Registry No.—**1**, 4544-23-4; **2**, 30896-86-7; **3**, 40922-91-6; **5**, 33530-27-7; **6**, 33530-26-6; **7**, 40811-43-6; **8**, 40811-42-5.

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Bridged Polycyclic Compounds. 84. Cationic Rearrangements Accompanying Addition of Acetic Acid to the Cyclopropane Dibenzotricyclo[3.2.2.0^{2,4}]nonadiene[1]

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Acid-catalyzed addition of acetic acid at reflux to 6,8-dibenzotricyclo[3.2.2.0^{2,4}]nonadiene (**1**) gives a mixture of *cis*-8-methyl-7-dibenzobicyclo[2.2.2]octadienyl acetate (**5**), the trans isomer (**6**), and 6,8-dibenzo-2-bicyclo-[3.2.2]nonadienyl acetate (**7**). Low temperature and deuterium-labeling experiments indicate that these products are thermodynamic sinks and that the initial products of addition are undoubtedly *syn*-8-methyl-*exo*-2-dibenzobicyclo[3.2.1]octadienyl acetate (**8**) and 3,6-dibenzo-2-bicyclo[3.2.2]nonadienyl acetate (**24**). The paths which are traversed in the acid-catalyzed rearrangements are explored, and rough rates of isomer interconversions are reported. The experimental results are discussed, with special attention paid to the differences between the isomeric [3.2.2] system and its demethylene analogue, the dibenzobicyclo[2.2.2]- and [3.2.1]octadienyl system.

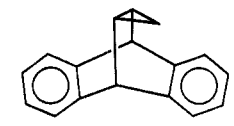
Our interest in the stereochemistries and mechanisms of electrophilic additions to cyclopropanes[2] led us to a study of additions to 6,8-dibenzotricyclo[3.2.2.0^{2,4}]nonadiene (**1**). This cyclopropane offers a variety of paths for ring-opening additions, and, as will be seen below, avails itself of several of these.

Several methods were attempted for the synthesis of **1**. Of these, the Gindig–Cross modification[3] of the Simmons–Smith reaction[4] with **2** gave **1** in about 70% yield. As the synthesis of **2** requires several steps, the following alternative synthesis was somewhat more convenient. Anthracene was condensed with *cis*- or *trans*-1,3-dichloropropene to give **3** or **4**, respectively. Treatment of either isomer with heavily coppered zinc–copper couple (1 g-atom of copper to 6 of zinc) gave **1** in good yield.[5]

When **1** was heated in acetic acid containing 0.1 M perchloric acid and 0.24 M water at 114 °C for 30 min, it reacted completely and gave a mixture containing about 33% of **5**, 22% of **6**, and 45% of **7**. This experiment showed that **1** was reactive, but the conditions are severe enough that it seemed likely that some or all of these products were not those of kinetic control in the ring-opening addition reaction.[7] A reaction run at room temperature with 0.11 M perchloric acid in acetic acid (containing a small amount of acetic anhydride) for 4.5 h gave (^{1}H NMR analysis) about 50% reaction with a ratio of about 5 parts of **8** and **9** to 4 parts of **7**. At this stage neither **5** nor **6** was apparent. The reaction was allowed to continue, with aliquots taken from time to time. After 9 h, a trace of **5** appeared; the amount of **5** grew, after the **1** was consumed, at the expense of **8** and **9**, while the amount of **7** remained constant.

Even after 200 h, no trace of **6** appeared, and **10** and **11**, which may be progenitors of **6** (see below), were also not detected, either in early or late experiments. Compound **12**, which is a possible product of ring opening and which would be stable under these experimental conditions,[8] was also not detected.

At the end of the experiment (200 h), the ratio of **8**:**9** was 33:67. It seemed likely, in view of previous work,[7,9] that the exo isomer **8** was formed first and was converted rapidly in the acid medium to the equilibrium mixture with **9**. This likelihood was increased by a study of the acetolysis of **13** in the presence of sodium acetate, which led, via the Wagner–Meerwein rearrangement common to these ring systems,[9a] to the exo isomer **8**. **8** was found to have a half-life for equilibration with **9** in 0.01 M perchloric acid in acetic acid of a few hours at 41 °C. The half-life for rearrangement of the **8**–**9** mixture, which went cleanly to **5** (no **6** being formed at room temperature), was 135 h at room temperature (25 ± 2 °C) in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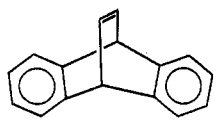
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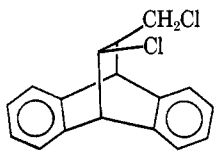

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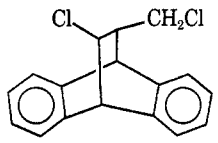

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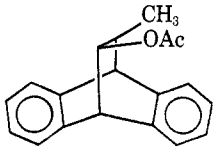

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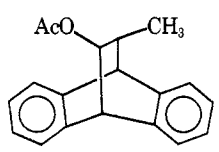

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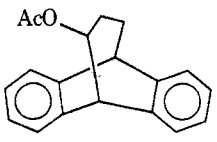

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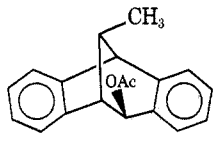

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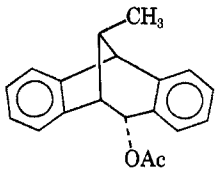

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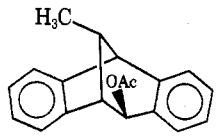

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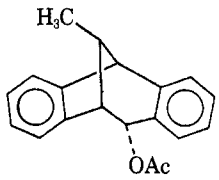

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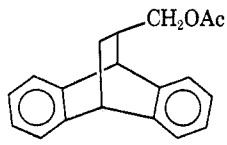

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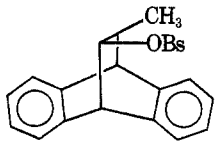

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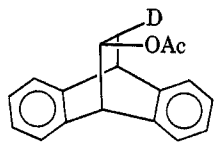

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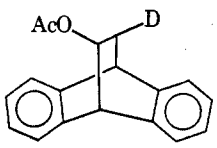

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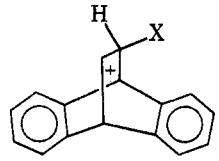

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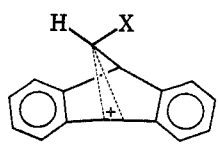

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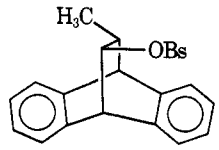

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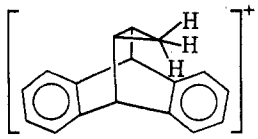

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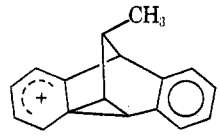

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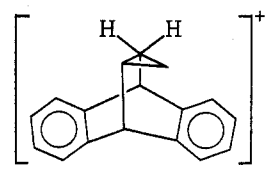
0.1 M perchloric acid in acetic acid containing excess acetic anhydride.

The results suggested that **6**, which was a substantial portion of the product of addition at reflux, arose as a result of acid-catalyzed rearrangement of **5**, and indeed **5** was found to rearrange rapidly with 0.1 M perchloric acid in acetic acid at reflux to mixtures with **6**. The rearrangement of **14** to **15** under severe conditions has been shown recently[7b] to involve the intermediacy of both **16**-*d* and **17**-*d*, and it seems likely that the rearrangement of **5** to **6** similarly involves either **16**-CH_3 or **17**-CH_3 or both.

The fact that the cis [2.2.2]–syn [3.2.1] and trans [2.2.2]–anti [3.2.1] systems maintain their integrities except under severe conditions was also demonstrated by starting with the trans-anti system. Thus acetolysis of **18** gave **10** which epimerized rapidly to a 1:1 mixture with **11** in acid solution and was then transformed to **6** with 0.1 M perchloric acid in dry acetic acid with a half-life of 7 h at room temperature, and without the formation of **5**.

Thus addition of acetic acid to **1** has two modes, one leading to the methylbicyclo[3.2.1] and [2.2.2] systems, which are converted among each other, and one to the [3.2.2] system, which is unrelated to the other set of products. The formation of **8** as the first stable intermediate in one of these systems is consistent with the intervention of the corner-protonated intermediate **19**,[10] whose opening is concerted with migration of the anti benzene ring to give[11] **20**, the precursor of **5**. As perhaps may be expected,[7,9,11] **19** does not suffer external nucleophilic attack to give acetate **6**. The formation of **7** is consistent with the intervention of the alternative corner-protonated intermediate **21**, which might be anticipated to suffer external nucleophilic attack by acetic acid to give **12** (not found) or to give **7**. Alternatively, **21** might open to the cation **22**. Capture of **22** by acetic acid would give **7**. More likely **22** would equilibrate with **23**[12] giving **24**, which, returning through the same set of cations, could give **7**.



