Bridged Polycyclic Compounds. LXXXI. Rearrangements in Dibenzobicyclooctadiene Systems. The Nature of the Low-Energy Intermediates[1]

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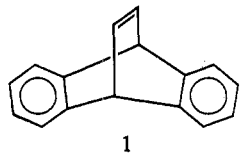
A number of addition reactions have been carried out with 10,11-dimethyldibenzobicyclo[2.2.2]octatriene (11) and with 10,11-dichlorodibenzobicyclo[2.2.2]octatriene (12). Some of these proceed without rearrangement and some with rearrangement to the dibenzobicyclo[3.2.1]octadiene ring system. This study was directed at determining whether reagents preferred attack at one side of the double bond or not and, if so, which orientation was preferred. No preference was noted with diborane, benzenesulfenyl chloride, iodine and silver acetate (Prevost reagent), or mercuric acetate. Of these, the first and the last give cis addition, the second trans addition, and the third addition with rearrangement. It is concluded that each of these reactions involves a cyclic process. On the other hand, bromine, chlorine, hydrogen bromide, and acetic acid show directional effects, with electrophilic attack preferred at the side anti to the dimethylbenzo ring in 11 and anti to the unsubstituted ring in 12. These results are rationalized as involving ring migration accompanying addition with the transition state resembling a phenyl-bridged ion (e.g., 6). The silver acetate assisted acetolyses of *trans*-7,8-dichloro-10,11,dimethyl- (or dichloro-) dibenzobicyclo[2.2.2]octadiene show similar migrating aptitude effects and are rationalized similarly.

Some time ago[2] we reported our initial results on the addition of a variety of electrophilic reagents to dibenzobicyclo[2.2.2]octatriene (1) which led, in general, to syn-8-exo- (or endo-) 4-substituted dibenzobicyclo[3.2.1]octadiene derivatives (2). The rearrangement reactions occurred with complete anti specificity. Similarly, solvolyses of cis-9,10 derivatives of dibenzobicyclo[2.2.2]octadiene (3) led stereospecifically to syn-8 compounds 2, while those of trans compounds 4 led only to the anti derivatives 5. In these solvolyses, the exo epimers of 2 or 5 were the principal products of kinetic control. When the exo epimers (Y = Cl, Br, $HOAc^+$) were allowed to stand or were warmed, they were rapidly converted to the endo epimers and, in most cases, were transformed more slowly, again sterospecifically and with anti migration, i.e. 2 to 3 and 5 to 4, to the thermodynamically stable [2.2.2] isomers.



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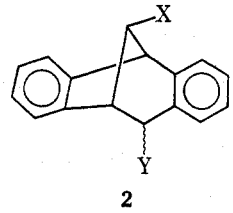

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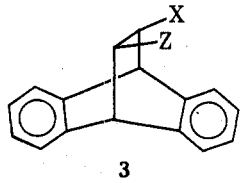

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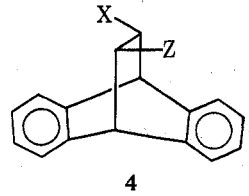

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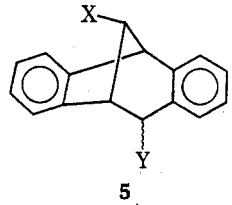

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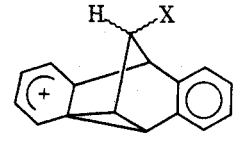
These results suggested[2] the intervention of the phenyl-bridged ions 6 and the benzylic ions 7 in the rearrangement reactions. The rapid exo–endo equilibration of 2 and 5 species, significantly faster than the [3.2.1] to [2.2.2] rearrangements, was interpreted as requiring the intermediacy of 7 species, as it was assumed that 6 could lead only to exo



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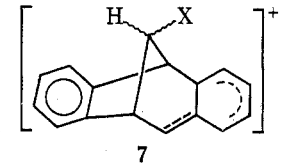

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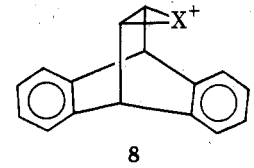

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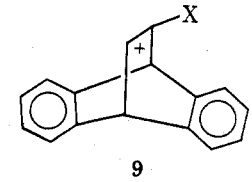

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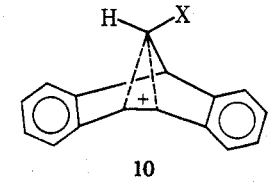

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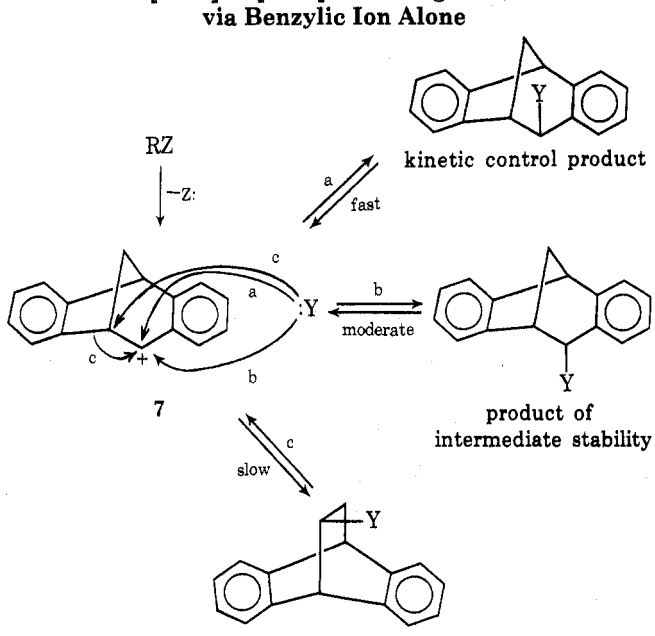
epimers or to [2.2.2] isomers. Thus, while 7 is required as an intermediate, 6 is not required. If in fact 6 is involved, it must be rapidly equilibrated with 7 to accommodate the exo–endo interconversion. On the other hand, as shown in Scheme I, the reactions may be interpreted by the assumption that 7 is the only cationic intermediate in the system, assuming the geitonodesmic[3] reaction (c). Since this early work, we have reported a number of experiments[4] consistent with these interpretations, with the further intervention of onium ions 8 in appropriate situations, and we have most recently noted[5] that cations of type 9 and 10, which are clearly not involved in most reactions, do intervene as high-energy species when the cationic systems are formed and consumed many times.

In this paper we return to the question of the number and nature of the low-energy cationic intermediates, and in particular to the question of the intermediacy of ions of type 6 in these rearrangements. We reasoned that we might be able to learn if the transition state for addition of X^+ to 1, or for loss of Z^- from 3 or 4, resembled 6 or 7, by appropriate nuclear substitution of 1, 3, or 4. Thus in additions to dimethyldibenzobarrelene (11), one would anticipate preferential migration of the substituted ring if the transition state for addition resembled 6 in electron distribution, while the unsubstituted ring should migrate preferentially if the transition state resembled 7. 12, which contains elec-

Scheme I
Pictorial Representation of [2.2.2] ⇄ [3.2.1] Rearrangement via Benzylic Ion Alone

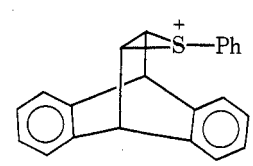


tron-withdrawing chlorine substituents, should react in an analogous fashion, but of course in the opposite sense. Similarly, if **13** were subjected to solvolysis, the chlorine anti to the substituted ring would react preferably if the transition state resembled **6**, and that anti to the unsubstituted ring would leave if the transition state resembled **7**. Again opposite predictions seemed reasonable for the dichloro derivative **14**.

Certain addition reactions involve cyclic processes, either via onium ions (π complexes) such as **8**, or via molecular cis additions. If the concepts described above are correct, if the substituents in **11** and **12** are small enough not to cause steric problems, and if the additions are irreversible, one might anticipate little or no directive influence upon the product mixture, whether the reaction leads to unrearranged [2.2.2] product or whether the intermediate analogous to **8** leads via **6** and/or **7** to [3.2.1] products. Thus study of **1**, **11**, and **12** with a variety of reagents offers not only an opportunity to learn about **6** and **7**, but also about the possibility of π complexes as product-determining intermediates in such reactions. Such intermediates are often used to rationalize stereochemical results (trans or cis addition), but our system allows a completely independent test for mechanism and may prove generally useful.

The addition of diborane to olefins involves a four-center transition state,[6] not involving cationic intermediates, and a study of its regioselectivity might be useful in testing the concept. Indeed **11**, when treated with diborane, followed by oxidation, gave equal amounts of the two alcohols **15**-OH and **16**-OH. Similarly **12** gave equal amounts of **17**-OH and **18**-OH.

Addition of sulfenyl chlorides is known to proceed via sulfonium ions,[7] and **1** has been shown[4a] to add benzenesulfenyl chloride stereospecifically trans and without rearrangement to give **4** (X = PhS; Y = Cl), obviously via attack of chloride ion on **19**. As anticipated, addition of benzenesulfenyl chloride to **11** gave equal amounts of **20** and **21**, confirming the intervention of the bis homologs of **19** as the product-forming intermediates.



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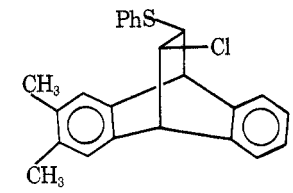

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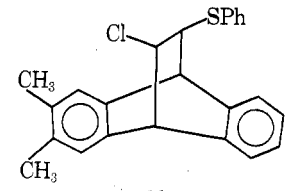

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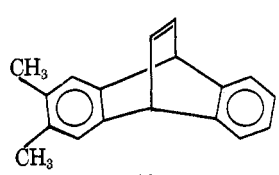
These three experiments thus seem to confirm the idea that processes involving cyclic additions to **1** and its analogs **11** and **12** will not show directive influences. Addition of positive halogen species to olefins may or may not involve cyclic onium intermediates,[8,9] and of the halogens, the likelihood of the formation of the **8** species decreases in the order iodine, bromine, chlorine. It has been reported[2d] that treatment of **1** with either iodine and silver acetate or bromine in acetic acid leads cleanly to syn-8-halo-4-exo acetate (**2**, X = halogen, Y = exo-OAc) and that[2b] chlorine gives the analogous dichloride (**2**, X = Cl, Y = exo-Cl), but the question remains open as to whether **8** (X = halogen) precedes **6** or **7** in the reaction scheme.

