potassium thiocyanate followed by analysis as in method I. In this manner four points could be obtained during the first three half-lives of the reaction. Attempts to slow down the reaction by carrying it out at lower concentrations failed due to complications in the analyses. In our solvent system one is, of course, limited in that lower temperatures are not accessible.

Method III. Relative rates were determined by means of competition experiments which were carried out in nmr tubes. The desired amounts of cyclopropanol substrates (a and b) were weighed out and dissolved in acetic acid-d_4. Mercury(II) acetate (c) was then added and the solution shaken until the reaction was complete. (The initial molar ratio of a:b:c was 1:1:0.9). The sample was then analyzed by nmr to determine the ratio of starting cyclopropyl compounds. From the known initial amounts of starting materials and the stoichiometry of the reaction the relative rate, k_a/k_b, could be determined using eq 8.

Acknowledgments. We wish to thank the National Science Foundation for a grant (No. GP 6536X) in support of this work. This investigation was also supported in part by a National Institutes of Health Fellowship (5-FO2-GM 37548) from the National Institutes of General Medical Sciences to A. D.

Bridged Polycyclic Compounds. LXII. Stereochemistry and Mechanisms of Electrophilic Additions to Cyclopropane Rings[1]

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Abstract: A number of electrophilic additions to the cyclopropane ring of dibenzotricyclo[3.3.0.0^{2,8}]octadiene (**4**) have been scrutinized. These include addition of bromine, the elements of methyl hypobromite (bromine in methanol), and hydrogen bromide. In addition, the latter reagent has been added to the dideuterio analog (**15**) of **4**. All reagents add to the bond between the benzylic carbon atoms. This system allows for study of the stereochemistry of attack by both electrophile and nucleophile. The results and those available in the literature are discussed in terms of plausible mechanisms for additions to cyclopropanes.

There has been much interest recently in the stereochemistry of additions to cyclopropane rings. Electrophilic additions recently described include: addition of deuterioacetic acid to nortricyclene,[2] which proceeds with 50% retention and 50% inversion at the site of electrophilic attack, and complete inversion at the site of nucleophilic attack, presumably *via* norbornyl cation; addition of deuterioacetic acid to 1-methylnortricyclene,[3] which occurs with 60% retention and 40% inversion at the site of electrophilic attack and 100% inversion by nucleophile; and addition of deuterioacetic acid to tricyclo[3.2.1.0^{2,4}]octane,[4] which gives largely inversion at each reaction site.

Addition of deuterioacetic acid to bicyclobutane[5a] proceeded with retention by the deuteron, a result opposite to that of addition of deuterium oxide to a more complex bicyclobutane,[5b] where inversion by both electrophile and nucleophile was observed.

Very recently it was reported[6] that deuterioacetic acid and deuterium bromide both add to a tricyclo[3.2.2.0^{2,4}]nonene with retention at the site of electrophilic attack. This is similar to additions of protic species to cyclopropanols and to cyclopropyl acetates, which appear to go largely (if not stereospecifically) with retention of configuration.[7-9] On the other hand, treatment of cyclopropanols with bromine appears to involve electrophilic attack with inversion.[7]

This confusing situation with respect to electrophilic ring cleavage is not paralleled by nucleophilic ring opening, where all of the cases studied[10,11] showed complete inversion by nucleophile.

Interest in this laboratory in the question of electrophilic attack upon cyclopropane rings began with our studies[12a] on the addition of bromine to quadricycloheptanedicarboxylic acid (**1**), where it was shown that addition of bromine led to **2**, a reaction involving inversion at both sites.[13] A similar situation obtained[12b] in addition of water to **1**, leading to **3**. The availability[14] of dibenzotricyclo[3.3.0.0^{2,8}]octadiene (**4**) made this an interesting candidate for studies of electrophilic additions, as, in general, it would be

(1) Paper LXI: S. J. Cristol and D. K. Pennelle, *J. Org. Chem.*, in press.