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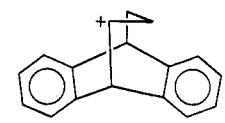

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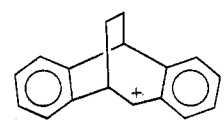

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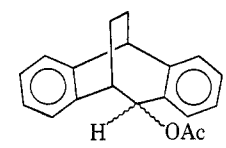

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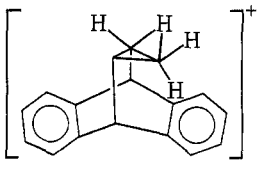
These considerations, plus the possibility[10] that an edge-protonated intermediate **25** was a common precursor to both systems, suggested that we look at the **24**–**7** system and that we study the addition of acetic acid-*O*-*d* to **1** to study the stereochemistry of the addition to give **7**. The ^1H NMR spectrum of the [3.2.2] alcohol **26** makes it convenient to check on the location of deuterium atoms at C-4. The NMR data show that **26** has the conformation indicated, with the hydroxyl group having an equatorial position. Thus the H-1 proton in **26** gives rise to a doublet with J = 2.4 Hz (coupling with the axial H-2 proton), while H-5 gives rise to a doublet of doublets with J = 2.4 and 6.0 Hz (coupling with the two protons on C-4). Similar data are produced with the acetate **7**. Thus the stereochemistry of the C-4 hydrogen atoms can be readily determined.

For a number of reasons we found it more convenient to add normal acetic acid to dideuterio-**1** (i.e., **27**) than to add deuterated acetic acid to **1**. Addition of ethyl propiolate-*3*-*d* to anthracene gave **28**, which, upon reduction with lithium alu-



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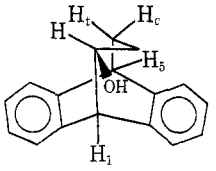

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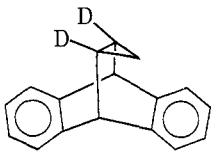

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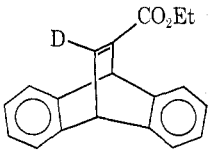

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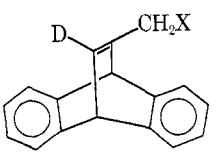
minum hydride–aluminum chloride as described[13] for the protio compound, gave **29**-OH. Treatment with thionyl chloride and tri-*n*-butylamine gave **29**-Cl which, upon acetophenone-sensitized irradiation[14] in acetonitrile, gave **30**. Treatment of **30** with triphenyltin deuteride (azoisobutyronitrile initiation) gave **27**.

27 was treated with 0.1 M perchloric acid in acetic acid at room temperature for 9 h. The resulting acetates were isolated and reduced with $LiAlH_4$ and the [3.2.2] alcohol (**26**-d_2) separated with TLC. ^1H NMR (100-MHz) spectroscopy (see Experimental Section) indicated that equal amounts of four dideuterio compounds resulted. These were **31**-OH, **32**-OH, **33**-OH, and **34**-OH. These results, plus the fact that the rearrangement of **35** to **36** was relatively slow, made it clear that



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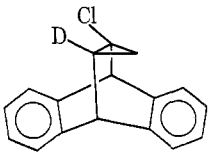

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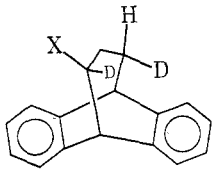

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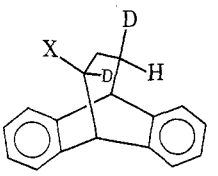

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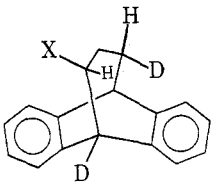

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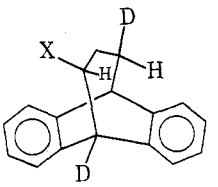

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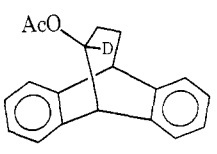

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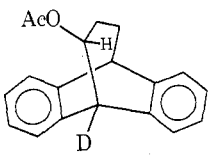
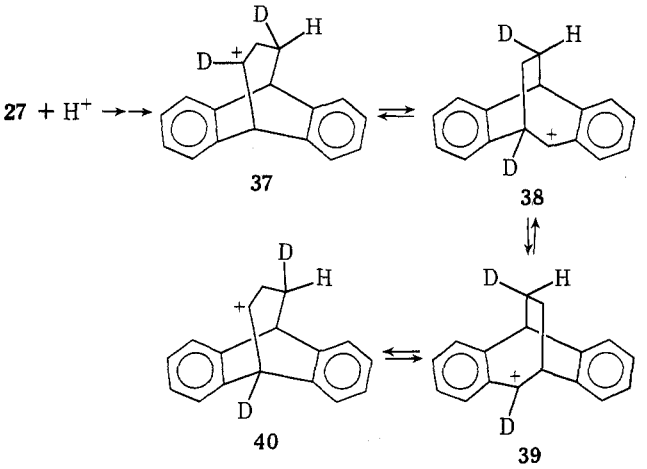


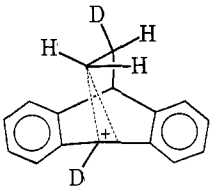
36

nucleophilic attack by solvent on protonated cyclopropane **21** or **25** did not lead directly to **7**, but that instead a more complicated process involving carbenium ions obtained. The fact that equal amounts of **31**-OAc and **32**-OAc, as well as **33**-OAc and **34**-OAc, were produced indicated that we would be unable to learn anything of stereochemical interest about this addition. However, the question of how the reaction proceeded still remained.

A likely rationalization for the production of the four isomers is shown in Scheme I. Ring opening of the protonated cyclopropane species leads to cation **37**,[12] which equilibrates rapidly with its presumably more stable isomer **38**. It is then necessary to assume the rapid migration of the two-carbon saturated bridge to give **39**, via the intermediate or transition state **41**, for the apparent deuterium migration to occur, a reaction which goes only very slowly with a one-carbon bridge (see above and ref 7 and 8), followed by equilibration of **39** with **40**. To learn whether this bridge migration was rapid, we studied the reaction of **42** in 0.1 M perchloric acid in acetic

Scheme I





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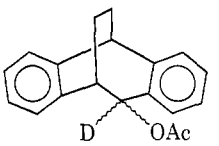

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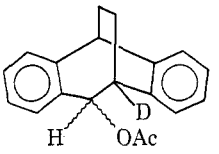

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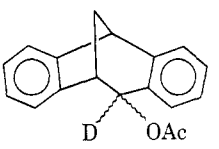
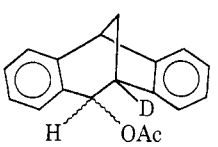


44

acid. Its complete interconversion with **43** occurred before the first NMR scan was taken (5–7 min at 25 °C). The subsequent rearrangement to deuterio-**7** had a half-life of about 50 min at 25 °C, and with no measurable **42** or **43** left at equilibrium. Thus the process outlined in Scheme I, with ions **38** and **39** being captured by acetic acid to give the dideuterio analogues of **42** and **43** and being regenerated from them, and with ions **37** and **40** ultimately being captured to give **31**, **32**, **33**, and **34**-OAc, is established.[15]

There remains to be discussed the remarkably large difference between the rate of isomerization in the [3.2.2] system, i.e., between **42** and **43** (complete in 0.1 M perchloric acid in acetic acid in <5 min at 25 °C), and that in the [3.2.1] system



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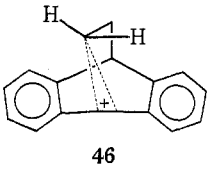

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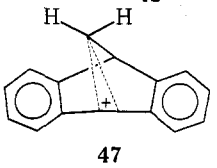
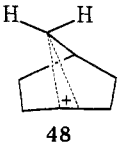
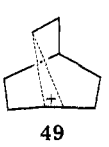


47



48

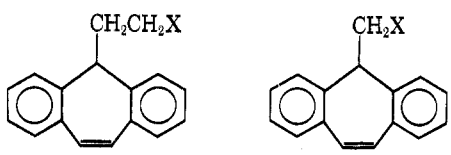


49

(half-life[7] for rearrangement of **44** to **45** under comparable conditions is of the order of 75 h at 85 °C). This must obviously relate to the relative stabilities of the two protonated cyclopropane intermediates or transition states **46** and **47**, which link the two isomeric pairs of cations in the [3.2.2] and [3.2.1] systems, respectively. It has been reported previously[17] that Professor Goering has commented on the difference between ion **47** and the corresponding saturated ion **48**, where the unsaturated ion **47** has serious additional strain associated with the tendency for a flatter system in the dibenzo compound than in the saturated one.