When **11** was treated with the Prevost reagent, the two rearranged iodoacetates **22**-I and **23**-I were obtained in equal amounts. The nature and amounts of the products allows the formulation of the ions **24**-I and **25**-I as product-determining intermediates, which then rearrange (**24** to **26** and/or **27** and **25** to **28** and/or **29**) on the path to product. On the other hand, addition of bromine in methylene chloride to **11** gave a mixture of **30** and **31** in a 2.1:1.0 ratio. Similarly **12** gave **32** and **33** in a ratio of 1.0:3.0. Thus, with bromine, rearrangement accompanies attack by electrophile and species analogous to **8** are bypassed. The facts that the dimethylbenzo ring migrates in preference to the



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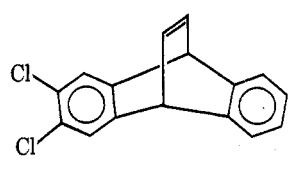

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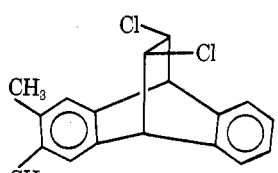

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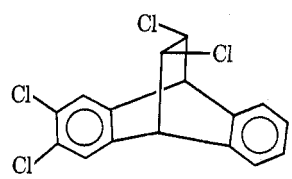

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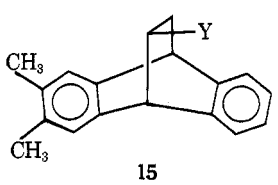

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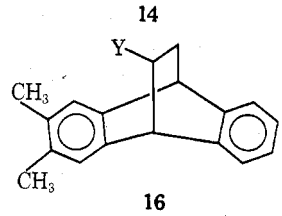

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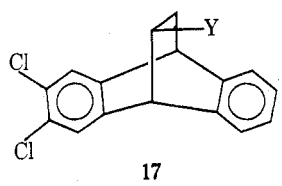

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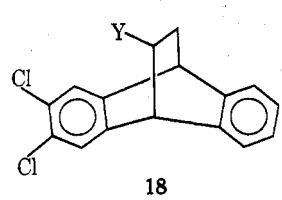

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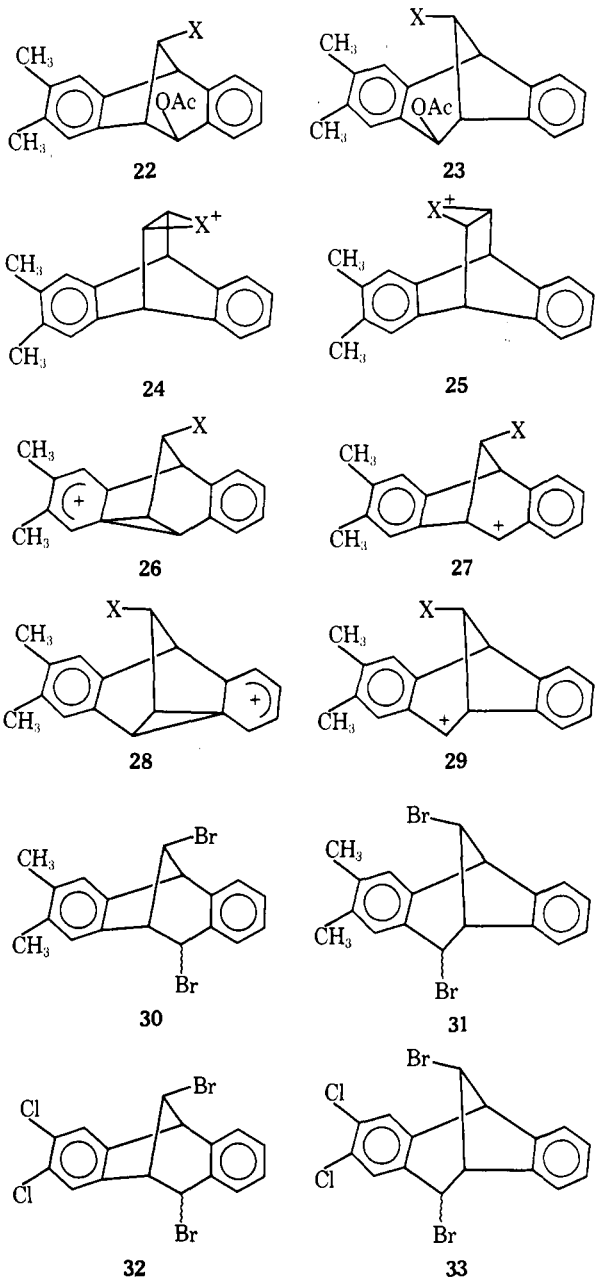
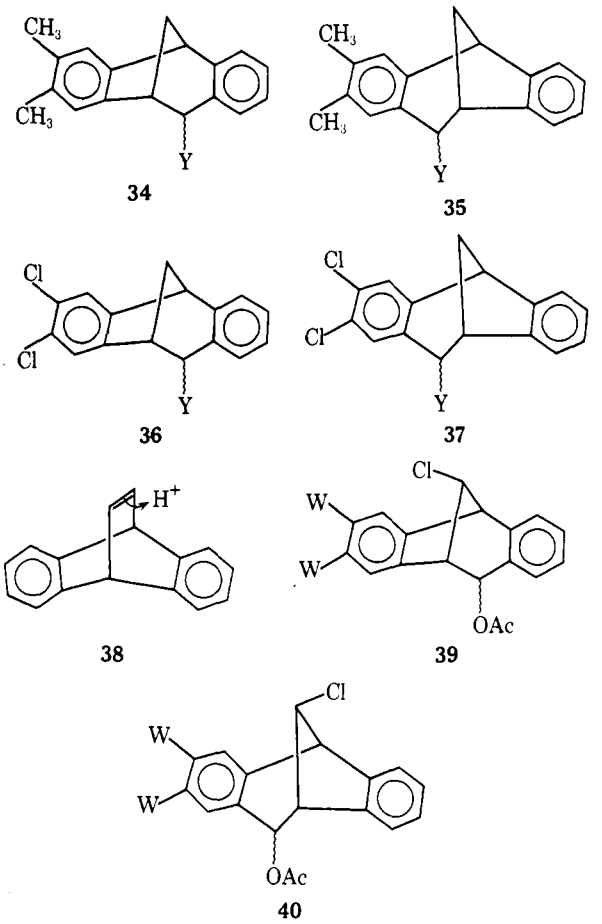


benzo ring, which in turn migrates in preference to the dichlorobenzo ring, furnish excellent evidence that the transition state for addition resembles the bridged ion **6** rather than the benzylic ion **7**. Similar conclusions may be reached for chlorine addition (in methylene chloride) where the dichlorides analogous to **30** and **31** were produced in a ratio of 1.7:1.0, and those analogous to **32** and **33** in a ratio of 1.0:2.3.

Addition of protic species generally is assumed to proceed via carbenium ions, although π complexes (protonated double bonds) have been suggested occasionally as reaction intermediates.[10] When **11** was treated with hydrogen bromide in ether, **34**-Br and **35**-Br were produced in a ratio of 1.8:1.0. **12** gave **36**-Br and **37**-Br in a 1.0:2.1 ratio. Acetic acid addition to **1** is so slow[4c,5] that the [3.2.1] acetates (**2**, X = H; Y = OAc) are not found in the reaction products, but are instead isomerized to the [2.2.2] acetate (**3**, X = H; Y = OAc). As this [2.2.2] to [3.2.1] rearrangement is largely stereoselective,[4c,5] the information we are seeking may still be observed by addition regioselectivity. Thus **11** gave (with 5% sulfuric acid in acetic acid) a mixture of **15**-OAc and **16**-OAc in a ratio of 2.0:1.0, and **12** gave **17**-OAc and **18**-OAc in a ratio of 1.0:2.5. Clearly, just as with Br^+ and



Cl^+ transfer, rearrangement accompanies proton transfer, and no protonated double bond species **38** intervenes. Again the migration aptitude results suggest the intervention of **6** rather than **7** as the first cationic intermediate.

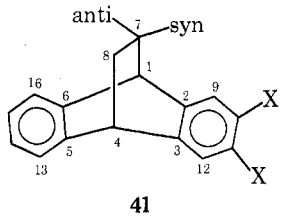
Oxymercuration of olefins, in particular addition of mercuric acetate, has been of considerable interest recently, with evidence adduced for[11] and against[12] cyclic processes, involving either mercurinium ions or concerted multicenter addition processes. A conservative viewpoint, to our mind, is that, as with other reactions, a multiplicity of mechanisms, often without large energy differences, is available so that evidence from one system is not necessarily transferable to others. Addition of mercuric acetate to **1** in acetic acid results in cis addition,[13] a result rationalized readily by the assumption of a concerted multicenter process. In accord with that assumption, similar treatment of **11**, followed by sodium borohydride reduction, gave equal amounts of acetates **15**-OAc and **16**-OAc. Treatment of **1** with mercuric acetate in aqueous acetone leads to trans addition without rearrangement,[13] probably via a mercurinium ion intermediate. It would be of interest to know how **11** reacts under these conditions, but we have not yet done that experiment. The results of such an experiment may be only difficultly interpretable, as mercurinium ions are known[14] to revert to olefin and mercuric ion, so that the requirement noted above of irreversible intermediate formation may not be met.

The data described above show clearly that migratory aptitude of groups is more important than benzylic stabilization, although the effects are not large. When the logarithms of relative k's are plotted against $\Sigma\sigma^+$ (we have used sums of σ^+_m and σ^+_p values[15] in these treatments), we get ρ values of -0.90, -0.67, -0.65, and -0.79 for addition of bromine, chlorine, hydrogen bromide, and acetic acid, respectively, under the conditions described above. These

rather low values suggest that the transition states for addition come quite early in the process, before much charge has leaked into the benzene rings. Solvolysis may be predicted to give a greater amount of benzene-ring participation, if results in the benzonorbornadiene–benzonorbornenyl system are applicable.[16] Accordingly the two trans dichlorides **13** and **14** were subjected to silver acetate assisted acetolysis. **13** gave a mixture of **39**-CH_3 and **40**-CH_3 in 5:1 ratio and **14** gave **39**-Cl and **40**-Cl in a 1:8 ratio. Again migratory aptitude leading to the phenyl-bridged species analogous to **6** prevailed; a ρ value of -1.8 resulted. This value is somewhat lower than those reported[16,17] for solvolysis of ring-substituted derivatives of 2-benzonorbornenyl chlorides or *p*-bromobenzenesulfonates, so that it would appear that π participation is somewhat less important in our system than in theirs. This may possibly be due in part to the silver ion assistance.