(2) A. Nickon and J. H. Hammons, *J. Amer. Chem. Soc.*, **86**, 3322 (1964).

(3) J. H. Hammons, E. K. Probasco, L. A. Sanders, and E. J. Whalen, *J. Org. Chem.*, **33**, 4493 (1968).

(4) R. T. LaLonde, J. Ding, and M. A. Tobias, *J. Amer. Chem. Soc.*, **89**, 6651 (1967).

(5) (a) K. B. Wiberg and G. Szeimies, *ibid.*, **90**, 4195 (1968); (b) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

(6) J. B. Hendrickson and R. K. Boeckman, Jr., *J. Amer. Chem. Soc.*, **91**, 3269 (1969).

(7) (a) C. H. DePuy and F. W. Breitbeil, *ibid.*, **85**, 2176 (1963); (b) C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *ibid.*, **88**, 3347 (1966); (c) C. H. DePuy, W. C. Arney, Jr., and D. H. Gibson, *ibid.*, **90**, 1830 (1968); (d) C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).

(8) A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *J. Amer. Chem. Soc.*, **85**, 3713 (1963).

(9) P. J. Wharton and T. I. Bair, *J. Org. Chem.*, **31**, 2480 (1966).

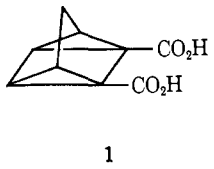
(10) J. Meinwald and J. K. Crandall, *J. Amer. Chem. Soc.*, **88**, 1292 (1966).

(11) (a) S. J. Cristol, J. K. Harrington, and M. S. Singer *ibid.*, **88**, 1529 (1966); (b) M. S. Singer, Ph.D. Thesis, University of Colorado, Boulder, Colo., 1966; (c) S. J. Cristol and B. B. Jarvis, *J. Amer. Chem. Soc.*, **89**, 5885 (1967).

(12) (a) S. J. Cristol and R. T. LaLonde, *ibid.*, **80**, 4355 (1958). (b) S. J. Cristol, P. S. Reeder, and J. K. Harrington, unpublished work.

(13) In the original paper, the stereochemistry of attachment of the bromine atom at C-5 (that is, the nucleophilic reagent) in **2** was not completely proven. Subsequent work[11a] has made it clear that **2** is in fact the correct structure of the dibromide.

(14) (a) G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 131 (1965); (b) E. Ciganek, *ibid.*, **88**, 2883, (1966); (c) S. J. Cristol and B. B. Jarvis, *ibid.*, **88**, 3095 (1966); **89**, 401 (1967).



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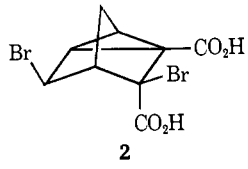

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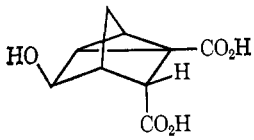

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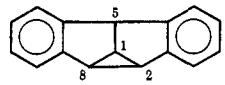

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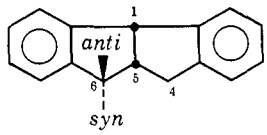
possible to learn the stereochemistry of incorporation of both electrophile and nucleophile from nmr studies, whether ring cleavage occurred by addition to the 1,2 bond to give bicyclo[3.2.1]octadiene derivatives or *via* addition to the 2,8 bond to give bicyclo[3.3.0]-octadiene (**5**) derivatives. In fact, all additions proceeded by cleavage of the bond between the benzylic carbon atoms, that is, to give derivatives of **5**. Structural information comes from the fact that protons at C-4 or C-6 *cis* to the C-5 proton have larger coupling constants with the C-5 proton than those *trans*. Struc-



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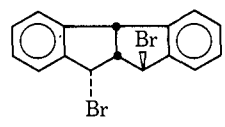

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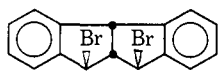

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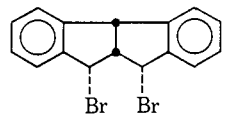


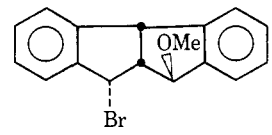
8

tural data on the products of our experiments are given in the Experimental Section.