Berson[18] has noted that, in the saturated bicyclo[3.2.2]nonanyl system, rearrangement via **49** occurs substantially less readily (compared with capture) than in the corresponding bicyclo[3.2.1]octanyl system via **48**, and has ascribed this to the additional strain imposed by the extra ring member in the [3.2.2] system vs. that in the smaller system in achieving proper orbital overlap. On extension of the Goering–Berson concept to the flatter dibenzo compounds, the [3.2.1] system does not allow significant overlap without considerable strain, while the additional ring member allows relatively strain-free overlap. Thus the situation is completely reversed from that of the saturated systems.

Consistent with these ideas are some results published by Nenitzescu and co-workers some time ago.[16,19] They reported that the buffered solvolysis of **50**-OTs in acetic acid containing sodium acetate led, via the "π-route" (that is via **46**), to mixtures containing mostly **24**-OAc epimers mixed with some **7**, and with only 9–22% of unrearranged **50**-OAc, while the corresponding analogue **51**-OTs, with one less carbon, gave only 6% of "π-route" products, ring expansion occurring instead. These authors discuss their results in similar, though not identical, terms.



50 **51**

Experimental Section

Except where otherwise mentioned, ^{1}H NMR spectra were taken with a Varian A-60A or A-60 60-MHz spectrometer.

Preparation of *trans*- (4) and *cis*-7-Chloro-8-chloromethyldibenzobicyclo[2.2.2]octadiene (3). A mixture of 35 g (0.19 mol) of anthracene, 110 ml of *trans*-1,3-dichloropropene, and 0.5 g of *p*-*tert*-butylcatechol was heated in a sealed tube at 195–200 °C for 2 days. After being cooled, the tube was opened and washed with 100 ml of methanol. The solution and washings were combined and the excess dichloropropene and methanol removed by evaporation. The resulting oil was dissolved in 100 ml of benzene, placed on an alumina column (ca. 800 ml of Merck 71707), and eluted with petroleum ether (bp 60–70 °C). Anthracene was eluted first and then the adduct. The solvent was evaporated and the resulting oil was crystallized from ethanol to give 23 g (42%) of **4**: mp 92–92.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.20 (m, 8, aromatic H), 4.39 (d, 2, $J_{1,7} = J_{4,8} = 2.5$ Hz, H-1 and H-4), 3.63 (t, 1, $J_{1,7} = J_{7,8} = 2.5$ Hz, H-7), 3.6–2.7 (septet, 2, CH_2Cl), 2.40 (bm, 1, H-8).

Anal. Calcd for $C_{17}H_{14}Cl_2$: C, 70.61; H, 4.85. Found: C, 70.67; H, 4.99.

The cis adduct **3** was prepared analogously, using *cis*-1,3-dichloropropene: yield 21 g, 40%; mp 176–177 °C; ^{1}H NMR ($CDCl_3$) δ 7.23 (m, 8, aromatic H), 4.66 (d, 1, $J_{1,7} = 2$ Hz, H-1), 4.50 (d, 1, $J_{4,8} = 2$ Hz, H-4), 4.44 (dd, 1, $J_{7,8} = 6$ Hz, $J_{1,7} = 2$ Hz, H-7), 2.6–3.8 (septet, 2, CH_2Cl), 2.50 (bm, 1, H-8).

Anal. Calcd for $C_{17}H_{14}Cl_2$: C, 70.61; H, 4.85. Found: C, 70.81; H, 4.63.

Preparation of Dibenzotricyclo[3.2.2.0^{2,4}]nonadiene (1). Powdered analytical grade zinc (38 g) was washed with 2% aqueous copper sulfate until the blue color persisted (about 1 g-atom of copper/6 g-atoms of zinc), then with 50 ml of 95% ethanol, and filtered. A mixture of either dichloride **3** or **4** (1 g, 3.5 mmol), 150 ml of 95% ethanol, and 1.5 g of the zinc–copper couple was heated at reflux with stirring for 48 h, cooled, and filtered. The residue was washed thoroughly with ether. The solvents were evaporated, and the residual oil was dissolved in a minimum amount of chloroform and placed on a silica gel column (ca. 150 ml, 60–200 mesh) and eluted with Skellysolve B. The first fractions contained the pure cyclopropane and later fractions contained small amounts (~5%) of **3** or **4**. Results were similar with both isomers. The solvent was removed by evaporation, and the cyclopropane **1** was fractionally crystallized from acetone: yield 620 mg (80%); mp 176–177 °C. An analytical sample melted at 179–180 °C;[20] ^{1}H NMR ($CDCl_3$) δ 7.10 (m, 8, aromatic H), 4.36 (t, 2, H-1 and H-5), 1.45 (sm, 2, H-2 and H-4), 0.55 (dd, 1 $J_{gem} = 6$ Hz, $J_{2,3} = J_{4,3} = 15$ Hz, exo-H-3), −0.27 (sm, 1, endo-H-3).

Anal.[20] Calcd for $C_{17}H_{14}$: C, 93.53; H, 6.47. Found: C, 93.59; H, 6.62.

Preparation of "Moist" Acetic Acid, 0.1 M in Perchloric Acid. A 1-l. volumetric flask was charged with 9 ml of 70% reagent grade perchloric acid (0.1 mol of perchloric acid and 0.24 mol of water), and filled to the mark with reagent grade acetic acid.

Addition of Acetic Acid to Dibenzotricyclo[3.2.2.0^{2,4}]nonadiene (1) at Reflux. A solution of 200 mg of dibenzotricyclo[3.2.2.0^{2,4}]nonadiene (**1**) in 25 ml of the perchloric acid–moist acetic acid mixture was heated at reflux for 30 min, then cooled, poured into 30 ml of water, and extracted several times with ether. The ether extracts were washed with water and aqueous sodium bicarbonate, dried ($MgSO_4$), and filtered, and the ether was evaporated. Addition and removal by evaporation of carbon tetrachloride three times left a yellow oil free of ether. The product composition was determined by ^{1}H NMR. The *cis*- to *trans*-8-methyl-7-dibenzobicyclo[2.2.2]octadienyl acetate (**5**:**6**) ratio was about 60:40 and the combined percentage of **5** and **6** was 55%. 6,8-Dibenzo-2-bicyclo[3.2.2]nonadienyl acetate (**7**) was the remaining 45%. No peaks due to other products were apparent.

Preparation of *cis*- and *trans*-8-Methyl-7-dibenzobicyclo[2.2.2]octadienyl Acetate (5 and 6) from Anthracene and 1-Propenyl Acetate. A Pyrex tube containing 19.5 g (0.112 mol) of anthracene (98%, Aldrich), 55 g (0.55 mol) of 1-propenyl acetate,[21,22] and 0.5 g of *p*-*tert*-butylpyrocatechol was sealed and heated at 200–210 °C for 96 h. The tube was cooled and opened and 4.5 g of anthracene removed by filtration. One hundred milliliters of methanol was used to wash the tube and solid. The filtrate and washings were combined and allowed to stand for 2 days at room temperature during which time 8.5 g of 95% pure (as determined by ^{1}H NMR) cis adduct **5** crystallized. The crystals were filtered and the flask was cooled in a freezer at −20 °C for 5 days. A second crop of crystals formed (10.5 g) which was 80% trans acetate **6** (as determined by ^{1}H NMR): total yield, 65%. The cis adduct **1** was recrystallized from aqueous ethanol giving 5.5 g of **5**: mp 122–123 °C; ^{1}H NMR (CCl_4) δ 7.08 (sm, 8, aromatic H), 5.02 (dd, 1, $J_{1,7} = 3$ Hz, $J_{7,8} = 7.0$ Hz, H-7), 4.30 (d, 1, $J_{1,7} = 3$ Hz, H-1), 3.84 (d, 1, $J_{4,8} = 2$ Hz, H-4), 2.20 (m, 1, H-8), 1.76 (s, 3, CH_3COO–), 0.59 (d, 3, $J_{8,9} = 7$ Hz, CH_3–).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.82; H, 6.74.