In all of the additions, and in the solvolyses as well, the products were largely exo at C-4. However, in most cases, small amounts of endo products accompanied the major epimers, as was noted in previous reactions with **1**.[2,4] We interpret these results as indicating that, while **6** is the first intermediate along the path from the [2.2.2] to [3.2.1] system, it comes into equilibrium with **7** (or begins to do so) before capture by nucleophile. Thus it may be assumed that bridged **6** ions lead to and from [2.2.2] molecules and may lead to and from exo [3.2.1] molecules, but that the latter species may arise from and give rise to benzyl cations **7**, as may the endo [3.2.1] molecules. There would appear to be no evidence requiring the intermediacy of geitonodesmic[3] reactions in these systems.

All of the product ratios were determined by ^1H NMR spectroscopy. In general, structure proof, other than syn-anti at C-8 or endo-exo at C-4 of the [3.2.1] systems, which are easily determined directly by ^1H NMR spectroscopy,[18] and often quantitative analysis as well, made use of conversion to the [3.2.1] 4-keto derivatives. We use the numbering systems shown in **41** and **42** in this paper, based upon the corresponding simple hydrocarbons.



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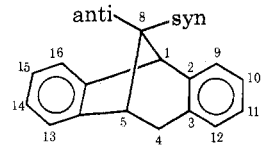

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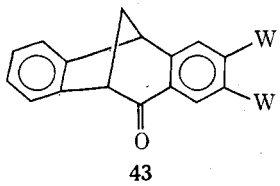
With the 4-keto substituent the ortho hydrogen (at C-12) resonance is shifted downfield by 0.4–0.9 ppm from the remainder of the aromatic multiplet and is therefore readily distinguishable. In ketones of type **43**, the proton resonance is a relatively sharp singlet, while in those of type **44**, the



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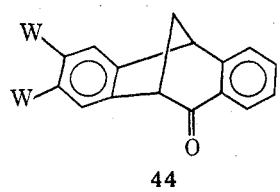

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proton resonance is seen as a doublet of doublets with important splittings between this proton and its ortho and meta neighbors. Once structures were established by conversion to ketones, we worked out procedures for analysis either by carrying out these conversions quantitatively and analyzing the ketone mixture, or by analysis of earlier product mixtures, again by ^1H NMR methods. The method used in each case is described in the Experimental Section.

Experimental Section

Proton magnetic resonance spectra were recorded with either Varian A-60A or HA-100 spectrometers, with tetramethylsilane as internal standard. Melting points were obtained with a Thomas-Hoover apparatus and are corrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of *trans*-7,8-Dichloro-10,11-dimethyldibenzobicyclo[2.2.2]octadiene (13). 2,3-Dimethylanthraquinone was prepared[19] and reduced with zinc and ammonia[20] to 2,3-dimethylanthracene. The reaction procedure was modified by using a two-phase system with a layer of toluene. The anthracene and *trans*-1,2-dichloroethene were combined to form **13** by the same method used for preparation of *trans*-7,8-dichlorodibenzobicyclo[2.2.2]octadiene.[2] Recrystallization of the product from petroleum ether (bp 60–70°) gave colorless crystals (mp 147.5–148.5°) with a ^1H NMR spectrum (CCl_4) indicating the assigned structure (δ 4.15, H-1, 4; 4.02, H-7, 8).

Anal. Calcd for $C_{18}H_{16}Cl_2$: C, 71.30; H, 5.32. Found: C, 71.23; H, 5.30.

Dehalogenation of 13 to 10,11-Dimethyldibenzobicyclo[2.2.2]octatriene (11). Dehalogenation of **13** by the established procedure in this laboratory[2] gave **11** (82%, mp 144–144.5°, recrystallized from ethanol). ^1H NMR analysis (CCl_4) confirmed the structure (δ 4.87).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.94; H, 6.95.

Preparation of *trans*-7,8,10,11-Tetrachloridibenzobicyclo[2.2.2]octadiene (14). 2,3-Dichloroanthraquinone was prepared from *o*-dichlorobenzene and phthalic anhydride by the method of Fieser.[21] Conversion to 2,3-dichloroanthracene was the same as for 2,3-dimethylanthracene above. Treatment of 2,3-dichloroanthracene with *trans*-1,2-dichloroethene as above gave colorless crystals of **14** (86%, mp 179–180°). ^1H NMR analysis ($CDCl_3$) confirmed the structure (δ 4.12, H-1, 4; 4.30, H-7, 8).

Anal. Calcd for $C_{16}H_{10}Cl_4$: C, 55.85; H, 2.93. Found: C, 55.72; H, 2.83.

Dehalogenation of 14 to 10,11-Dichlorodibenzobicyclo[2.2.2]octatriene (12). Treatment of **14** in the same manner as **13** above resulted in **12** (90%, mp 227–228°). ^1H NMR analysis agreed with the assigned structure (δ 5.05, H-1, 4).

Anal. Calcd for $C_{16}H_{10}Cl_2$: C, 70.35; H, 3.69. Found: C, 70.13; H, 3.76.

Addition of Bromine to 11. The olefin **11** (348 mg, 1.5 mmol) was dissolved in 50 ml of methylene chloride. A solution of bromine (240 mg, 1.5 mmol) in 3 ml of CCl_4 was added dropwise with stirring in the dark over a 10-min period. The pale yellow solution was stirred for 10 min after the addition was completed. Sodium acetate (126 mg, 1.54 mmol) and 25 ml of glacial acetic acid were added, and the solution was heated on the steam bath until the chlorinated solvents were removed. The solution was then heated at reflux for 6 hr. The reaction mixture was poured into 25 ml of water and extracted with chloroform. The chloroform solution was washed with water and then neutralized with sodium bicarbonate. The chloroform was evaporated leaving a pale yellow oil containing by ^1H NMR analysis 90% *syn*-8-bromo-14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate and *syn*-8-bromo-10,11-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate and 10% of their endo epimers. The oil was dissolved in 25 ml of anhydrous ether, and excess $LiAlH_4$ was added. The reaction mixture was stirred overnight. Water was then added dropwise until the excess $LiAlH_4$ was consumed, and magnesium sulfate was added. The ether solution was filtered and the reaction flask was rinsed with ether. Evaporation of the solvent left 459 mg (93%) of a colorless oil shown to be a mixture of 90% *syn*-8-bromo-14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol and *syn*-8-bromo-10,11-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol with 10% of their endo epimers. The oil was dissolved in 5 ml of benzene, 5 ml of 0.33 *M* solution of sodium dichromate in acetic acid was added, and the solution was heated for 5 min on a steam bath, forming a dark green solution. Water was added, and the solution was extracted with benzene. The benzene solution was washed with water until the green color was removed. Evaporation of the benzene gave 417 mg (85.5% overall) of a pale yellow oil shown by ^1H NMR analysis to be the ketones *syn*-8-bromo-14,15-dimethyl-4-dibenzobicyclo[3.2.1]octadienone and *syn*-8-bromo-10,11-dimethyl-4-dibenzobicyclo[3.2.1]octadienone in a 2.1:1 ratio.

Preparation of the Bromine Derivatives of 11. Bromine was added to **11** as described above. The solvent was evaporated leaving a pale yellow oil, which was then dissolved in petroleum ether

(bp 85–100°). The dibromide **30** (***endo*-4-*syn*-8-dibromo-14,15-dimethyldibenzobicyclo[3.2.1]octadiene**) crystallized upon concentration of the solution: mp 150–151°; ^{1}H NMR (CCl_4) δ 3.79 (H-1), 5.80 (H-4), 3.57 (H-5), 4.63 (H-8), $J_{1,8}$ = 4.5, $J_{4,5}$ = 4.5 Hz.

Anal. Calcd for $C_{18}H_{16}Br_2$: C, 55.13; H, 4.11. Found: C, 55.46; H, 4.05.

Repeated crystallization of **30** and concentration of the mother liquor produced a small amount of **31** (***endo*-4-*syn*-8-dibromo-10,11-dimethyldibenzobicyclo[3.2.1]octadiene**), mp 154–157°, identified by the difference in the chemical shift for the C-8 proton: a mixture melting point with **30** was depressed; ^{1}H NMR (CCl_4) δ 3.79 (H-1), 5.80 (H-4), 3.57 (H-5), 4.68 (H-8), $J_{1,8}$ = 4.5, $J_{4,5}$ = 4.5 Hz.

Anal. Found: C, 55.28; H, 4.16.

Dibromide **30** was treated with 1 equiv of AgOAc in refluxing acetic acid for 4 hr. The reaction mixture was cooled, filtered, poured into an equal volume of water, and neutralized with aqueous $NaHCO_3$. Extraction with chloroform, followed by filtration of the chloroform solution through $MgSO_4$ and evaporation of the solvent under a stream of nitrogen, left a colorless oil, which crystallized upon dissolution in aqueous ethanol and standing. Recrystallization from ethanol gave ***syn*-8-bromo-14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate:** mp 139–141°; ^{1}H NMR (CCl_4) δ 3.90 (H-1), 5.58 (H-4), 3.55 (H-5), 4.63 (H-8), $J_{1,8}$ = 3.8, $J_{4,5}$ = 1.4 Hz.

Anal. Calcd for $C_{20}H_{19}O_2Br$: C, 64.70; H, 5.15. Found: C, 64.89; H, 5.17.

$LiAlH_4$ reduction as described above gave ***syn*-8-bromo-14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol:** mp 173.5–175° (recrystallized from ethanol); ^{1}H NMR (CCl_4) δ 3.89 (H-1), 4.23 (H-4), 3.53 (H-5), 4.73 (H-8), $J_{1,8}$ = 4.4 Hz.

Anal. Calcd for $C_{18}H_{17}OBr$: C, 65.67; H, 5.20. Found: C, 65.49; H, 5.16.

Oxidation was carried out in the manner described above. Crystallization from EtOH gave a compound which was identified from its ^{1}H NMR spectrum as ***syn*-8-bromo-14,15-dimethyl-4-dibenzobicyclo[3.2.1]octadienone,** mp 171–172°, thus confirming the structure of **30**: ^{1}H NMR (CCl_4) δ 3.96 (H-1), 4.13 (H-5), 5.03 (H-8), $J_{1,8}$ = 4.6 Hz.

Anal. Calcd for $C_{18}H_{15}OBr$: C, 66.01; H, 4.62. Found: C, 66.23; H, 4.51.