When **4** was treated with bromine in ethyl acetate, it reacted rapidly and cleanly to give the *trans*-dibromide **6**. It could be epimerized readily by warming (presumably *via* a carbonium ion process) to a 30:70 mixture of **6** with its *anti-cis* isomer **7**. In neither the kinetic product nor the thermodynamic mixture could any of the *syn-cis* isomer **8** be detected.[15] The result shows that ring opening involves one inversion and one retention, but does not sort out which is which. However, addition of bromine in methanol gave the *syn*-6-bromo-*anti*-4-methoxy ether **9**, a reaction in which electrophilic attack has occurred with retention and nucleophilic attack with inversion. The stereochemistry of the carbon atoms bearing the bromine and methoxy groups was demonstrated on the bromo ether and that bearing the methoxyl group was confirmed by reduction to the *anti*-methyl ether **10**. **10** was prepared for comparison, along with its epimer **11**, by methanolysis of monobromides **12** and **13**.

We next decided to look at addition of hydrogen bromide (in methylene chloride) to **4**. To our surprise the *syn* bromide **13** was obtained (*i.e.*, nucleophilic attack occurred with retention), almost pure after about 10% reaction. By the time the reaction was complete the ratio of **13** to **12** was 57:43, and, after 12 hr standing in a solution saturated with hydrogen

(15) Models of **8** show very large steric interference between bromine atoms. The steric interactions are less in **6** and still less in **7**.



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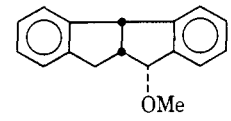

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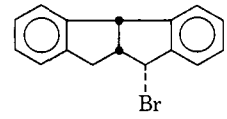

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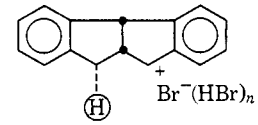
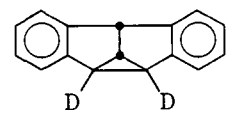


14

bromide, the equilibrium mixture (21:79 of **13**:**12**) was formed. As this appeared to be the first addition in which predominant retention at the site of attack by nucleophile has been observed in either electrophilic or nucleophilic ring opening, it seemed important to scrutinize this more closely. It seemed possible that the retention might be due to collapse of a tight ion pair such as **14**, formed by proton transfer (with retention), before epimerization of that ion pair, to give the equivalent of a *cis* addition (both with retention).[16] Problems of sorting out proton frequencies made it simpler to analyze the product by addition of hydrogen bromide to the dideuterio compound **15** rather than by the addition of deuterium bromide to **4**. The synthesis of **15** *via* the hydrolysis of **6** and **7** to the corresponding



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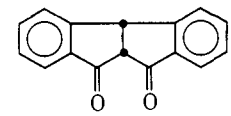

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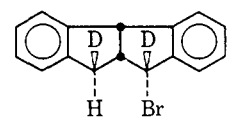

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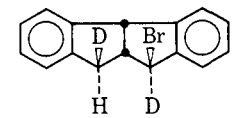

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diols, oxidation to the diketone **16**, reduction with lithium aluminum deuteride to the dideuterio diols, conversion to the dideuterio dibromides, and 1,3 elimination of bromine to **15** is described in the Experimental Section.

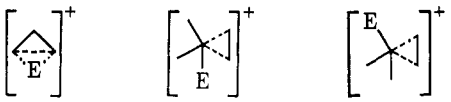
Addition of hydrogen bromide in methylene chloride to **15** gave protolysis of the ring with retention to give **17**. The structure of **17** was established by pmr studies, and was confirmed by conversion of **17** to **18** and consideration of its spectrum. These data show that a carbonium ion intervenes in the addition process and that the Dewar–Fahey-like intermediate **14** may also be involved.