The crude trans isomer was converted to the alcohol (the procedure follows) and separated on a preparative silica gel plate using 10% ether in benzene to develop the plate. Alternatively, fractional crystallization of the alcohol (80% trans isomer from acetates) from aqueous ethanol was successful, but the yields were rather low. The alcohol was converted to the acetate using acetic anhydride and pyridine. Recrystallization from aqueous ethanol gave pure trans acetate **6**: mp 96.5–97.5 °C; ^{1}H NMR (CCl_4) δ 7.09 (sm, 8, aromatic H), 4.46 (dd, 1, $J_{1,7} = 2.5$ Hz, $J_{7,8} = 3.0$ Hz, H-7), 4.37 (d, 1, $J_{1,7} = 2.5$ Hz, H-1), 3.83 (d, 1, $J_{4,8} = 2.5$ Hz, H-4), 1.82 (s, 3, CH_3COO–), 1.72 (bm, 1, H-8), 0.91 (d, 3, $J_{8,9} = 6.5$ Hz, CH_3–).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 82.02; H, 6.47.

Preparation of *cis*- and *trans*-8-Methyl-7-dibenzobicyclo[2.2.2]octadienols. Each acetate was converted to the corresponding alcohol with sodium methoxide in methanol at reflux. Recrystallization from aqueous ethanol gave the alcohols as follows.

The cis isomer: mp 145–147 °C; ^{1}H NMR (CCl_4) δ 7.05 (sm, 8, aromatic H), 4.20 (d, 1, $J_{1,7} = 3.5$ Hz, H-1), 4.0 (bm, 1, H-7, not resolved due to OH coupling), 3.81 (d, 1, $J_{4,8} = 2$ Hz, H-4), 3.19 (m, 1, $J_{8,9} = 7$, $J_{4,8} = 2$ Hz, H-8), 0.83 (bd, 1, $J = 11$ Hz, OH), 0.64 (d, 3, $J_{8,9} = 7$ Hz, CH_3–).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.43; H, 7.01.

The trans isomer: mp 114–115.5 °C; ^{1}H NMR (CCl_4) δ 7.08 (sm, 8, aromatic H), 4.09 (d, 1, $J_{1,7} = 3$ Hz, H-1), 3.77 (d, 1, $J_{4,8} = 2.5$ Hz, H-1),

3.32 (dd, 1, $J_{7,8}$ = 3, $J_{1,7}$ = 3 Hz, H-7), 1.39 (sm, 1, H-8), 1.13 (s, 1, OH), 0.82 (d, 3, $J_{8,9}$ = 6.5 Hz, CH_3–).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.14; H, 6.73.

Addition of "Moist" Acetic Acid (0.1 M in Perchloric Acid) to Dibenzotricyclo[3.2.2.0^{2,4}]nonadiene (1) at Room Temperature. A solution of dibenzotricyclo[3.2.2.0^{2,4}]nonadiene (750 mg, 2.7 mmol) in 100 ml of "moist" acetic acid containing 0.1 M perchloric acid and 0.24 M water was allowed to stand at room temperature. Aliquots (20 ml) were taken at various times and worked up in normal fashion. ^{1}H NMR analysis of the crude oils showed no starting material after 150 h. There was no *trans*-8-methyl-7-dibenzobicyclo[2.2.2]octadienyl acetate (**6**) nor anti [3.2.1] acetates (**10** or **11**) visible during the reaction. The presence of *exo*- and *endo-syn*-8-methyl-2-dibenzobicyclo[3.2.1]octadienyl acetates (**8** and **9**) was monitored by the appearance of two sets of doublets near δ 6.0. The subsequent rearrangement of **8** and **9** to the cis [2.2.2] acetate **5** as a function of time was apparent. When runs similar to the one described above were made with the water concentration varied, the rate of ring opening was found to be markedly dependent on the amount of water present. Thus, with water molarities of 0.17, 0.24, and 0.46 the percent reaction of **1** after 24 h (as determined by ^{1}H NMR) was 43, 40, and 32, respectively. The rearrangement of the [3.2.1] acetates to cis [2.2.2] acetate was similarly affected, but since the half-lives were approximately 12 times longer than the ring opening the effect appeared magnified.

Preparation of "Dry" Acetic Acid, 0.1 M in Perchloric Acid. In a 1-l. volumetric flask was placed 9 ml of 70% reagent grade perchloric acid (0.1 mol of perchloric acid, and 0.24 mol of water) and 50 ml of reagent grade acetic anhydride, before it was filled to the mark with reagent grade acetic acid. The final solution had about 3 vol % excess acetic anhydride. Titration with potassium acetate, using bromothymol blue indicator, gave a value of 0.108 ± 0.005 M in perchloric acid.

Equilibration of *cis*- and *trans*-8-Methyl-7-dibenzobicyclo[2.2.2]octadienyl Acetates (5 and 6). A two-necked 50-ml round-bottom flask was equipped with a reflux condenser. Twenty milliliters of "dry" acetic acid, 0.108 M in perchloric acid, was added. The solution was heated to reflux, and 200 mg of a mixture of 90% **5** and 10% **6** was added. The solution was heated at reflux for 20 min and half of the solution was withdrawn and worked up in the normal manner. After 60 min the second half of the reaction solution was worked up. ^{1}H NMR analysis of the resultant oils showed a **5** to **6** ratio of 30:70 and 20:80 after 20 and 60 min, respectively.

Preparation of *p*-Bromobenzenesulfonates 13 and 18. A solution of 3.8 g (16 mmol) of *cis*-8-methyl-7-dibenzobicyclo[2.2.2]octadienol, 8.2 g (32 mmol) of *p*-bromobenzenesulfonyl chloride, and 150 ml of dry reagent-grade pyridine was stirred at room temperature for 3 days. The solution was poured into 200 ml of water. The *p*-bromobenzenesulfonate crystallized immediately. The white crystals were filtered and washed with 5% hydrochloric acid (50 ml), 50 ml of water, and 25 ml of cold ether. The *cis*-8-methyl-7-dibenzobicyclo-[2.2.2]octadienyl *p*-bromobenzenesulfonate (**13**) was recrystallized from acetone to give 5.5 g (75%): mp 114–117 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.70 (s, 4 aromatic H's on *p*-bromobenzenesulfonate), 7.18 (sm, 8 benzo protons), 4.97 (dd, 1, $J_{1,7}$ = 3.5, $J_{7,8}$ = 6.5 Hz, H-7), 4.42 (d, 1, $J_{1,7}$ = 3.5 Hz, H-1), 3.96 (d, 1, $J_{1,7}$ = 2 Hz, H-4), 1.60 (bm, 1, H-7), 0.68 (d, 3, $J_{8,9}$ = 7.5 Hz, CH_3–).

Anal. Calcd for $C_{23}H_{19}BrO_3S$: C, 60.67; H, 4.20. Found: C, 60.97; H, 4.06.

The trans isomer was prepared using similar proportions, but it did not crystallize when poured into water. The solution was extracted with ether (3 × 100 ml). The combined ether extracts were washed with 5% hydrochloric acid (2 × 75 ml) and water (2 × 75 ml), dried ($MgSO_4$), and filtered. The ether was evaporated and the crude product was recrystallized from heptane to give **18**: yield 83%; mp 90–100 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.60 (s, 4, aromatic protons on *p*-bromobenzenesulfonate), 7.13 (sm, 8, benzo protons), 4.44 (d, 1, $J_{1,7}$ = 3 Hz, H-1), 4.32 (dd, 1, $J_{1,7}$ = 3, $J_{7,8}$ = 3 Hz, H-7), 3.88 (d, 1, $J_{4,8}$ = 2.5 Hz, H-4), 1.88 (bm, 1, H-8), 0.73 (d, 3, $J_{8,9}$ = 7.5 Hz, CH_3–). An analysis of this compound was not obtained because the compound decomposed on standing at room temperature for several days.

Buffered Acetolyses of *cis*- (13) and *trans*-8-Methyl-7-dibenzobicyclo[2.2.2]octadienyl *p*-Bromobenzenesulfonate (18). A solution of acetic anhydride (4 ml), 8.2 g (0.1 mol) of sodium acetate, 2.37 g (5.2 mmol) of *cis*-8-methyl-7-dibenzobicyclo[2.2.2]octadienyl *p*-bromobenzenesulfonate (**13**), and 96 ml of acetic acid was stirred at room temperature for 12 h. At this time it was noted that all of the **13** had not dissolved, and the temperature was maintained at 60 °C for 3.5 more days. The solution was poured into 50 ml of water, and extracted with ether (3 × 100 ml). The combined ether extracts were washed with cold water and saturated aqueous sodium bicarbonate, dried ($MgSO_4$), filtered, and evaporated to dryness. The crude yellow oil (1.14 g, 80% yield) was dissolved in ethanol, treated with charcoal, and crystallized by adding water to the cloud point, heating to 80 °C by a steam bath, and slow cooling. The only important product by ^{1}H NMR of the oil was *syn*-8-methyl-*exo*-2-dibenzobicyclo[3.2.1]octadienyl acetate (**8**): mp 109.5–111 °C after recrystallization; ^{1}H NMR (CCl_4) δ 7.25 (sm, 1, benzo proton α to carbon number 3), 7.00 (sm, 7, remaining benzo protons), 5.71 (d, 1, $J_{1,2}$ = 2 Hz, H-2 endo), 3.61 (d, 1, $J_{5,8}$ = 4 Hz, H-5), 3.35 (dd, 1, $J_{1,8}$ = 4 Hz, H-1), 2.75 (bm, 1, H-8 anti), 2.00 (s, 3, CH_3COO–), 1.13 (d, 3, $J_{8,9}$ = 7 Hz, CH_3–).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.95; H, 6.72.