Fractional crystallization (EtOH) of the ketone mixture from the product ratio determinations produced ***syn*-8-bromo-10,11-dimethyl-4-dibenzobicyclo[3.2.1]octadienone:** mp 185–188°; ^{1}H NMR (CCl_4) δ 3.96 (H-1), 4.13 (H-5), 4.98 (H-8), $J_{1,8}$ = 4.6 Hz.

Anal. Found: C, 66.16; H, 4.72.

$LiAlH_4$ reduction of this ketone gave ***syn*-8-bromo-10,11-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol:** mp 146–148°; ^{1}H NMR (CCl_4) δ 3.89 (H-1), 4.23 (H-4), 3.53 (H-5), 4.73 (H-8), $J_{1,8}$ = 4.4 Hz.

Anal. Calcd for $C_{18}H_{17}OBr$: C, 65.67; H, 5.20. Found: C, 65.45; H, 5.24.

Acetylation of this alcohol in a 10:1 acetic anhydride–pyridine solution on a steam bath overnight gave the corresponding exo acetate, which after work-up and recrystallization from aqueous ethanol melted at 128–129°: ^{1}H NMR (CCl_4) δ 3.90 (H-1), 5.58 (H-4), 3.55 (H-5), 4.63 (H-8), $J_{1,8}$ = 3.8, $J_{4,5}$ = 1.4 Hz.

Anal. Found: C, 64.70; H, 5.15.

Addition of Bromine to 12. The addition of bromine to **12** was accomplished quantitatively when 15 ml of a 1 *M* solution of bromine was added over a 45-min period with an addition funnel to a stirred solution of 3.57 g (13 mmol) of **12** dissolved in 50 ml of methylene chloride and shielded from the light. Removal of the solvent by rotary evaporation left a colorless oil shown by ^{1}H NMR analysis to contain 53% *exo*-4-*syn*-8-dibromo-10,11-dichlorodibenzobicyclo[3.2.1]octadiene (*exo*-**33**), 13% *exo*-4-*syn*-8-dibromo-14,15-dichlorodibenzobicyclo[3.2.1]octadiene (*exo*-**32**), 22% *endo*-4-*syn*-8-dibromo-10,11-dichlorodibenzobicyclo[3.2.1]octadiene (*endo*-**33**), and 11% *endo*-4-*syn*-8-dibromo-14,15-dichlorodibenzobicyclo[3.2.1]octadiene (*endo*-**32**). These percentages were obtained upon expansion of the ^{1}H NMR spectrum of the exo and endo protons at C-4 with the HA-100 spectrometer. Fractional crystallization from petroleum ether (bp 85–100°) separated the four isomers.

***exo*-32:** mp 165–170°; ^{1}H NMR ($CDCl_3$) δ 4.00 (H-1), 5.21 (H-4), 3.88 (H-5), 4.81 (H-8), $J_{1,8}$ = 4.5 Hz.

Anal. Calcd for $C_{16}H_{10}Cl_2Br_2$: C, 44.38; H, 2.33. Found: C, 44.40; H, 2.15.

***endo*-32:** mp 156–157°; ^{1}H NMR ($CDCl_3$) δ 4.00 (H-1), 5.90 (H-4), 3.62 (H-5), 4.75 (H-8), $J_{1,8}$ = 5.0, $J_{4,5}$ = 5.0 Hz.

Anal. Found: C, 44.46; H, 2.29.

***exo*-33:** mp 178–182°; ^{1}H NMR ($CDCl_3$) δ 4.00 (H-1), 5.15 (H-4), 3.88 (H-5), 4.83 (H-8), $J_{1,8}$ = 4.5 Hz.

Anal. Found: C, 44.09; H, 2.32.

***endo*-33:** mp 140–160°; ^{1}H NMR ($CDCl_3$) δ 4.00 (H-1), 5.82 (H-4), 3.62 (H-5), 4.76 (H-8), $J_{1,8}$ = 5.0, $J_{4,5}$ = 5.00 Hz.

Anal. Found: C, 44.24; H, 2.30.

Each of the four dibromides was subjected to the reactions used for the structure proof of and the preparation of analytical samples from **30** above. The bromides of **33** were acetolyzed to ***syn*-8-bromo-10,11-dichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate:** mp 141–146°; ^{1}H NMR ($CDCl_3$) δ 4.05 (H-1), 5.67 (H-4), 3.74 (H-5), 4.78 (H-8), $J_{1,8}$ = 4.5 Hz.

Anal. Calcd for $C_{18}H_{13}O_2Cl_2Br$: C, 52.46; H, 3.18. Found: C, 52.34; H, 3.14.

Reduction of the acetate gave ***syn*-8-bromo-10,11-dichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol:** mp 172–173°; ^{1}H NMR ($CDCl_3$) δ 4.03 (H-1), 4.44 (H-4), 3.65 (H-5), 4.86 (H-8), $J_{1,8}$ = 4.2 Hz.

Anal. Calcd for $C_{16}H_{11}OCl_2Br$: C, 51.93; H, 3.00. Found: C, 51.76; H, 2.93.

Oxidation produced ***syn*-8-bromo-10,11-dichloro-4-dibenzobicyclo[3.2.1]octadienone:** mp 200–201°; ^{1}H NMR ($CDCl_3$) δ 4.31 (H-1), 4.21 (H-5), 5.17 (H-8), $J_{1,8}$ = 5.0 Hz.

Anal. Calcd for $C_{16}H_9OCl_2Br$; C, 52.21; H, 2.46. Found: C, 52.40; H, 2.48.

The bromides of **32** formed upon acetolysis ***syn*-8-bromo-14,15-dichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate:** mp 138–139°; ^{1}H NMR ($CDCl_3$) δ 3.99 (H-1), 5.71 (H-4), 3.74 (H-5), 4.76 (H-8), $J_{1,8}$ = 4.5 Hz.

Anal. Found: C, 52.51; H, 3.22.

Upon reduction the acetate was converted to ***syn*-8-bromo-14,15-dichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol:** mp 167–168°; ^{1}H NMR ($CDCl_3$) δ 3.95 (H-1), 4.48 (H-4), 3.65 (H-5), 4.89 (H-8), $J_{1,8}$ = 4.2 Hz.

Anal. Found: C, 51.86; H, 3.01.

Conversion was then accomplished to ***syn*-8-bromo-14,15-dichloro-4-dibenzobicyclo[3.2.1]octadienone:** mp 177–178°; ^{1}H NMR ($CDCl_3$) δ 4.33 (H-1), 4.23 (H-5), 5.10 (H-8), $J_{1,8}$ = 5.0 Hz.

Anal. Found: C, 52.26, H, 2.46.

Addition of Chlorine to 11. Elemental chlorine was bubbled through a sulfuric acid drying tower calibrated for known flow rate into a stirred solution of 238 mg (1.03 mmol) of **11** in 25 ml of methylene chloride until 2.0 equiv of chlorine had been delivered. The solvent was evaporated, leaving a colorless oil containing 80% of the dichlorides *endo*-4-*syn*-8-dichloro-14,15-dimethyldibenzobicyclo[3.2.1]octadiene and *endo*-4-*syn*-8-dichloro-10,11-dimethyldibenzobicyclo[3.2.1]octadiene and 20% of their exo epimers (^{1}H NMR analysis).

Conversion to the acetates, reduction to the alcohols, and oxidation to the ketones was accomplished by the procedure described above for bromine addition (89% overall yield). The ketone ratio was determined by ^{1}H NMR. The chlorine derivatives of **11** were isolated by fractional crystallization of the product mixtures. The following compounds were prepared in the course of this work.

***endo*-4-*syn*-8-Dichloro-14,15-dimethyldibenzobicyclo[3.2.1]octadiene:** mp 137–138°; ^{1}H NMR (CCl_4) δ 3.78 (H-1), 5.58 (H-4), 3.50 (H-5), 4.63 (H-8), $J_{1,8}$ = 4.5, $J_{4,5}$ = 5.0 Hz.

Anal. Calcd for $C_{18}H_{16}Cl_2$: C, 71.30; H, 5.32. Found: C, 71.03; H, 5.31.

***endo*-4-*syn*-8-Dichloro-10,11-dimethyldibenzobicyclo[3.2.1]octadiene:** mp 133–140°; ^{1}H NMR (CCl_4) δ 3.78 (H-1), 5.58 (H-4), 3.50 (H-5), 4.67 (H-8), $J_{1,8}$ = 4.5, $J_{4,5}$ = 5.0 Hz.

Anal. Found: C, 71.36; H, 5.33.

***syn*-8-Chloro-14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]-octadienol acetate:** mp 139–140°; ^{1}H NMR (CCl_4) δ 3.90 (H-1), 5.65 (H-4), 3.57 (H-5), 4.63 (H-8), $J_{1,8}$ = 5.0 Hz.

Anal. Calcd for $C_{20}H_{19}O_2Cl$: C, 73.50; H, 5.86. Found: C, 73.49; H, 5.91.

***syn*-8-Chloro-10,11-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]-octadienol acetate:** mp 149–149.5°; ^{1}H NMR (CCl_4) δ 3.90 (H-1), 5.65 (H-4), 3.57 (H-5), 4.63 (H-8), $J_{1,8}$ = 5.0 Hz.

Anal. Found: C, 73.45; H, 5.86.

***syn*-8-Chloro-14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]-octadienol:** mp 184–185°; ^{1}H NMR (CCl_4) δ 3.87 (H-1), 4.37 (H-4), 3.48 (H-5), 4.72 (H-8), $J_{1,8}$ = 4.0 Hz.

Anal. Calcd for $C_{18}H_{17}OCl$: C, 75.92; H, 6.17. Found: C, 75.96; H, 5.90.

***syn*-8-Chloro-10,11-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]-octadienol:** mp 158–158.5°; ^{1}H NMR (CCl_4) δ 3.87 (H-1), 4.37

(H-4), 3.48 (H-5), 4.72 (H-8), $J_{1,8}$ = 4.0 Hz.

Anal. Found: C, 76.12; H, 5.99.

***syn*-8-Chloro-14,15-dimethyl-4-dibenzobicyclo[3.2.1]octadienone:** mp 160–161°; ^{1}H NMR (CCl_4) δ 3.93 (H-1), 4.12 (H-5), 4.90 (H-8), $J_{1,8}$ = 4.4 Hz.

Anal. Calcd for $C_{18}H_{15}OCl$: C, 76.46; H, 5.35. Found: C, 76.27; H, 5.51.

***syn*-8-Chloro-10,11-dimethyl-4-dibenzobicyclo[3.2.1]octadienone:** mp 174–175°; ^{1}H NMR (CCl_4) δ 3.93 (H-1), 4.12 (H-5), 4.93 (H-8), $J_{1,8}$ = 4.4 Hz.