To summarize briefly, it is clear that stereochemical inversion or retention of configuration by electrophile and by nucleophile may attend electrophilic addition to cyclopropanes, and that no single mechanism can accommodate these data.

(16) This is analogous to the proposal made by Dewar and Fahey[17] to explain *cis* addition to certain olefins.

(17) M. J. S. Dewar and R. C. Fahey, *Angew. Chem. Intern. Ed. Engl.*, 3, 245 (1964).

It has become clear recently, from both theoretical and experimental results, that "edge-protonated" (or hydrogen-bridged) cyclopropanes (**19**) and "corner- or point-protonated" cyclopropanes (**20**) do not differ substantially in energy and that the same is undoubtedly true for complexes between other electrophiles and cyclopropanes. For example, Klopman's calculations



19 **20a** **20b**

on protonated nortricyclene[18] suggest that edge- and corner-protonated species may have essentially identical energies, and Olah's[19] work shows that these differ by not more than 6 kcal/mol, with corner-protonated nortricyclene (nonclassical norbornyl cation) the more stable species. The 7-norbornadienyl cation described in detail by Winstein and his students[20] is a further example of a stable corner-protonated cyclopropane.

Presumably similar small differences in energy obtain between edge and corner species with other cyclopropanes. Indeed this has been suggested to explain mixing in addition of deuterium oxide and deuterium sulfate to cyclopropane,[21] where the 1-propanol mixture had molecules labeled at C-3, as anticipated, but also others labeled at C-2 or at C-1. A similar explanation has been set forth[22] to rationalize the formation of 1,1- and 1,2-, as well as the anticipated 1,3-dibromopropane from bromine, ferric bromide, and cyclopropane, and for analogous compounds produced in the aluminum chloride catalyzed addition of acetyl chloride to cyclopropane.[23] Calculations on protonated cyclopropane itself suggest that the edge-protonated species may be 10 kcal/mol more stable than the corner-protonated species,[24] but whether these calculations will be corroborated experimentally may be questioned in view of Olah's results.[19] In any case, the proton migrations accompanying the additions described above show that energy barriers between the generalized species **19** and **20** are small.

Our present system, as well as those described earlier,[2-9,12] shows no scrambling of protons, so that the stereochemistry of reagent attack is the only evidence available for discussion. Hendrickson and Boeckman[6] have most recently and quite lucidly discussed retention *vs.* inversion in electrophilic attack as involving reaction of electrophile with either the front lobe or the rear lobe of the σ bond *undergoing cleavage*. This may be an unnecessarily restrictive assumption, as initial attack may in fact involve an *edge which does not finally suffer cleavage*, with cleavage occurring after edge-to-corner isomerization.[25]

(18) G. Klopman, *J. Amer. Chem. Soc.*, **91**, 89 (1969).

(19) G. A. Olah, Abstracts of the 21st National Organic Chemistry Symposium, Salt Lake City, Utah, June 1969, p 100; G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3954, 3956 (1969).

(20) See R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **90**, 7364 (1968), and references therein.

(21) R. L. Baird and A. A. Aboderin, *ibid.*, **86**, 252 (1964).

(22) N. C. Deno and D. N. Lincoln, *ibid.*, **88**, 5357 (1966).

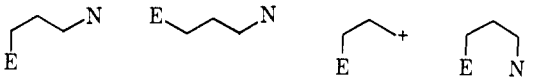
(23) H. Hart and R. H. Schlosberg, *ibid.*, **88**, 5030 (1966); **90**, 5189 (1968).

(24) H. Fischer, H. Kollmar, H. O. Smith, and K. Miller, *Tetrahedron Lett.*, 5821 (1968).