The trans isomer **18** was solvolyzed at room temperature using the same proportions as for the cis isomer. The product, *anti*-8-methyl-*exo*-2-dibenzobicyclo[3.2.1]octadienyl acetate (**10**), was purified by sublimation at 90 °C and 0.5 mm: yield 80%; mp 98.5–100 °C; ^{1}H NMR (CCl_4) δ 7.32 (sm, 1, benzo proton α to carbon number 3), 7.0 (sm, 7, remaining benzo protons), 5.79 (d, 1, $J_{1,2}$ = 2 Hz, H-2 endo), 3.55 (s, 1, H-5), 3.13 (bs, 1, H-1, this is probably a poorly resolved dd), 2.82 (q, $J_{8,9}$ = 6.5 Hz, H-8 anti), 2.02 (s, 3, CH_3COO–), 1.00 (d, 3, CH_3–).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 82.21; H, 6.64.

Lithium Aluminum Hydride Reduction of *syn*- and *anti*-8-Methyl-2-dibenzobicyclo[3.2.1]octadienyl Acetates (8 and 10) to the Corresponding Alcohols. A solution of 1.14 g (4 mmol) of **8**, 60 ml of anhydrous ether, and 240 mg (6 mmol) of lithium aluminum hydride was stirred at room temperature for 4 hr. Saturated aqueous sodium sulfate was added very slowly until a white granular precipitate was formed. The precipitate was filtered and washed with anhydrous ether. The washings and filtrate were combined and evaporated to dryness. The product, ***syn*-8-*exo*-2-dibenzobicyclo[3.2.1]-octadienol,** was recrystallized from ethanol–water: yield 900 mg (95%); mp 143–145 °C; ^{1}H NMR ($CDCl_3$) δ 7.15 (sm, 8, aromatic H), 4.54 (d, 1, $J_{1,2}$ = 1.8 Hz, H-2 endo), 3.68 (d, 1, $J_{5,8}$ = 3.5 Hz, H-5), 3.29 (dd, 1, $J_{1,8}$ = 3.5 Hz, H-1), 2.85 (m, 1, H-8 anti), 1.95 (s, 1, –OH), 1.09 (d, 3, $J_{8,9}$ = 7 Hz, CH_3).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.45; H, 7.12.

The reduction of **10** was carried out in a similar manner to give ***anti*-8-methyl-*exo*-2-dibenzobicyclo[3.2.1]octadienol** in 90% yield (after recrystallization from aqueous ethanol): mp 135–138 °C; ^{1}H NMR ($CDCl_3$) δ 7.20 (sm, 8, aromatic H), 4.65 (d, 1, $J_{1,2}$ = 2 Hz, H-2 endo), 3.59 (s, 1, H-5), 3.17 (bd, 1, $J_{1,2}$ = 2 Hz, H-1), 2.72 (q, 1, $J_{8,9}$ = 7 Hz, H-8 syn), 2.47 (s, 1, –OH), 1.03 (d, 3, $J_{8,9}$ = 7 Hz, CH_3).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.49; H, 7.04.

Preparation of *syn*- and *anti*-8-Methyl-2-dibenzobicyclo[3.2.1]octadienone. A solution of 50.00 g (0.168 mol) of sodium dichromate dihydrate, 27.5 ml of concentrated sulfuric acid, and water to 250 ml was prepared. A 150-ml round-bottom flask was charged with 1.10 g (4.62 mmol) of *syn*-8-methyl-*exo*-2-dibenzobicyclo[3.2.1]-octadienol, 50 ml of ether, and 5.0 ml of the above aqueous acidic chromic acid solution. The reaction mixture was stirred at room temperature for 24 h. The solution was washed repeatedly with water (6 × 25 ml), dried ($MgSO_4$), filtered, and evaporated to dryness. The product, ***syn*-8-methyl-2-dibenzobicyclo[3.2.1]octadienone,** was recrystallized from aqueous ethanol: yield 770 mg (61%); mp 100–102 °C; ^{1}H NMR ($CDCl_3$) δ 7.83 (sm, 1, benzo proton α to C-3), 7.18 (sm, 7, remaining aromatic H), 3.91 (d, 1, $J_{5,8}$ = 5 Hz, H-5), 3.80 (d, 1, $J_{1,8}$ = 4 Hz, H-1), 3.28 (sm, 1, H-8 anti), 1.10 (d, 3, $J_{8,9}$ = 7 Hz, CH_3–).

Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.96; H, 5.94.

Similarly, the oxidation of the corresponding anti alcohol gave ***anti*-8-methyl-2-dibenzobicyclo[3.2.1]octadienone** in 60% yield: mp 109–110.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.90 (sm, 1, benzo proton α to C-3), 7.25 (sm, 7, remaining aromatic H), 3.89 (bs, 1, H-1), 3.78 (s, 1, H-5), 3.18 (q, 1, $J_{8,9}$ = 7 Hz, H-8 syn), 1.10 (d, 3, $J_{8,9}$ = 7 Hz, CH_3).

Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.95; H, 6.02.

Lithium Aluminum Hydride Reduction of *syn*- and *anti*-8-Methyl-2-dibenzobicyclo[3.2.1]octadienones. A solution of 472 mg (2 mmol) of *syn*-8-methyl-2-dibenzobicyclo[3.2.1]octadienone, 30 ml of anhydrous ether, and 40 mg (1 mmol) of lithium aluminum hydride was stirred at room temperature for 30 min. Saturated aqueous sodium sulfate was added very slowly until a white granular precipitate was formed. The mixture was filtered, and the filtered precipitate was washed with additional ether. The washings and filtrate were combined and evaporated to dryness. A ^{1}H NMR spectrum

of the colorless oil (470 mg, yield 95%) showed an exo to endo alcohol ratio of 1:1. The isomers were separated by preparative thin layer chromatography on PF-254 (Brinkmann) silica gel, developed with 10 vol % ether in benzene. The bands were visible under uv light. The upper band contained the endo isomer and was removed and extracted with ether to give 170 mg of ***syn*-8-methyl-*endo*-2-dibenzobicyclo[3.2.1]octadienol,** which after recrystallization from aqueous ethanol melted at 96–97.5 °C: ^{1}H NMR ($CDCl_3$) δ 7.78 (sm, 8, aromatic H's), 4.86 (d, 1, $J_{1,2}$ = 5.5 Hz, H-2 exo) (this proton is frequently broad or a dd with J = 11 due to the slowness of the OH exchange, but addition of D_2O to the sample eliminates the problem), 3.58 (d, 1, $J_{5,8}$ = 4 Hz, H-5), 3.29 (dd, 1, $J_{1,8}$ = $J_{1,2}$ = 5.5 Hz, H-1), 2.93 (bm, 1, H-8 anti), 2.50 (bs, 1, –OH), 1.00 (d, 3, $J_{8,9}$ = 7 Hz, CH_3–).

Similarly, the reduction of *anti*-8-methyl-2-dibenzobicyclo[3.2.1]-octadienone gave exo and endo 4-alcohols in a 25:75 ratio (as determined by ^{1}H NMR) in a 95% yield. ***anti*-8-Methyl-*endo*-2-dibenzobicyclo[3.2.1]octadienol** was recrystallized from aqueous ethanol: mp 121–122.7 °C; ^{1}H NMR ($CDCl_3$) δ 7.16 (sm, 8, aromatic H's), 4.96 (d, 1, $J_{1,2}$ = 5.5 Hz, H-2 exo), 3.55 (s, 1, H-5), 6.68 (d, 1, $J_{1,2}$ = 5.5 Hz, H-1), 2.60 (q, 1, $J_{8,9}$ = 7 Hz, H-8 syn), 1.58 (s, 1, –OH), 1.20 (d, 3, $J_{8,9}$ = 7 Hz, CH_3).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.37; H, 6.99.

