[3.2.1]octadien-2-one (IX).—Compound VII (149 mg., 0.580 mmole) was subjected to the permanganate oxidation procedure previously reported for the *syn*-8-chloro-*exo*-2-alcohol.² The product, 130 mg. (87%) of a white crystalline compound, showed a melting point of 121–122°. A mixture melting point with known *syn*-8-chlorodibenzobicyclo[3.2.1]octadien-2-one (IX)² showed no depression. Infrared spectra of both samples were identical.

The Epimerization of *syn*-8-Chlorodibenzobicyclo[3.2.1]octadien-*exo*-2-yl Acetate (IV) to *syn*-8-Chlorodibenzobicyclo[3.2.1]octadien-*endo*-2-yl Acetate (VIII).—A mixture of 1.54 g. of 70% perchloric acid (1.54 mmoles), 10 ml. of glacial acetic acid, and 438 mg. (1.46 mmoles) of IV was heated at 85° for 4 hr. The solution was then poured into 200 ml. of water and extracted with two 100-ml. portions of benzene. The organic layer was washed with a 5% sodium bicarbonate solution and then twice with water. The benzene extract was then dried over anhydrous sodium sulfate, filtered, and the solvent was removed by rotary evaporation, leaving 432 mg. of a clear yellow oil. A spectrum of the crude product was identical with that of the *endo*-acetate VIII. The product was recrystallized from petroleum ether (b.p. 60–70°) twice, and 114 mg. of a compound melting at 141–142° was obtained. A mixture melting point with a sample of VIII showed no depression. A solution spectrum of the product in carbon disulfide was taken from 2–25 μ and was found to be identical with that of VIII.

The mother liquors from the recrystallizations were combined and subjected to elution chromatography on an alumina column packed with 10 g. of Woelm neutral alumina. The chromatogram was eluted with petroleum ether (b.p. 60–70°), carbon tetrachloride, and chloroform. The fractions eluted with chloroform (217 mg.) yielded upon recrystallization 120 mg. of a compound melting at 121–139° and having a solution spectrum identical with that of VIII. The impurity seemed, from the crude infrared spectrum, to be a small amount of the hydrolysis product *syn*-8-chlorodibenzobicyclo[3.2.1]octadien-*endo*-2-ol (VII). When the mother liquors were combined and the solvent removed by rotary evaporation, an oil weighing 23 mg. was obtained. The oily product was dissolved in 10 ml. of acetic anhydride, and 2 drops of concentrated sulfuric acid was added. The mixture was warmed for several minutes and then poured slowly into water. The aqueous mixture was extracted twice with benzene, and the combined organic layers were decolorized with Norit and dried over anhydrous sodium sulfate. When the solvent was removed by rotary evaporation, 27 mg. of a compound having a melting point of 121–135° was obtained. Upon recrystallization from petroleum ether (b.p. 60–70°), 15 mg. of a compound, m.p. 128–140°, was recovered. An infrared spectrum of this compound showed it to be VIII. The crude yield of VIII was 58%.

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Dipole Moments, Configuration, and Conformation of Tricyclo[5.1.0.0^{3,5}]octane Derivatives and Related Compounds¹

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Tricyclo[5.1.0.0^{3,5}]octane (VI), 4,4-dibromotricyclo[5.1.0.0^{3,5}]octane (V), and 4,4,8,8-tetrabromotricyclo[5.1.0.0^{3,5}]octane (III) have been prepared. The dipole moments of these compounds as well as those of norcaradiene (VII), Δ^3 -norcaradiene (IV), 7,7-dibromobicyclo[4.1.0]heptane (VIII), Δ^3 -7,7-dibromobicyclo[4.1.0]heptane (II), 1,4-cyclohexadiene (I), cyclohexene, and cyclopentene have been measured. Zero dipole moment for III proves its configuration is *trans* and the six-membered ring has a relatively flat conformation. The methods of preparation indicate a *trans* configuration for VI and V and the dipole moment values favor nearly flat conformations for the six-membered rings in these compounds. Cyclohexene and cyclopentene were found to have dipole moments of 0.21 D, which are considerably smaller than most values in the literature. Norcaradiene has a moment of 0.44 D. The evidence indicates the central ring is relatively flat when either cyclopropane or olefinic groups are on opposite sides of a six-membered ring.

In the course of another study² it was necessary to determine the configurations of the bismethylene adducts (VI) of 1,4-cyclohexadiene (I). One of the bis-

adducts can be derived from the crystalline tetrabromide³ III, the bisdibromocarbene adduct of 1,4-cyclohexadiene. As a guide to configuration, the dipole moment of the tetrabromide was determined, and in

(1) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 9–14, 1962; Abstracts, p. 80Q.

(2) P. Bruck and R. Boikess, unpublished work.

(3) (a) K. Hofmann, *et al.*, *J. Am. Chem. Soc.*, **81**, 992 (1959); (b) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961).