(25) This is explicity shown and discussed in the paper of Nickon and Hammons,[2] and we would agree with those authors that there is a possibility that the edge protonation may be bypassed, that is, corner protonation may occur directly.

This unfortunately exchanges one problem for another, that is, why does electrophilic attack occur on the side of the bond to be cleaved in some cases and on an opposite side in others? The data described above show that in some cases, proton and bromine cation donor attacks occur from the same direction, and in others in opposite directions, but without an obvious pattern. Clearly there are no gross preferences involved, but rather some subtle admixture of non-overwhelming factors. Presumably these may be steric and bridging abilities. Our present knowledge does not appear to warrant more detailed discussion.

With respect to nucleophilic attack, it is possible to assume that an edge-protonated species **19** may suffer nucleophilic displacement giving the stereochemical result of electrophilic retention and nucleophilic inversion, *i.e.*, to **21**. A similar stereochemical result could occur by nucleophilic attack at one of the electron-deficient centers in **20a** or **20b**. The opposite stereochemistry would be observed for the electrophile, but inversion again by nucleophile to give **22**, if attack occurred at the other position in **20a** or **20b**.



21 **22** **23** **24**

These account for all of the stereochemical results described in the literature, but not for our addition of hydrogen bromide to **4** to give **13**, or that of hydrogen bromide to **15** to give **17**, where nucleophilic attack with retention is the major stereochemical outcome. This must be the result of protonation at a corner or at an edge *syn* to the bond ultimately cleaved (to give electrophilic retention) followed by transformation of **19** or **20a** to a carbonium ion **23**. This, in principle, could suffer capture from either side. In our case, attack from one side (*syn*) is kinetically preferred, although the rapid epimerization of **13** to **12** teaches us that capture from the *anti* side does occur fairly readily. In the dibenzotricyclooctane ring system we have been working with, isomerization from the electrophile–cyclopropane complex (**19** or **20**) to the carbonium ion can occur readily, as a relatively stable secondary benzylic cation, analogous to **14**, is formed. Such isomerization may in fact also occur in the bromine addition to give a cation **23**-Br, which for steric reasons chooses to react with nucleophile from the *anti* side,[15] although this is not presently distinguishable from direct nucleophilic attack on **19** or **20a**. The analogous isomerization of the corner-protonated norbornyl cation to a carbonium ion has been proposed[26] as the reaction path involved in the transformation of *exo*-2-norbornyl derivatives to *endo*. Alternatively, addition of electrophile could bypass the three-membered ring complex, that is, proceed directly to carbonium ion, *via* an S$_E$2 process.

There has been much interest recently in the stereochemistry of the S$_E$2 process at saturated carbon atoms, and it has been suggested[7b] that electrophilic cleavage of cyclopropanes might offer a good possibility for determining such stereochemistry. It is apparent that most cleavages of cyclopropanes do not furnish useful

(26) See H. L. Goering and C. B. Schewene, *J. Amer. Chem. Soc.*, 87, 3516 (1965), and ref 2–5 therein.

models for the SE2 process, assuming that this process, analogous to the SN2 process, does not involve an intermediate, but rather is a direct displacement of electrofuge by electrophile. It would appear that cyclopropanol systems, such as DePuy has studied,[7] and systems such as those described in this paper, would offer the best possibilities of ring cleavage synchronous with electrophilic attack, *i.e.*, of an SE2 process. However, it is now apparent[7] that cyclopropanol ring cleavages do not furnish clear-cut patterns for stereochemical preferences, and it remains to be seen whether electrophilic retention will be generally observable with other compounds with the ring system of **4** and with all electrophilic reagents.