Anal. Found: C, 76.17; H, 5.46.

Addition of Chlorine to 12. When 229 mg (0.84 mmol) of **12** was treated under the same reaction conditions as described above, 200 mg (73% overall) of the ketones were obtained and used in the product ratio determination by ^{1}H NMR. The following compounds were prepared.

***exo*-4-*syn*-8,10,11-Tetrachlorodibenzobicyclo[3.2.1]octadiene:** mp 168–188°; ^{1}H NMR ($CDCl_3$) δ 3.97 (H-1), 4.92 (H-4), 3.77 (H-5), 4.77 (H-8), $J_{1,8}$ = 4.5 Hz.

Anal. Calcd for $C_{16}H_{10}Cl_4$: C, 55.85; H, 2.88. Found: C, 55.75; H, 2.88.

***exo*-4-*syn*-8,14,15-Tetrachlorodibenzobicyclo[3.2.1]octadiene:** mp 190.5–191.5°; ^{1}H NMR ($CDCl_3$) δ 3.97 (H-1), 4.94 (H-4), 3.77 (H-5), 4.73 (H-8), $J_{1,8}$ = 4.5 Hz.

Anal. Found: C, 56.04; H, 2.91.

***syn*-8,10,11-Trichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate:** mp 141–143°; ^{1}H NMR ($CDCl_3$) δ 4.08 (H-1), 5.72 (H-4), 3.72 (H-5), 4.77 (H-8), $J_{1,8}$ = 4.5 Hz.

Anal. Calcd for $C_{18}H_{13}O_2Cl_3$: C, 58.80; H, 3.56. Found: C, 58.92; H, 3.36.

***syn*-8,14,15-Trichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate:** mp 167–167.5°; ^{1}H NMR ($CDCl_3$) δ 4.08 (H-1), 5.73 (H-4), 3.72 (H-5), 4.75 (H-8), $J_{1,8}$ = 4.5 Hz.

Anal. Found: C, 58.69; H, 3.46.

***syn*-8,10,11-Trichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol:** mp 169–178°; ^{1}H NMR ($CDCl_3$) δ 3.97 (H-1), 4.40 (H-4), 3.63 (H-5), 4.85 (H-8), $J_{1,8}$ = 4.5 Hz.

Anal. Calcd for $C_{16}H_{11}OCl_3$: C, 59.02; H, 3.40. Found: C, 59.22; H, 3.29.

***syn*-8,14,15-Trichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol:** mp 166–167°; ^{1}H NMR ($CDCl_3$) δ 3.97 (H-1), 4.40 (H-4), 3.63 (H-5), 4.80 (H-8), $J_{1,8}$ = 4.5 Hz.

Anal. Found: C, 58.87; H, 3.30.

***syn*-8,10,11-Trichloro-4-dibenzobicyclo[3.2.1]octadienone:** mp 163–164°; ^{1}H NMR ($CDCl_3$) δ 4.17 (H-1), 4.28 (H-5), 5.12 (H-8), $J_{1,8}$ = 4.7 Hz.

Anal. Calcd for $C_{16}H_9OCl_3$: C, 59.40; H, 2.78. Found: C, 59.37; H, 2.92.

***syn*-8,14,15-Trichloro-4-dibenzobicyclo[3.2.1]octadienone:** mp 215–216°; ^{1}H NMR ($CDCl_3$) δ 4.17 (H-1), 4.28 (H-5), 5.11 (H-8), $J_{1,8}$ = 4.7 Hz.

Anal. Found: C, 59.10; H, 2.60.

Addition of Hydrogen Bromide to 11. In a two-necked flask (gas-inlet tube, Dry Ice condenser, magnetic stirrer) were placed 454 mg (1.95 mmol) of **11** and 5 ml of ether. Hydrogen bromide gas was bubbled from a lecture bottle until the volume of solution in the flask reached 15 ml. The reaction was stopped 45 min from the start of gas delivery by pouring the contents of the flask over ice. Extraction with ether, neutralization with $NaHCO_3$, and drying over $MgSO_4$ left an ether solution containing the exo bromides **34** (*exo*-4-bromo-14,15-dimethyldibenzobicyclo[3.2.1]octadiene) and **35** (*exo*-4-bromo-10,11-dimethyldibenzobicyclo[3.2.1]octadiene). Evaporation of the ether left a colorless oil, 560 mg (92%). A portion of the oil (331 mg, 1.06 mmol) was dissolved in 20 ml of acetone and water was added until the solution became cloudy. The solution was clarified with acetone and 0.5 ml of pyridine was added. The mixture was allowed to stand overnight. The acetone was removed by rotary evaporation and the contents of the flask were extracted with benzene. Evaporation of the benzene left a colorless oil which was dissolved in ether. Oxidation for 5 hr with 10 ml of the sodium dichromate solution described above gave a mixture of ketones 14,15-dimethyl-4-dibenzobicyclo[3.2.1]octadienone (**44-Me**) and 10,11-dimethyl-4-dibenzobicyclo[3.2.1]octadienone (**43-Me**) in 90% overall yield; these were used for the product ratio determination by ^{1}H NMR. The derivatives were prepared from compounds **34** and **35**, which were obtained by fractional crystallization from petroleum ether (bp 60–70°) solution of the oil obtained from HBr addition to **11**.

***exo*-34:** mp 115–116°; ^{1}H NMR ($CDCl_3$) δ 3.77 (H-1), 5.37 (H-4), 3.77 (H-5), 2.68 (H-8).

Anal. Calcd for $C_{18}H_{17}Br$: C, 69.02; H, 5.47. Found: C, 69.13; H, 5.40.

***exo*-35:** mp 107–108°; ^{1}H NMR ($CDCl_3$) δ 3.77 (H-1), 5.37 (H-4), 3.77 (H-5), 2.68 (H-8).

Anal. Found: C, 68.92; H, 5.55.

Treatment of **34** with acetone–H_2O gave 14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol, which was purified by sublimation at 130° (0.5 Torr): mp 169–170°; ^{1}H NMR ($CDCl_3$) δ 3.75 (H-1), 4.48 (H-4), 3.33 (H-5), 2.37 (H-8).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.52; H, 7.31.

Oxidation as described above gave 14,15-dimethyl-4-dibenzobicyclo[3.2.1]octadienone: mp 109–110°; ^{1}H NMR ($CDCl_3$) δ 3.97 (H-1), 4.10 (H-5), 2.71 (H-8a), 2.69 (H-8s).

10,11-Dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol: mol wt 250 (mass spectrum) (calcd 250); ^{1}H NMR ($CDCl_3$) δ 3.75 (H-1), 4.48 (H-4), 3.37 (H-5), 2.37 (H-8).

10,11-Dimethyl-4-dibenzobicyclo[3.2.1]octadienone: mol wt 248 (mass spectrum) (calcd 248); ^{1}H NMR ($CDCl_3$) δ 3.97 (H-1), 4.10 (H-5), 2.71 (H-8a), 2.69 (H-8s).

Addition of Hydrogen Bromide to 12. Under the conditions described above **12** showed no reaction with HBr. A heavy-walled Pyrex tube containing 410 mg (1.5 mmol) of **12** in 10 ml of ether was immersed in Dry Ice–acetone and hydrogen bromide gas was added until the total volume of solution was 30 ml. The tube was sealed and placed in a large Dewar flask at −30°. The tube was removed after 50 min, cooled to −70° and opened, and its contents were poured onto ice. The mixture was extracted with ether. The ethereal solution was neutralized with sodium bicarbonate. Evaporation of the ether left a colorless oil (405 mg, 93.5%) containing the bromides **37** (*exo*-4-bromo-10,11-dichlorodibenzobicyclo[3.2.1]octadiene) and **36** (*exo*-4-bromo-14,15-dichlorodibenzobicyclo[3.2.1]octadiene). Conversion to the ketones for ^{1}H NMR analysis was carried out as described above. The hydrolysis in aqueous acetone required 2 days at reflux for completion. The derivatives from this reaction were prepared from the [2.2.2] alcohols obtained in the hydroboration of **12**. Their preparation is described in the details of that reaction.

Addition of Acetyl Hypoiodite to 11. A mixture of 176 mg (0.76 mmol) of **11**, 201 mg (0.79 mmol), of iodine, and 263 mg (1.57 mmol) of AgOAc was stirred overnight in 25 ml of refluxing benzene. The solution was cooled to room temperature and filtered. Evaporation of the benzene under a stream of nitrogen left a pale yellow oil composed of 80% of the iodoacetates **22-I** (*syn*-8-iodo-14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate) and 20% of their endo epimers. The oil was dissolved in ether and excess lithium aluminum hydride was added. The mixture was stirred for 5 hr. Water was carefully added until the excess hydride had been consumed, and magnesium sulfate was added. The ether was filtered, and the reaction flask was washed with dry ether. The ether was evaporated, and the resulting oil was dissolved in dry acetone. Oxidation with 0.3 ml of Jones reagent[22] for 10 min was followed by addition of 10 ml of water. The mixture was extracted with benzene. The benzene layer was washed with water and then evaporated to give a pale yellow oil (216 mg, 76% overall) containing the two ketones in a 1:1 ratio by ^{1}H NMR analysis. The ketones were separated by chromatography on Merck 71707 aluminum oxide, eluting with petroleum ether (bp 60–70°) and 20% benzene. The alcohols and acetates were prepared from the two ketones by $LiAlH_4$ reduction, then acetylation in acetic anhydride and pyridine as described. Each was recrystallized from EtOH.

22-I: mp 154–155°; ^{1}H NMR ($CDCl_3$) δ 4.00 (H-1), 5.75 (H-4), 3.72 (H-5), 4.78 (H-8), $J_{1,8}$ = 4.4 Hz.

Anal. Calcd for $C_{20}H_{19}O_2I$: C, 57.43; H, 4.58. Found: C, 57.62; H, 4.47.

23-I: mp 147–148°; ^{1}H NMR ($CDCl_3$) δ 4.00 (H-1), 5.75 (H-4), 3.72 (H-5), 4.78 (H-8), $J_{1,8}$ = 4.4 Hz.

Anal. Found: C, 57.30; H, 4.61.

***syn*-8-Iodo-14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol:** mp 180–182°; ^{1}H NMR ($CDCl_3$) δ 4.02 (H-1), 4.57 (H-4), 3.69 (H-5), 4.85 (H-8), $J_{1,8}$ = 4.5 Hz.