This alcohol was converted to the corresponding acetate with acetic anhydride in pyridine. After aqueous extraction of an ether solution and appropriate workup including preparative TLC on silica gel and recrystallization, the ***anti*-8-methyl-*endo*-2-dibenzobicyclo-[3.2.1]octadienyl acetate (11),** mp 95–96 °C, was obtained: ^{1}H NMR ($CDCl_3$) δ 7.18 (s, 8, aromatic H's), 6.25 (d, 1, $J_{1,2}$ = 5.5 Hz, H-2 exo), 3.60 (s, 1, H-5), 3.55 (d, 1, $J_{1,2}$ = 5.5 Hz, H-1), 2.68 (q, 1, $J_{8,9}$ = 7 Hz, H-8 syn), 2.12 (s, 3, CH_3COO–), 1.03 (d, 3, $J_{8,9}$ = 7 Hz, CH_3–).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.71; H, 6.50.

Acid-Catalyzed Equilibration of Exo (8) and Endo (9) Isomers of *syn*-8-Methyl-2-dibenzobicyclo[3.2.1]octadienyl Acetates. Preparation of the Endo Isomer 9. A solution of 500 mg of **8** in 70 ml of 0.1 M perchloric acid in "dry" acetic acid was stirred at room temperature for 30 min. The solution was poured into 75 ml of water and extracted with four 100-ml portions of ether. The ether washings were combined and extracted with aqueous sodium bicarbonate until the washings were basic. The ether layer was treated with charcoal, dried ($MgSO_4$), and evaporated to dryness. The ^{1}H NMR spectrum of the resulting oil showed the **8**:**9** ratio to be 35:65. The oil was fractionally crystallized from aqueous ethanol to give 140 mg of **8.** The mother liquor was concentrated, and **9** crystallized. It was recrystallized from aqueous ethanol to give 100 mg of **9:** mp 129–130 °C; ^{1}H NMR ($CDCl_3$) δ 7.12 (s, 8, aromatic H), 6.16 (d, 1, $J_{1,2}$ = 5 Hz, H-1), 3.68 (d, 1, $J_{5,8}$ = 4 Hz, H-5), 3.53 (dd, 1, $J_{1,2}$ = $J_{1,8}$ = 5 Hz, H-1), 2.95 (sm, 1, H-8 anti), 2.08 (s, 3, CH_3COO–), 1.11 (d, 3, $J_{8,9}$ = 7 Hz, CH_3).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 82.22; H, 6.63.

6,8-Dibenzo-2-bicyclo[3.2.2]nonadienol (26)[16] has been previously prepared in this laboratory:[23] mp 157–158 °C; ^{1}H NMR ($CDCl_3$) δ 7.23 (sm, 8, aromatic H's), 4.00 (m, 2, H-1 and H-5), 3.80 (bm, 1, H-2), 1.79 (sm, 2, H-4 and cis H-3), 1.50 (s, 1, OH), 1.3–0.7 (bm, 1, trans H-3). The δ 4.00 region was resolved on an HA-100 (100 MHz) spectrometer as follows: the absorbance due to H-1 lies at lower field and is a doublet with $J_{1,2}$ = 2.4 Hz and that of H-5 at about 10 Hz higher field is a doublet of doublets with J_{4c5} = 6 Hz, J_{4t} = 2.4 Hz. The 2-deuterio alcohol[23] **35** had a ^{1}H NMR spectrum differing from that of **26** as follows: δ 4.02 (s, 1, H-1), 3.96 (dd, J = 6, 2.5 Hz), and with no peak at 3.80.

The acetate **7**[16,20] was used for structure verification: ^{1}H NMR ($CDCl_3$) δ 7.10 (sm, 8, aromatic H), 4.72 (sm, 1, H-2), 4.46 (d, 1, $J_{1,2}$ = 2.5 Hz, H-1), 3.82 (dd, $J_{4,5}$ = 2.5, 5 Hz), 2.2–1.0 (bm, 4, H_3 and H_4), 1.88 (s, 3, CH_3COO–).

3,6-Dibenzo-2-bicyclo[3.2.2]nonadienols and their acetates have been prepared previously,[16,20] as has the corresponding ketone.[20] Appropriate data are given below.

3,6-Dibenzo-*exo*-2-bicyclo[3.2.2]nonadienyl Acetate (*exo*-24): colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.10 (sm, 8, aromatic H's), 6.05 (d, 1, $J_{1,2}$ = 5 Hz, H-2 endo), 3.90 (m, 1, H-5), 3.57 (bm, 1, H-1), 2.0 (m, H-8 and H-9), 1.94 (s, 3, CH_3COO–).

***endo*-24:** mp 90–90.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.20 (sm, 8, aromatic H), 6.16 (d, 1, $J_{1,2}$ = 3.5 Hz, H-2 exo), 3.88 (dd, 1, H-5), 3.45 (dd, 1, H-1), 2.5–1.9 (m, 4, H-8 and H-9), 1.94 (s, 3, CH_3COO–).

3,6-Dibenzo-*exo*-2-bicyclo[3.2.2]nonadienol: mp 120–121.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.20 (sm, 8, aromatic H's), 4.94 (d, 1, $J_{1,2}$ = 5 Hz, H-2 endo), 3.87 (m, 1, H-5), 3.30 (m, 1, H-1), 2.6–1.7 (bm, H-8 and H-9), 1.60 (s, 1, –OH).

Table I. Analysis of Reaction Products from Treatment of 1 with Acetic Acid–Perchloric Acid

Time, h	% 1	% 8 + 9	% 5	% 7
4.5	50	28	0	22
9	25	39	Trace	36
18	5	52	5	41
22	0	50	7	45
30	0	43	12	45
89	0	34	21	45
120	0	30	25	45
167	0	13	42	45

3,6-Dibenzo-*endo*-2-bicyclo[3.2.2]nonadienol: ^{1}H NMR ($CDCl_3$) δ 7.20 (sm, 8, aromatic H's), 4.76 (d, 1, $J_{1,2}$ = 5 Hz, H-2, exo), 3.93 (dd, 1, H-5), 3.43 (dd, 1, H-1), 2.15–1.85 (m, 4, H-8 and H-9), 1.67 (s, 1, –OH).

3,6-Dibenzo-2-bicyclo[3.2.2]nonadienone: mp 113–114.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.07 (sm, 1, benzo proton α to C-3), 7.25 (sm, 7, aromatic H protons), 4.22 (m, 2, H-1 and H-5), 2.11 (m, H-8 and H-9). Reduction of this ketone with lithium aluminum deuteride (same procedure as given above) gave a 50:50 mixture of exo and endo isomers of 2-deuterio-3,6-dibenzo-2-bicyclo[3.2.2]nonadienols.

Treatment of 1 with 0.1 M Perchloric Acid in "Dry" Acetic Acid at Room Temperature. A solution of 4.5 g (21 mmol) of **1** in 750 ml of "dry" acetic acid, 0.108 M in perchloric acid, was prepared. Aliquots (25 ml) were withdrawn from time to time, poured into 25 ml of water, and extracted with ether (3 × 50 ml). The ether extracts were combined and washed with cold water (3 × 75 ml), saturated aqueous sodium bicarbonate (3 × 75 ml), and water (2 × 75 ml). The ether layer was dried ($MgSO_4$), filtered, and evaporated to dryness. After several additions and evaporations of carbon tetrachloride, ^{1}H NMR analysis was performed on each residue, based on ^{1}H NMR data from the independently synthesized compounds. These are reported in Table I.

Rough Kinetic Studies. Rates of isomer interconversion or of additions to **1** were measured in NMR tubes by ^{1}H NMR spectroscopy, following the reactions by integrations of absorptions due to the protons α to the acetoxy groups. The temperature of the NMR probe was 41 ± 1 °C, and runs were made either in a constant temperature bath at that temperature or at room temperature (~25 °C). In the latter case, the tubes were kept in the NMR probe for as short a time as possible. Runs were made with approximately 30 mg of material in "dry" acetic acid containing 0.103 M perchloric acid. For the additions and the skeletal rearrangements, reactions were complete, while for the exo–endo isomerizations, appropriate kinetic treatments suitable for equilibria were used.[24] For the rearrangements **8** ⇄ **9** and **10** ⇄ **11,** 0.01 M perchloric acid was used, as reactions were otherwise too fast.

Deuterium Scrambling Studies. A solution of 48 mg (0.20 mmol) of 2-deuterio-6,8-dibenzo-2-bicyclo[3.2.2]nonadienol in 0.3 ml of "dry" acetic acid containing 0.099 M perchloric acid was placed in an NMR tube at 40 °C. The excess acetic anhydride converted the alcohol to the acetate **35** immediately. An initial ^{1}H NMR spectrum was recorded, and the rate of **35** scrambling of the C-2 deuterium to the C-1 position (i.e., to give **36**) was followed at 41 °C. After 4 h there was 8 ± 2% protium at C-2. After 6.5 h there was 13 ± 2% and after 11 h there was 20 ± 2%. A second run was made at 25 ± 2 °C. After 26 h there was 4–5% protium at C-2.