Experimental Section

Melting points are uncorrected. Proton magnetic resonance spectra were obtained with a Varian A-60-A or Varian HA-100. Apparent coupling constants are given in hertz. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

trans-**4,6-Dibromodibenzobicyclo[3.3.0]octadiene (6).** A solution of 320 mg (2.00 mmol) of bromine in 25 ml of ethyl acetate was added slowly, with stirring, to a solution of 408 mg (2.00 mmol) of dibenzotricyclo[3.3.0.$0^{2,8}$]octadiene (**4**)[14b] in 150 ml of ethyl acetate. The solvent was removed under reduced pressure at water bath temperatures of 35–45°. Recrystallization from acetone yielded 550 mg (76%) of *trans*-4,6-dibromodibenzobicyclo[3.3.0]-octadiene (**6**): mp 160–161°; pmr ($CDCl_3$) τ 5.08 (1 H, d, C-1 H), 4.22 (1 H, d, C-6 bearing *anti*-bromine H), 4.28 (1 H, d, C-4 bearing *syn*-bromine H), and 6.12 (1 H, sextet, C-5 H); J_{45} = 7, J_{15} = 8, and J_{56} = 3.

Anal. Calcd for $C_{16}H_{12}Br_2$: C, 52.78; H, 3.32. Found: C, 52.74; H, 3.46.

cis-anti-**4,6-Dibromodibenzobicyclo[3.3.0]octadiene (7).** When a solution prepared as above was allowed to stand for 12 hr in the presence of a small amount of excess bromine, it was partially converted to the *anti-cis*-dibromide **7**. The solvent was removed and the remaining oil dissolved in acetone from which the *trans*-dibromide (**6**) was removed by repeated crystallizations. The *cis*-dibromide (**7**) was precipitated by addition of petroleum ether (bp 60–70°). Successive recrystallizations from petroleum ether and carbon tetrachloride yielded pure **7**: mp 115–116°; pmr (CCl_4) τ 5.04 (1 H, d, C-1 H), 4.68 (2 H, d, C-4 H and C-6 H), and 5.90 (1 H, sextet, C-5 H); J_{15} = 7 and J_{45} = J_{56} = 4.

Anal. Calcd for $C_{16}H_{12}Br_2$: C, 52.78; H, 3.32. Found: C, 52.96; H, 3.50.

Complete equilibration (in ethyl acetate at room temperature, 16 hr) gave a mixture of 30% of **6** and 70% of **7**.

syn-4-**Bromodibenzobicyclo[3.3.0]octadiene (13).** Hydrogen bromide was bubbled through a solution of 400 mg (1.96 mmol) of **4** in 75 ml of dichloromethane for 4 hr at 25°. The solvent was removed at 30–40° (aspirator). Acetone was added to the residual orange syrup and **13** crystallized. Recrystallization from acetone yielded 102 mg (38%) of **13**: mp 119–120.5°; pmr ($CDCl_3$) τ 4.36 (1 H, d, C-4 H), 5.42 (1 H, d, C-1 H), 6.40 (1 H, octet, C-5 H), and ~6.88 (2 H, triplet, C-6 *syn*-H and C-6 *anti*-H); J_{15} = 7, J_{45} = 7, J_{56anti} = 8.5, J_{56syn} = 7, $J_{6anti6syn}$ = 0, C-5 H multiplet width = 29. For analysis of this spectrum, see below.

Anal. Calcd for $C_{16}H_{13}Br$: C, 67.37; H, 4.56. Found: C, 67.22; H, 4.66.

anti-**4-Bromodibenzobicyclo[3.3.0]octadiene (12).** A solution of **13** prepared as above was allowed to equilibrate for 12 hr at 25° before removal of dichloromethane. The *syn*-bromide **13** was partially removed by crystallization from acetone, and the acetone removed at 30–40° (aspirator). The residual orange syrup was dissolved in pentane and eluted with pentane from a 100-g silica gel column (1-in. diameter). Pentane was removed (aspirator). The clear syrup remaining contained some **13** (7%) and this amount was reduced by crystallization from acetone. Acetone was removed at aspirator pressures and the remaining oil crystallized at 0° after several weeks. Traces of solvent were removed at 10-Torr pressure to leave 41 mg (15%) of **12**: mp 39°; pmr ($CDCl_3$) τ 4.75 (1 H, d, C-4 H), 5.28 (1 H, d, C-1 H), 6.32 (1 H, m, C-5 H), 6.82 (1 H, quartet, C-6 *anti*-H), and 7.39 (1 H, quartet, C-6 *syn*-H); J_{15} = 7.0, J_{45} = 3.0, J_{56anti} = 6.5, J_{56syn} = 8.5, and $J_{6anti6syn}$ = 15.5, C-5 H multiplet width = 25. For analysis of this spectrum, see below.