Anal. Calcd for $C_{18}H_{17}OI$: C, 57.46; H, 4.55. Found: C, 57.37; H, 4.61.

***syn*-8-Iodo-10,11-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol:** mp 184.5–185°; ^{1}H NMR ($CDCl_3$) δ 4.02 (H-1), 4.57 (H-4), 3.69 (H-5), 4.85 (H-8), $J_{1,8}$ = 4.5 Hz.

Anal. Found: C, 57.40; H, 4.61.

***syn*-8-Iodo-14,15-dimethyl-4-dibenzobicyclo[3.2.1]octadienone:** mp 182–183°; ^{1}H NMR ($CDCl_3$) δ 4.13 (H-1), 3.97 (H-5), 5.00 (H-8), $J_{1,8}$ = 4.5 Hz.

Anal. Calcd for $C_{18}H_{15}OI$: C, 57.77; H, 4.04. Found: C, 57.50; H, 3.92.

***syn*-8-Iodo-10,11-dimethyl-4-dibenzobicyclo[3.2.1]octadienone:** mp 188–189°; ^1H NMR ($CDCl_3$) δ 4.13 (H-1), 3.97 (H-5), 5.03 (H-8), $J_{1,8}$ = 4.5 Hz.

Anal. Found: C, 57.93; H, 3.89.

Addition of Acetic Acid to 11. Into a 1.25 × 15 cm Pyrex tube were placed 1.04 g (4.5 mmol) of **11** and 5 ml of 0.5 *M* H_2SO_4 in HOAc. The tube was cooled, sealed, and then placed in a steam bath at 94° for 5 hr. The tube was cooled and opened, and its contents were poured into 5 ml of water. The mixture was extracted with CCl_4 which was then washed with water and neutralized with sodium bicarbonate. The carbon tetrachloride was removed by rotary evaporation, leaving 1.07 g (81.5%) of a brown oil which was shown by its ^1H NMR spectrum to be a 2:1 mixture of **15**-OAc and **16**-OAc. Analysis was by expansion and integration of the acetate methyl peak by HA-100 NMR. The peaks were also cut from the spectrum and weighed to determine the product ratio. The reaction was followed over a 3-day period and no significant change in the product ratio was detected.

Reduction of the acetate mixture with $LiAlH_4$ gave 915 mg (81.5%) of an oil, which contained the alcohols **15**-OH (10,11-dimethyl-*anti*-7-dibenzobicyclo[2.2.2]octadienol) and **16**-OH (10,11-dimethyl-*syn*-7-dibenzobicyclo[2.2.2]octadienol). Some separation of this mixture was effected by chromatography on silica gel (PF_{254} with $CaSO_4$), developing with 10% ether in benzene three times. The band with the smaller R_f value was removed and extracted with CH_2Cl_2, leaving a colorless oil upon evaporation of the solvent. A portion of the oil was acetylated and after work-up left an oil shown by ^1H NMR spectral analysis to be the acetate **15**-OAc. The remaining portion of the alcohol was converted to the *p*-toluenesulfonate using *p*-toluenesulfonyl chloride in dry pyridine for 2 days at room temperature. The solution was poured into water and extracted with ether. The ether was washed with cold dilute HCl, neutralized with aqueous $NaHCO_3$, and filtered through $MgSO_4$. The ether was evaporated and the oil which remained was dissolved in acetic acid containing 1 equiv of NaOAc and heated at reflux for 2 days. The solution was then poured into an equal amount of water and extracted with $CHCl_3$. After washing with $NaHCO_3$, the $CHCl_3$ was evaporated, giving a colorless oil which was then dissolved in ether. Excess lithium aluminum hydride was added to give the alcohol, which was converted with Jones reagent[22] to the ketone **44**-Me, identified by its ^1H NMR spectrum.

The analytical samples were prepared by recrystallizing the alcohols obtained in the TLC separation from CCl_4. Acetylation of the alcohols in acetic anhydride and pyridine gave the acetates **15**- and **16**-OAc, which were then recrystallized from EtOH–H_2O.

15-OAc: mp 140–141°; ^1H NMR ($CDCl_3$) δ 4.47 (H-1), 4.15 (H-4), 5.07 (H-7), 2.23 (H-8s), 1.45 (H-8a), 2.17 (CH_3), 1.83 (OAc).

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 81.83; H, 6.85.

16-OAc: mp 132–133°; ^1H NMR ($CDCl_3$) δ 4.47 (H-1), 4.15 (H-4), 5.07 (H-7), 2.23 (H-8a), 1.45 (H-8s), 2.20 (CH_3), 1.86 (OAc).

Anal. Found: C, 81.94; H, 7.02.

15-OH: mp 188–189°; ^1H NMR ($CDCl_3$) δ 4.07 (H-1), 4.10 (H-4), 4.00 (H-7), 2.20 (H-8s), 1.23 (H-8a).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.48; H, 7.40.

16-OH: mp 230–231°; ^1H NMR ($CDCl_3$) δ 4.07 (H-1), 4.10 (H-4), 4.00 (H-7), 2.20 (H-8a), 1.23 (H-8s).

Anal. Found: C, 86.23; H, 7.32.

Addition of Acetic Acid to 12. The addition of HOAc to **12** was carried out in 0.5 *M* H_2SO_4 in HOAc at 110° in a sealed tube in an oil bath. The work-up was the same as in the addition to **11**, resulting in mixtures of the acetates **18**-OAc (10,11-dichloro-*syn*-7-dibenzobicyclo[2.2.2]octadienol acetate) and **17**-OAc (10,11-dichloro-*anti*-7-dibenzobicyclo[2.2.2]octadienol acetate). Reduction of the acetates to the alcohols was the same as above. TLC separation under the same conditions was possible to some extent. The band with the larger R_f value was removed and identified as **18**-OH in the same manner as **15**-OH. The addition of HOAc was followed for 3 days and the ratio of **18**-OAc to **17**-OAc decreased from over 2.5:1 to 1.5:1.[5]

17-OAc: mp 109–110°; ^1H NMR ($CDCl_3$) δ 4.47 (H-1), 4.17 (H-4), 5.02 (H-7), 2.22 (H-8s), 1.45 (H-8a), 1.85 (OAc).

Anal. Calcd for $C_{18}H_{14}O_2Cl_2$: C, 64.88; H, 4.23. Found: C, 64.70; H, 4.26.

18-OAc: mp 138.5–139°; ^1H NMR ($CDCl_3$) δ 4.47 (H-1), 4.17 (H-4), 4.97 (H-7), 2.22 (H-8a), 1.45 (H-8s), 1.88 (OAc).

Anal. Found: C, 65.01; H, 4.28.

17-OH: mp 191–193°; ^1H NMR ($CDCl_3$) δ 4.30 (H-1), 4.20 (H-4), 4.25 (H-7), 2.33 (H-8s), 1.37 (H-8a).

Anal. Calcd for $C_{16}H_{12}OCl_2$: C, 66.00; H, 4.15. Found: C, 65.84; H, 4.03.

18-OH: mp 206–207°; ^1H NMR ($CDCl_3$) δ 4.30 (H-1), 4.20 (H-4), 4.25 (H-7), 2.33 (H-8a), 1.37 (H-8s).

Anal. Found: C, 65.93; H, 4.19.

Addition of Mercuric Acetate to 11. Compound **11** (116 mg, 0.5 mmol) and 162 mg (0.5 mmol) of mercuric acetate were stirred in 20 ml of acetic acid for 4 hr at room temperature. The acetic acid was removed by rotary evaporation and 10 mg of sodium borohydride was added to the colorless oil in the flask. The mixture was stirred for 5 min in 5 ml of tetrahydrofuran and then 3 ml of 2 *M* NaOH was added. Stirring was continued for another 1 min. Water was added (10 ml) and the solution was extracted with $CHCl_3$. The $CHCl_3$ was evaporated to give 136 mg (93%) of an oil shown by its ^1H NMR spectrum to be a 1:1 mixture of the acetates **15**-OAc and **16**-OAc.

Hydroboration of 11. Hydroboration of **11** occurred when 232 mg (1.0 mmol) of **11** and 20 mg (0.62 mmol) of sodium borohydride were dissolved in 10 ml of dry diglyme and a solution of 100 mg of boron trifluoride etherate in 5 ml of diglyme was added dropwise with stirring. After addition had been completed the solution was stirred for 2 hr. Ten milliliters of 6 *M* NaOH was added very slowly and then 10 ml of 30% H_2O_2 was added. Stirring was continued for 15 min. The mixture was extracted with benzene and the benzene was evaporated, leaving a colorless oil which was acetylated in acetic anhydride and pyridine overnight at room temperature. Work-up as usual gave 251 mg (86% overall) of the acetates **15**-OAc and **16**-OAc in a 1:1 ratio by ^1H NMR analysis.

Hydroboration of 12. Hydroboration of **12** was carried out in the same way as that of **11**. In this case 273 mg (1.0 mmol) of **12** after hydroboration and acetylation yielded 249 mg (75%) of the acetates **17**-OAc and **18**-OAc in a 1:1 ratio by ^1H NMR analysis.

The alcohols **17**-OH and **18**-OH were separated by TLC. Formation of their *p*-toluenesulfonates and rearrangement to the [3.2.1] acetates followed by $LiAlH_4$ reduction and oxidation to ketones was the same as described above. The ketones were purified by crystallization from EtOH. PBr_3 reaction with the [3.2.1] alcohols gave the bromides **36**-Br and **37**-Br.

37-Br: ^1H NMR ($CDCl_3$) δ 3.83 (H-1), 5.26 (H-4), 3.83 (H-5), 2.67 (H-8), $J_{4,5}$ = 2.0 Hz; mol wt (mass spectrum) 354 (calcd 354).

36-Br: mp 182–184°; ^1H NMR ($CDCl_3$) δ 3.83 (H-1), 5.37 (H-4), 3.83 (H-5), 2.67 (H-8), $J_{4,5}$ = 2.0 Hz; mol wt (mass spectrum) 354 (calcd 354).

10,11-Dichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol (*exo*-37-OH): mp 116–117°; ^1H NMR ($CDCl_3$) δ 3.85 (H-1), 4.55 (H-4), 3.47 (H-5), 2.58 (H-8), $J_{4,5}$ = 2.0 Hz.

Anal. Calcd for $C_{16}H_{12}OCl_2$: C, 66.00; H, 4.15. Found: C, 65.73; H, 4.26.

14,15-Dichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol (*exo*-36-OH): mp 127–131°; ^1H NMR ($CDCl_3$) δ 3.85 (H-1), 4.60 (H-4), 3.47 (H-5), 2.58 (H-8), $J_{4,5}$ = 2.0 Hz.