A similar run was made on 2-deuterio-3,6-dibenzo-2-bicyclo[3.2.2]-nonadienol (exo:endo mixture from the lithium aluminum deuteride reduction of the ketone). The alcohol was converted to the acetate **42** immediately. By the time (5–7 min) the first scan was recorded the bridge migration had occurred so that a 50:50 mixture of **42** and **43** was observed. The subsequent rearrangement to deuterio-6,8-dibenzo-2-bicyclo[3.2.2]nonadienol acetates (**35** and **36**) was monitored. The half-life at 41 ± 1 °C was 13 ± 2 min and the half-life at 25 ± 2 °C was 50 ± 5 min.

Preparation of Ethyl Propiolate-*3-d*. A mixture of 10.1 ml (9.8 g, 0.10 mol) of ethyl propiolate (Aldrich Chemical Co.), 100 mg of barium oxide, and 18 ml (20 g, 1.0 mol) of 99.8% deuterium oxide (Mallinckrodt) was placed in a small oven-dried flask and stirred for 24 h at room temperature. ^{1}H NMR analysis of the organic phase showed ~95% deuterium at C-3 (δ 3.0). The layers were separated and the ester salted out of the aqueous layer with sodium chloride. The combined ester layers were treated again with deuterium oxide and

barium oxide for a day, after which no C-3 protons were noted by ^{1}H NMR. The deuterated ester was dried ($MgSO_4$) and distilled to give 8.4 g (86%) of ethyl propiolate-*3-d*.

Preparation of Ethyl 8-Deuterio-7-dibenzobicyclo[2.2.2]-octatriene Carboxylate (28). A Pyrex tube (15 × 1 in. o.d., 5/32 wall) was washed with deuterium oxide containing 0.5% barium oxide (by weight), then dried at 110 °C for 6 h. The tube was charged with 9.9 g (0.10 mol) of ethyl propiolate-*3-d*, 8.7 g (0.05 mol) of anthracene, 15 ml of "dry" benzene, and 100 mg of *p-tert*-butyldideuteriocatechol (prepared by an exchange reaction). The tube was sealed and heated at 200–210 °C for 4 h. The tube was cooled and opened. Unreacted anthracene (2.5 g, 0.014 mol) precipitated from the solution and was filtered. The filtrate was subjected to distillation at reduced pressure. The distillate contained benzene and ca. 5 g of ethyl propiolate-*3-d* which was recovered and recycled. ^{1}H NMR analysis of the yellow-orange residue (9.8 g) showed that there was ~4% of anthracene, 10% of ethyl propiolate-*3-d*, and the desired Diels–Alder adduct. The mixture was dissolved in a minimum amount of chloroform and placed on a silica gel column (800 ml of silica gel, 60–200 mesh). The column was eluted with benzene. The first fraction contained 400 mg of anthracene. Subsequent fractions contained ethyl propiolate and the adduct. The ethyl propiolate was removed at 90 °C under reduced pressure. The fractions containing the adduct (8.2 g) were combined and evaporated to dryness. The residue was dissolved in a minimum amount of ethanol and crystallized to give 7.7 g (56%) of **28**. Mass spectral analysis showed 98.5% deuterium incorporation: mp 111–112 °C; ^{1}H NMR ($CDCl_3$) δ 7.13 (m, 8, aromatic H), 5.70 (s, 1, H-1) 5.23 (s, 1, H-4), H-1 and H-4 shift with concentration ±0.1 ppm, 4.18 (q, 2, CH_3CH_2O–), 1.25 (t, 3, CH_3CH_2O–).

Preparation of 7-Hydroxymethyl-8-deuteriodibenzobicyclo[2.2.2]octatriene (29-OH). A solution of 3.4 g (12 mmol) of **28** in 40 ml of anhydrous ether was added dropwise over a period of 30 min, with stirring, to a solution of 0.80 g (6 mmol) of aluminum chloride, *caution*, and 0.70 g (18 mmol) of lithium aluminum hydride in 150 ml of anhydrous ether. The reaction mixture was stirred at room temperature for 2 h and then worked up as described for the protio analogue.[13,14] The best yields of crystalline product were obtained by dissolving the oil in a minimum amount of ethanol and pouring the solution into an evaporating dish. Evaporation of the solvent at room temperature and atmospheric pressure gave white crystals which were dried in a vacuum desiccator (24 h, aspirator pressure) to give 2.6 g (91%) of **29-OH**. A small amound of material was recrystallized from ethanol for melting point comparison with the undeuterated compound:[13] mp 124–125 °C; ^{1}H NMR ($CDCl_3$) δ 7.06 (m, 8, aromatic H), 4.98 (bs, 2, H-1 and H-4), 4.13 (s, 2, $-CH_2OH$), 1.70 (bs, 1, –OH).

Preparation of 7-Chloromethyl-8-deuteriodibenzobicyclo[2.2.2]octatriene (29-Cl).[14] To a solution of 1.3 g (5.6 mmol) of **29-OH** and 1.1 g (5.9 mmol) of tri-*n*-butylamine in 175 ml of anhydrous ether, stirred at room temperature, a solution of 0.70 g (5.9 mmol) of thionyl chloride in 40 ml of anhydrous ether was added dropwise over a period of 20 min. After another 1 h, the reaction mixture was poured into 100 ml of cold water in a separatory funnel. Three extractions with 75 ml each of ether were followed by washing of the ether layers several times with dilute hydrochloric acid, water, and saturated aqueous sodium bicarbonate solution. The ethereal solution was dried ($MgSO_4$) and evaporated to dryness. The crude product (1.1 g, 78%) was dissolved in a minimum amount of chloroform and placed on a silica gel column (100 ml of silica gel 60–200 mesh) and eluted with 10 vol % benzene in Skellysolve B (petroleum ether bp 60–70 °C). The solvent was evaporated and the product was recrystallized from Skellysolve B: mp 147–148.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.13 (m, 8, aromatic H), 5.11 (s, 1, H-1), 5.05 (s, 1, H-4), 4.22 (s, 2, $-CH_2Cl$).

Photorearrangement of 7-Chloromethyl-3-deuteriodibenzobicyclo[2.2.2]octatriene (29-Cl). Preparation of 2-Chloro-4-deuteriodibenzotricyclo[3.2.2.0^{2,4}]nonadiene (30).[14] A quartz tube (7 × 5/16 in o.d.) was charged with 450 mg (1.78 mmol) of **29-Cl**, 0.60 ml of reagent grade acetophenone, and 3.4 ml of spectral quality acetonitrile. The tube was deaerated by bubbling prepurified nitrogen through it for 30 min, stoppered, and irradiated with a 450-W medium-pressure mercury lamp for 48 h. The tube was opened, and the contents were washed into a 125-ml Erlenmeyer flask with acetone. The acetonitrile and acetone were removed at aspirator pressure. The residue was dissolved in a minimum amount of chloroform and placed on a silica gel column (150 ml of silica gel, 60–200 mesh). Elution of the column with 10 vol % benzene in Skellysolve B gave 185 mg (40%) of **30**: mp 115–116.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.22 (sm, 8, aromatic H), 4.51 (s, 1, H-1), 4.37 (s, 1, H-5), 1.19 (d, 1, J_{gem} = 7 Hz, exo H-3), 0.55 (d, 1, J_{gem} = 7 Hz, endo H-3).

Reduction of 30 to 2,4-Dideuteriodibenzotricyclo[3.2.2.0^{2,4}]nonadiene (27). The experimental procedure described here was developed after several trials. Careful exclusion of water was required to obtain high deuterium incorporation, and all glassware was dried at 110 °C for 4–8 h.

Triphenyltin deuteride was prepared by the method of Kuivila,[25] using lithium aluminum deuteride. It was distilled at 162 °C (0.5 mm) and 12.7 g was dissolved in 6 ml of carefully dried benzene, and stored as such in a freezer. One milliliter of this solution, which was fluid enough to handle in a syringe at room temperature, contained 850 mg (2.5 mmol) of triphenyltin deuteride.