Anal. Calcd for $C_{16}H_{13}Br$: C, 67.37; H, 4.56. Found: C, 67.12; H, 4.43.

syn-**4-Methoxydibenzobicyclo[3.3.0]octadiene (11) and** *anti*-**4-Methoxydibenzobicyclo[3.3.0]octadiene (10).** A solution of 2.0 g (7.0 mmol) of a mixture of **12** and **13** in 100 ml of anhydrous methanol containing a few drops of pyridine was stirred for 3 days at 25°. The methanol was evaporated (aspirator) at 40–50°. The residue was dissolved in petroleum ether (bp 60–70°) and eluted with petroleum ether from a 100-g alumina column (1-in. diameter). Two distinct fractions were eluted. The solvent from the first fraction was evaporated (aspirator) at 30–40°, yielding 520 mg (31%) of *syn*-methoxide (**11**): mp 137–139.5°; pmr ($CDCl_3$) τ 6.40 (1 H, m, C-5 H), 6.48 (3 H, s, methoxy H), 7.00 (1 H, d, C-6 *syn* H), 7.04 (1 H, d, C-6 *anti* H), 5.52 (1 H, d, C-1 H), and 5.06 (1 H, d, C-4 H); J_{15} = 7.5, J_{45} = 7, J_{56anti} = 10, J_{56syn} = 7, and $J_{6anti6syn}$ = 0.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.45; H, 6.77. Found: C, 86.18; H, 6.69.

The solvent from the second fraction was similarly evaporated yielding 710 mg (48%) of the *anti*-methoxide (**10**): mp 83–85°; pmr ($CDCl_3$) τ 5.26 (1 H, d, C-1 H), 5.38 (1 H, d, C-4 H), 6.59 (3 H, s, methoxy H), 7.28 (1 H, quartet, C-7 *syn* H), ~6.68 (2 H, m, C-5 H and C-6 *anti* H); J_{15} = 7, J_{45} = 2.5, J_{56syn} = 9.5, $J_{6anti6syn}$ = 18, J_{56anti} indeterminate due to peak overlap.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.45; H, 6.77. Found: C, 86.67; H, 6.58.

Dibenzobicyclo[3.3.0]octadiene-4,6-dione (16) and 2,8-Dideuteriodibenzotricyclo[3.3.0.$0^{2,8}$]octadiene (15). A solution of 3.64 g (10 mmol) of **6** in 100 ml of acetone, 10 ml of water, and 0.5 ml of pyridine was stirred for 12 hr at 25°. The reaction mixture was concentrated (aspirator) at 40–50°. Dichloromethane (100 ml) and 100 ml of dilute hydrochloric acid were added. The solvent was evaporated from the organic phase (aspirator) at 25–30°. A solution of 3.00 g (10 mmol) of sodium dichromate dihydrate was added to a solution of the residue in 100 ml of acetone during 1 hr; the solution was stirred for 6 hr at 25°. The solution was concentrated to 50 ml (aspirator) at 40–50°. Dichloromethane (100 ml) was added and the solution was washed with five 100-ml portions of water and once with 100 ml of 10% sodium bicarbonate solution. The organic phase was dried ($MgSO_4$). The solvent was distilled (aspirator). The crude product was recrystallized from acetone and water yielding 1.98 g (85%) of dione **16**: mp 257–259°; pmr ($CDCl_3$) τ 4.92 (1 H, d, C-1 H), 5.97 (1 H, d, C-5 H); J_{15} = 6.