Anal. Found: C, 65.72; H, 4.24.

10,11-Dichloro-4-dibenzobicyclo[3.2.1]octadienone (43-Cl): mp 135–137°; ^1H NMR ($CDCl_3$) δ 4.02 (H-1), 4.12 (H-5), 2.78 (H-8).

Anal. Calcd for $C_{16}H_{10}OCl_2$: C, 66.46; H, 3.49. Found: C, 66.43; H, 3.49.

14,15-Dichloro-4-dibenzobicyclo[3.2.1]octadienone (44-Cl): mp 178.5–180°; ^1H NMR ($CDCl_3$) δ 4.02 (H-1), 4.12 (H-5), 2.78 (H-8).

Anal. Found: C, 66.49; H, 3.36.

Silver Acetate Assisted Solvolysis of 13. Trans dichloride **13** (613 mg, 2.02 mmol) and 341 mg (2.04 mmol) of silver acetate were stirred for 4 hr in 25 ml of refluxing glacial acetic acid. The solution was cooled and the silver chloride was removed by filtration. The solution was poured into 25 ml of water and extracted with $CHCl_3$. The $CHCl_3$ solution was washed with water and dilute $NaHCO_3$. Evaporation of the $CHCl_3$ gave a colorless oil containing 33% unreacted **13** (^1H NMR analysis). The oil was dissolved in 25 ml of ether and excess $LiAlH_4$ was added. The mixture was stirred for 6 hr and water was carefully dropped in until the excess hydride had been consumed. The ether solution was dried over $MgSO_4$ and then filtered. The reaction flask was carefully rinsed with dry ether. Evaporation of the ether left 601 mg (94% based on initial percent reaction) of a colorless oil containing alcohols corresponding to **39** and **40** and the unreacted **13** by ^1H NMR analysis. Oxidation of this mixture by the Jones procedure gave 172 mg of a

mixture of the ketones (90% overall yield) which was analyzed by ^{1}H NMR. The major isomer of the two mixtures could be crystallized from EtOH solutions of the reaction mixtures. The minor isomers were not isolated, and their ^{1}H NMR spectra are taken from the mixtures with the other isomer. The mixture of alcohols was separated from the unreacted **13** by chromatography on Merck 71707 alumina. The trans dichloride was eluted with petroleum ether (bp 60–70°) and the alcohols were removed with benzene.

***anti*-8-Chloro-14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]-octadienol:** mp 217–218°; ^{1}H NMR (CCl_4) δ 3.94 (H-1), 4.65 (H-4), 3.47 (H-5), 4.83 (H-8), $J_{4,5}$ = 2.0 Hz.

Anal. Calcd for $C_{18}H_{17}OCl$: C, 75.92; H, 6.17. Found: C, 76.09; H, 5.94.

***anti*-8-Chloro-10,11-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]-octadienol:** ^{1}H NMR (CCl_4) δ 3.94 (H-1), 4.65 (H-4), 3.47 (H-5), 4.83 (H-8), $J_{4,5}$ = 2.0 Hz.

***anti*-8-Chloro-14,15-dimethyl-4-dibenzobicyclo[3.2.1]octadienone:** mp 172–173°; ^{1}H NMR (CCl_4) δ 4.07 (H-1), 4.23 (H-5), 4.88 (H-8).

Anal. Calcd for $C_{18}H_{15}OCl$: C, 76.46; H, 5.35. Found: C, 76.32; H, 5.43.

***anti*-8-Chloro-10,11-dimethyl-4-dibenzobicyclo[3.2.1]octadienone:** ^{1}H NMR (CCl_4) δ 4.07 (H-1), 4.23 (H-5), 4.88 (H-8).

Silver Acetate Assisted Acetolysis of 14. Solvolysis of 688 mg (2.00 mmol) of **14** with 335 mg (2.00 mmol) of silver acetate in 15 ml of refluxing glacial acetic acid with stirring for 7 days was 75% complete by ^{1}H NMR analysis after work-up as described for **13**. The product was a colorless oil, 743 mg. ^{1}H NMR analysis of the acetates was used in determining the ρ values. The acetates were converted to the alcohols and ketones in the same procedure used for the derivatives of **13** in order to prove the structural assignments (overall yield 80%). The major isomer could be crystallized from an ethanol solution of the mixture obtained at each stage of the reaction sequence. The minor isomers were not separated, and ^{1}H NMR data are taken from mixtures.

***anti*-8,10,11-Trichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate:** mp 199.5–200°; ^{1}H NMR ($CDCl_3$) δ 4.10 (H-1), 5.90 (H-4), 3.89 (H-5), 4.92 (H-8), $J_{4,5}$ = 2.5 Hz.

Anal. Calcd for $C_{18}H_{13}O_2Cl_3$: C, 58.80; H, 3.56. Found: C, 58.53; H, 3.48.

***anti*-8,14,15-Trichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate:** ^{1}H NMR ($CDCl_3$) δ 4.10 (H-1), 5.95 (H-4), 3.89 (H-5), 4.98 (H-8).

***anti*-8,10,11-Trichloro-4-dibenzobicyclo[3.2.1]octadienone:** mp 204–205°; ^{1}H NMR ($CDCl_3$) δ 4.25 (H-1), 4.13 (H-5), 4.83 (H-8).

Anal. Calcd for $C_{16}H_9OCl_3$: C, 59.40; H, 2.78. Found: C, 59.21; H, 2.89.

***anti*-8,14,15-Trichloro-4-dibenzobicyclo[3.2.1]octadienone:** ^{1}H NMR ($CDCl_3$) δ 4.25 (H-1), 4.13 (H-5), 4.88 (H-8).

Addition of Benzenesulfenyl Chloride to 11. Benzenesulfenyl chloride (1.96 g, 13.6 mmol) in 50 ml of CCl_4 was added dropwise to 2.90 g (12.5 mmol) of **11** stirring in 50 ml of CCl_4. The orange color of the reagent disappeared instantly. Upon evaporation of the CCl_4 a pale yellow oil remained, 4.67 g (96%). The oil was dissolved in petroleum ether (bp 85–100°) and the two trans isomers **21** and **20** could be separated by fractional crystallization. Approximately equal amounts of each were obtained in this way.

In another reaction the mixture of trans isomers from the addition (476 mg, 1.27 mmol) and 227 mg (1.35 mmol) of AgOAc was refluxed with stirring in 25 ml of glacial acetic acid for 43 hr. Work-up as before, reduction with $LiAlH_4$, and oxidation gave a 97% yield of a mixture of syn and anti [3.2.1] ketones. When **20** was subjected to the reaction sequence above only *anti*-8-thiophenoxy-14,15-dimethyl-4-dibenzobicyclo[3.2.1]octadienone was formed, based on the ^{1}H NMR spectrum.

***anti*-8-Chloro-*syn*-7-thiophenoxy-10,11-dimethyldibenzobicyclo[2.2.2]octatriene (20):** mp 174–175°; ^{1}H NMR ($CDCl_3$) δ 4.23 (H-1), 4.12 (H-5), 3.95 (H-7), 3.42 (H-8).

Anal. Calcd for $C_{24}H_{21}SCl$: C, 76.46; H, 5.63. Found: C, 76.61; H, 5.77.

***syn*-8-Chloro-*anti*-7-thiophenoxy-10,11-dimethyldibenzobicyclo[2.2.2]octadiene (21):** mp 152–153.5°; ^{1}H NMR ($CDCl_3$) δ 4.23 (H-1), 4.12 (H-5), 3.95 (H-7), 3.42 (H-8).

Anal. Found: C, 76.26; H, 5.85.