To a test tube containing 300 mg (1.18 mmol) of **30** and 150 mg of azoisobutyronitrile (AIBN), fitted with a stirring bar and a serum stopper, was added 2 ml of the triphenyltin deuteride solution. The tube was deaerated with nitrogen, then held in a 70 °C bath for 6 h. The tube was then cooled, the stopper removed, and an additional 150 mg of AIBN added. The tube was resealed, then 2 ml of the tin deuteride solution and 1 ml of benzene were added. The tube was degassed with nitrogen for 15 min and heated at 70 °C for another 6 h. The tube was opened; the contents were washed into a 50-ml round-bottom flask with acetone, and 5 ml of carbon tetrachloride was added. The solution was heated to 70 °C for 15 min, destroying any remaining triphenyltin deuteride, and the solvents were removed at aspirator pressure. The residue was taken up in about 10 ml of hot chloroform (not all the material went into solution). The mixture was filtered onto a 350-ml silica gel, 60–200 mesh column. An additional 5–7 ml of hot chloroform was used to wash the flask and precipitate. The column was eluted with about 2 l. of petroleum ether (bp 60–70 °C), giving ca. 230 mg (88%) of 2,4-dideuteriodibenzotricyclo[3.2.2.0^{2,4}]nonadiene (**27**). The material was recrystallized from petroleum ether. Mass spectral analysis showed ~2% d_0, ~10% d_1, and ~88% d_2 present: mp 176–177 °C; ^{1}H NMR ($CDCl_3$) δ 7.17 (sm, 8, aromatic H), 4.36 (s, 2, H-1 and H-5), 0.50 (bd, 1, J_{gem} = 6 Hz, exo H-3), −0.17 (d, 1, J_{gem} = 6 Hz, endo H-3).

Addition of Acetic Acid to 2,4-Dideuteriodibenzotricyclo[3.2.2.0^{2,4}]nonadiene (27). A solution of 500 mg (4.4 mmol) of **27** in 90 ml of "dry" acetic acid, 0.105 M in perchloric acid, was kept at room temperature (25 ± 2 °C) for 9 h (2 half-lives for the reaction with **1**). The solution was then poured into 50 ml of water in a 250-ml separatory funnel. The solution was extracted with 200 ml of pentane. The pentane layer was washed with two 100-ml portions of cold water, two 75-ml portions of saturated aqueous sodium bicarbonate, and twice with water, then dried ($MgSO_4$), filtered, and evaporated to dryness to give 502 mg of product. The ^{1}H NMR spectrum of the product showed about 25% of **27**. The ^{1}H NMR spectrum of the crude reaction mixture was quite complex but it was clear that 50% deuterium was at the bridgehead of the [3.2.2] product indicating phenyl migration in the ring opening. The acetates were converted to the alcohols with lithium aluminum hydride, and the [3.2.2] alcohol was separated by preparative thin layer chromatography and submitted for mass spectral analysis and HA-100 ^{1}H NMR analysis. The deuterium incorporation was 3–4% d_0, 10% d_1, and 87% d_2.

The ^{1}H NMR spectrum showed[26] that the product contained equal amounts of **31-OH**, **32-OH**, **33-OH**, and **34-OH**. We were able to separate the absorptions due to protons at C-1, C-2, and C-5. The integration of absorption for the C-1 proton was 0.5 H, and the peak was a slightly broadened singlet (this is due to the bridgehead proton in **31-OH** and **32-OH** which is vicinal to a deuterium atom at C-2—the other half of the alcohol mixture has D at C-1—hence the 0.5 intensity). The next higher field peak had an intensity of 1, and had two equal doublets, one a set of exterior peaks, with J = 6–7 Hz, caused by coupling of H-5 with the equatorial (cis to acetoxy) protons at C-4 in **31-OH** and **33-OH**, and the other, a set of interior peaks, with J = 2.4 Hz, due to coupling of H-5 with the axial (trans to acetoxy) proton at C-4 in **32-OH** and **34-OH**. The H-2 proton absorption gives rise to a doublet of doublets (J = 9 and 5 Hz) with the hydrogens at C-3. As the substituent at C-1 is a deuteron when the proton is at C-2, there is no further important coupling. The intensity of this peak was 0.5, and the peak is attributed to the **33-OH–34-OH** equimolar mixture.

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Registry No.—**1**, 30122-20-4; **3**, 59938-53-3; **4**, 59938-54-4; **5**, 59938-55-5; **5** OH analogue, 53483-04-8; **6**, 59938-56-6; **6** OH analogue, 53483-08-2; **7**, 24330-16-3; **8**, 59938-57-7; **8** OH analogue, 59938-58-8; **9**, 59981-06-5; **9** OH analogue, 59981-07-6; **10**, 59981-08-7; **10** OH analogue, 59981-09-8; **11**, 59981-10-1; **11** OH analogue, 59981-11-2; **13**, 59938-59-9; **18**, 59938-60-2; *exo*-**24**, 24332-09-0; *exo*-**24** OH analogue, 23445-14-9; *endo*-**24**, 24332-08-9; *endo*-**24** OH analogue,

23445-15-0; **26**, 23417-00-7; **27**, 59938-61-3; **28**, 59938-62-4; **29**-OH, 59938-63-5; **29**-Cl, 59938-64-6; **30**, 59938-65-7; anthracene, 120-12-7; *trans*-1,3-dichloropropene, 10061-02-6; *cis*-1,3-dichloropropene, 10061-01-5; acetic acid, 64-19-7; *cis*-1-propenyl acetate, 3102-47-4; *trans*-1-propenyl acetate, 1528-10-5; *p*-bromobenzenesulfonyl chloride, 98-58-8; *syn*-8-methyl-2-dibenzobicyclo[3.2.1]octadienone, 59938-66-8; *anti*-8-methyl-2-dibenzobicyclo[3.2.1]octadienone, 59981-12-3; lithium aluminum hydride, 16853-85-3; 3,6-dibenzo-2-bicyclo[3.2.2]nonadienone, 24330-03-8; ethyl propiolate-*3-d*, 59938-67-9.

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Ionic Reactions in Bicyclic Systems. 9. Preparation of Optically Active 1,2-Dimethyl-*exo*-2-norbornyl, 1,2-Dimethyl-*exo*-2-benzonorbornenyl, and 6,7-Dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl Chloride

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Hydrochlorination of optically active 1-methyl-2-methylenenorbornane (1) in pentane at −78 °C gives active 1,2-dimethyl-*exo*-2-norbornyl chloride (2) with ~27% retention of optical configuration. Under similar conditions active 1-methyl-2-methylenebenzonorbornene (3) gives active 1,2-dimethyl-*exo*-2-benzonorbornenyl chloride (4) (~80% retention) and active 6,7-dimethoxy-1-methyl-2-methylenebenzonorbornene (5) gives 6,7-dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl chloride (6) with about 13% retention of optical configuration.

Recently we reported results of solvolytic studies of optically active 1,2-dimethyl-*exo*-2-norbornyl chloride (**2**)[1] and 1,2-dimethyl-*exo*-2-benzonorbornenyl chloride (**4**).[2] We have also investigated the 6,7-dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl system[3] including the optically active tertiary chloride (**6**). We now present details of the preparation of these optically active tertiary chlorides.

A possible route to the optically active tertiary chlorides was suggested by the work of Brown and Liu,[4] who observed that under carefully controlled conditions, hydrochlorination of deuterium labeled 1-methyl-2-methylenenorbornane (**1**) gives **2** with only partial scrambling of the methyl groups. Exposure of the product to hydrogen chloride at 0 or −78 °C results in randomization of the methyl groups (hydrogen chloride catalyzed isomeric Wagner–Meerwein rearrangement[5]). A corollary of that work is that optically active **1** should lead to active **2**; however, **2** racemizes under the conditions of the hydrochlorination.

The preparation and determination of absolute configurations and rotations of optically active 1-methyl-2-methylenenorbornane (**1**),[6] 1-methyl-2-methylenebenzonorbornene (**3**),[7] and 6,7-dimethoxy-1-methyl-2-methylenebenzonorbornene (**5**)[8] have been reported elsewhere.[9] Attempts to prepare optically active **2** from active **1** under conditions reported[4] to give minimum scrambling of the methyl groups (hydrochlorination of neat **1**, 0 °C, 1–2 min) were unsuccessful. Hydrogen chloride uptake ceased at about 60% reaction—the remaining liquid **1** was encapsulated by the solid adduct (**2**)—and active chloride could not be separated from the mixture. Evidently, in the earlier work[4b] unreacted **1** in the product did not interfere with NMR analysis of the tertiary chloride. In the present work the additional handling required for separation of pure **2** resulted in racemization.

Hydrochlorination of (−)-**1** in pentane at −78 °C is complete in a few minutes—the reaction is somewhat slower at 0 °C. Removal of the pentane and excess hydrogen chloride under high vacuum at <0 °C gave homogeneous (−)-**2**. The purity of racemic and optically active **2** obtained by this procedure was established by the NMR spectrum, solvolysis equivalent, elemental analysis, and mass spectrum. Efficient