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Registry No.—**11,** 55089-35-5; **12,** 55089-36-6; **13,** 55124-45-3; **14,** 55089-37-7; **15**-OAc, 55089-38-8; **15**-OH, 55089-39-9; **16**-OAc, 55123-06-3; **16**-OH, 55123-07-4; **17**-OAc, 55089-40-2; 17-OH, 55089-41-3; **18**-OAc, 55123-08-5; **18**-OH, 55123-09-6; **20,** 55089-42-4; **21,** 55123-10-9; **22**-I, 55089-43-5; **23**-I, 55089-44-6; **30,** 55089-45-7; **31,** 55089-46-8; *exo*-**32,** 55089-47-9; *endo*-**32,** 55123-11-0; *exo*-**33,** 55089-48-0; *endo*-**33,** 55123-12-1; *exo*-**34,** 55089-49-1; *exo*-**35,** 55089-50-4; *exo*-**36**-Br, 55089-51-5; *exo*-**36**-OH, 55089-52-6; *exo*-**37**-Br, 55089-53-7; *exo*-**37**-OH, 55089-54-8; **43**-Cl, 55089-55-9; **44**-Cl, 55089-56-0; *syn*-8-bromo-14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate, 55089-57-1; *syn*-8-bromo-14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol, 55089-58-2; *syn*-8-bromo-14,15-dimethyl-4-dibenzobicyclo[3.2.1]octadienone, 55089-59-3; *syn*-8-bromo-10,11-dimethyl-4-dibenzobicyclo[3.2.1]octadienone, 55089-60-6; *syn*-8-bromo-10,11-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol, 55089-61-7; *syn*-8-bromo-10,11-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate, 55089-62-8; *syn*-8-bromo-10,11-dichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate, 55089-63-9; *syn*-8-bromo-10,11-dichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol, 55089-64-0; *syn*-8-bromo-10,11-dichloro-4-dibenzobicyclo[3.2.1]octadienone, 55089-65-1; *syn*-8-bromo-14,15-dichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate, 55089-66-2; *syn*-8-bromo-14,15-dichloro-*exo*-4-dibenzobicyclo-[3.2.1]octadienol, 55089-67-3; *syn*-8-bromo-14,15-dichloro-4-dibenzobicyclo[3.2.1]octadienone, 55089-68-4; *endo*-**4**-*syn*-8-dichloro-14,15-dimethyldibenzobicyclo[3.2.1]octadiene, 55089-69-5; *endo*-4-*syn*-8-dichloro-10,11-dimethyldibenzobicyclo[3.2.1]octadiene, 55124-04-4; *syn*-8-chloro-14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate, 55089-70-8; *syn*-8-chloro-10,11-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate, 55089-71-9; *syn*-8-chloro-14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol, 55089-72-0; *syn*-8-chloro-10,11-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol, 55089-73-1; *syn*-8-chloro-14,15-dimethyl-4-dibenzobicyclo[3.2.1]octadienone, 55089-74-2; *syn*-8-chloro-10,11-dimethyl-4-dibenzobicyclo[3.2.1]octadienone, 55089-75-3; *exo*-4-*syn*-8,10,11-tetrachlorodibenzobicyclo[3.2.1]octadiene, 55089-76-4; *exo*-4-*syn*-8,14,15-tetrachlorodibenzobicyclo[3.2.1]octadiene, 55089-77-5; *syn*-8,10,11-trichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate, 55089-78-6; *syn*-8,14,15-trichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate, 55089-79-7; *syn*-8,10,11-trichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol, 55089-80-0; *syn*-8,14,15-trichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol, 55089-81-1; *syn*-8,10,11-trichloro-4-dibenzobicyclo[3.2.1]octadiene, 55089-82-2; *syn*-8,14,15-trichloro-4-dibenzobicyclo[3.2.1]octadienone, 55089-83-3; 14,15-dimethyl-*exo*-4-dibenzobicyclo-[3.2.1]octadienol, 55089-84-4; 14,15-dimethyl-4-dibenzobicyclo-[3.2.1]octadienone, 55089-85-5; 10,11-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol, 55089-86-6; 10,11-dimethyl-4-dibenzobicyclo[3.2.1]octadienone, 55089-87-7; *syn*-8-iodo-14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol, 55089-88-8; *syn*-8-iodo-10,11-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol, 55089-89-9; *syn*-8-iodo-14,15-dimethyl-4-dibenzobicyclo[3.2.1]octadienone, 55089-90-2; *syn*-8-iodo-10,11-dimethyl-4-dibenzobicyclo-[3.2.1]octadienone, 55089-91-3; *anti*-8-chloro-14,15-dimethyl-*exo*-4-dibenzobicyclo[3.2.1]octadienol, 55123-13-2; *anti*-8-chloro-10,11-dimethyl-exo-4-dibenzobicyclo[3.2.1]octadienol, 55123-14-3; *anti*-8-chloro-14,15-dimethyl-4-dibenzobicyclo[3.2.1]octadienone, 55123-15-4; *anti*-8-chloro-10,11-dimethyl-4-dibenzobicyclo[3.2.1]-octadienone, 55123-16-5; *anti*-8,10,11-trichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate, 55123-17-6; *anti*-8,14,15-trichloro-*exo*-4-dibenzobicyclo[3.2.1]octadienol acetate, 55123-18-7; anti-8,10,11-trichloro-4-dibenzobicyclo[3.2.1]octadienone, 55123-19-8; *anti*-8,14,15-trichloro-4-dibenzobicyclo[3.2.1]octadienone, 55123-20-1; 2,3-dimethylanthracene, 613-06-9; *trans*-1,2-dichloroethene, 156-60-5; 2,3-dichloroanthracene, 613-07-0; bromine, 7726-95-6; AgOAc, 563-63-3; chlorine, 7782-50-5; hydrogen bromide, 10035-10-6; acetyl hypoiodite, 6540-76-7; acetic acid, 64-19-7; mercuric acetate, 1600-27-7; sodium borohydride, 16940-66-2; benzenesulfenyl chloride, 931-59-9.

References and Notes

(1) Part LXXX: S. J. Cristol and R. J. Bopp, *J. Org. Chem.*, **39,** 1336 (1974).
(2) (a) S. J. Cristol and R. K. Bly, *J. Am. Chem. Soc.*, **82,** 6155 (1960); (b) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, **28,** 1374 (1963); (c) S. J. Cristol and D. D. Tanner, *J. Am. Chem. Soc.*, **86,** 3122 (1964); (d) S. J. Cristol, F. P. Parungo, and D. E. Plorde, *ibid.*, **87,** 2870 (1965); (e) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **87,** 2879 (1965).
(3) A geitonodesmic reaction has been defined[2e] as one in which a nucleophile attacks a cation at an atom neighboring the cationic center with coincident migration of the anti bond to the cationic center.
(4) (a) S. J. Cristol, R. Caple, R. M. Sequeira, and L. O. Smith, Jr., *J. Am.*

Chem. Soc., **87**, 5679 (1965); (b) S. J. Cristol and B. B. Jarvis, *ibid.*, **88**, 3091 (1966); (c) S. J. Cristol, R. J. Bopp, and A. E. Johnson, *J. Org. Chem.*, **34**, 3574 (1969).
(5) S. J. Cristol and R. J. Bopp, *J. Org. Chem.*, **39**, 1336 (1974).
(6) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972, p 265 ff.
(7) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", Elsevier, Amsterdam, 1966, p 166 ff.
(8) Reference 7, Chapters 6 and 7.
(9) R. C. Fahey and H.-J. Schneider, *J. Am. Chem. Soc.*, **90**, 4429 (1968); M.-F. Ruasse and J.-E. Dubois, *J. Org. Chem.*, **39**, 2441 (1974).
(10) Reference 7, Chapters 4 and 5.
(11) See, for example, (a) T. G. Traylor, *Acc. Chem. Res.*, **2**, 152 (1969); (b) R. D. Bach and R. F. Richter, *J. Am. Chem. Soc.*, **94**, 4747 (1972); (c) G. A. Olah and P. R. Clifford, *ibid.*, **95**, 6067 (1973); (d) R. D. Bach and R. F. Richter, *J. Org. Chem.*, **38**, 3442 (1973).
(12) (a) J. G. Traynham, G. R. Franzen, G. A. Knesel, and D. J. Northington, Jr., *J. Org. Chem.*, **32**, 3285 (1967); (b) H. C. Brown and J. H. Kawakami, *J. Am. Chem. Soc.*, **92**, 201 (1970); (c) H. C. Brown and K.-T. Liu, *ibid.*, **93**, 7335 (1971); (d) J. G. Traynham and H. H. Hsieh, *J. Org. Chem.*, **38**, 868 (1973).
(13) (a) V. I. Sokolov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1285 (1968); (b) F. R. Jensen, J. J. Miller, S. J. Cristol, and R. S. Beckley, *J. Org. Chem.*, **37**, 4341 (1972).
(14) (a) S. Bentham, P. Chamberlain, and G. H. Whitham, *Chem. Commun.*, 1528 (1970); (b) R. D. Bach and R. F. Richter, *Tetrahedron Lett.*, 4099 (1973).
(15) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).
(16) (a) H. Tanida, H. Ishitobi, and T. Irie, *J. Am. Chem. Soc.*, **90**, 2688 (1968); (b) H. Tanida, *Acc. Chem. Res.*, **1**, 239 (1968).
(17) (a) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 1901 (1968); (b) H. C. Brown and G. L. Tritle, *ibid.*, **90**, 2689 (1968).
(18) S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **30**, 1956 (1965).
(19) C. F. H. Allen and A. Bell, *Org. Synth.*, **22**, 37 (1942).
(20) E. de Barry Barnett, M. A. Matthews, and J. L. Wiltshire, *Recl. Trav. Chim. Pays-Bas*, **45**, 558 (1926).
(21) L. F. Fieser, "Experiments in Organic Chemistry", 3rd ed, D. C. Heath, Boston, Mass., 1957, p 157.
(22) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

Photochemical Transformations. XII. Photochemical Reduction of Some Dehydronorbornyl Derivatives[1]

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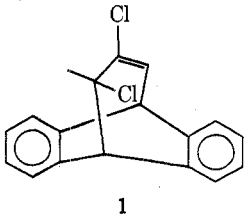
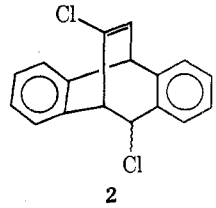
The photosensitized irradiation of exo and endo isomers of 5-chloronorbornene, 5-hydroxynorbornene, and 5-acetoxynorbornene, as well as of 5,5-dichloronorbornene, with a variety of sensitizers and solvents led to saturation of the double bond to give the corresponding norbornanes. No rearrangements, epimerizations, or solvolyses were observed.

Some years ago, it was discovered[3] that sensitized irradiation of **1** led to **2**, which is the photochemical equivalent of a Wagner–Meerwein rearrangement. That this is a true photochemical process, rather than a chain process, was clear from the fact that **1** is thermally stable with respect to **2**. The possibility that the photorearrangement involved carbenium ion–chloride ion pairs was suggested at that time and led to the idea that other systems which could accept triplet energy from photosensitizers and could undergo carbenium-ion formation readily might show similar interesting chemistry. Although the idea of carbenium-ion intervention remains to be proven or disproven,[4] it led to the discovery[5] that photosensitization of allylic chlorides and bromides results in the formation not only of products of 1,3-sigmatropic (allylic) rearrangement, but also of 1,2-rearrangement–cyclizations (allyl to cyclopropyl rearrangements). These reactions have been shown to be quite general.[1,4,6]



1



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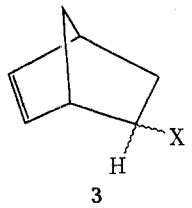

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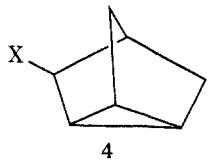
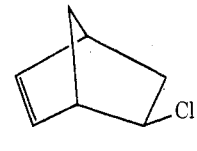
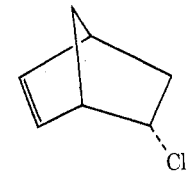


4

As the dehydronorbornyl (**3**)–nortricyclyl (**4**) system represents one in which reversible rearrangements attend carbenium ion processes,[7] we thought that photosensitized rearrangement of **3** to **4** might occur and that one might also possibly see some interesting stereochemical consequences of exo (**5**) and endo (**6**) isomerism in the halides. Accordingly, we subjected **5** and **6** to irradiation in acetone using thin-walled Pyrex filters ($\lambda > 280$ nm, $T\% > 10\%$). Both compounds were reactive under these conditions, but no trace of the isomeric nortricyclyl chloride (**4**-Cl) could be found. Instead, photoreduction occurred to give norbornyl chloride of retained stereochemistry (i.e., **5** → **7** and **6** → **8**) in yields of 10–20% as the only products of this volatility. Nortricyclyl chloride (**4**-Cl) was not reactive under similar conditions.



5



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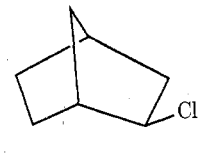

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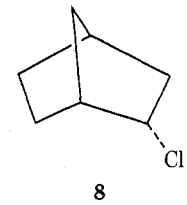

8

Sensitization of **6** with *m*-xylene (λ 254 nm) or with *p*-methoxyacetophenone ($\lambda > 280$ nm)[8] in pentane also gave