Anal. Calcd for $C_{16}H_{10}O_2$: C, 82.06; H, 4.27. Found: C, 82.26; H, 4.20.

The dione **16**, 1.98 g, 8.5 mmol, was dissolved in 150 ml of anhydrous ether and 420 mg (10 mmol) of lithium aluminum deuteride was added. Ethyl acetate was added to the solution after 12 hr of stirring at 25°, followed by addition of hydrochloric acid. The mixture was filtered and the insoluble portion was washed with ether and dichloromethane. The filtrate and washings were concentrated to 150 ml (aspirator) at 30–40°. The concentrate was washed twice with 100-ml portions of dichloromethane. The combined organic phases were concentrated to 75 ml (aspirator) at 30–40° and dried ($MgSO_4$ and $NaHCO_3$). The solvent was evaporated (aspirator). The residue was dissolved in phosphorus tribromide (40 ml) and the solution was held for 12 hr at 25°. The reaction mixture was slowly poured onto 300 g of ice and stirred until the excess phosphorus tribromide had reacted. The reaction mixture was extracted with three 100-ml portions of chloroform. The combined organic phases were concentrated to 100 ml (aspirator) and dried ($MgSO_4$ and $NaHCO_3$). The residue from evaporation of solvent (containing 4,6-dideuterio dibromides analogous to **6** and **7**) was dissolved in 50 ml of dry dimethoxyethane (glyme). Sodium (460 mg, 20 g-atoms) was added to 25 ml of toluene in a three-necked Morton flask equipped with a nitrogen inlet, magnetic stirrer, and reflux condenser. The toluene was heated to reflux and the molten sodium was dispersed by stirring. Continued stirring and rapid cooling provided finely particulated sodium to which was added the glyme solution of the 4,6-dideuterio dibromides. The mixture was stirred for 3 hr at 25°. The mixture was filtered, the solids were washed with dry glyme, and 200 ml of water was added. The solution was extracted with three 100-ml portions of ether. The ether was evaporated (aspirator). The oily residue crystallized upon addition of alcohol. Recrystallization from alcohol yielded 880 mg (43%) of 2,8-dideuteriodibenzotricyclo[3.3.-0.$0^{2,8}$]octadiene (**15**): mp 98–100°; pmr ($CDCl_3$) τ 5.60 (1 H,

d, C-5 H), 6.42 (1 H, broad d, C-1 H); $J_{15} = 6$. We estimate (pmr analysis) that there was less than 5% of hydrogen at the 2 (or 8) positions.

anti-**4-Methoxy-*syn*-6-bromodibenzobicyclo[3.3.0]octadiene (9) and *anti*-4-Methoxydibenzobicyclo[3.3.0]octadiene (10).** Bromine (150 mg, 0.94 mmol) was added at 0° to a solution of 204 mg (1.00 mmol) of **4** in 25 ml of anhydrous methanol. After 1 min, the solution was poured into 100 ml of chilled (0°) carbon tetrachloride. Chilled 0.2 *M* sodium thiosulfate solution (100 ml) was added; the mixture was shaken vigorously. The organic layer was washed with two 100-ml portions of ice water, and swirled for 1 min with magnesium sulfate. The solution was filtered, and the solvent was evaporated (aspirator) at 20°. Pmr analysis ($CDCl_3$) revealed that most of the product (89%) was *anti*-4-methoxy-*syn*-6-bromodibenzobicyclo[3.3.0]octadiene (**9**) as judged by the ratio of protons at τ 4.38 (1 H, d, C-6 H), $J_{56} = 8$, compared to total aromatic protons (8 H). Other major resonances were at τ 4.98 (1 H, d, C-4 H), $J_{45} = 3.5$, 5.28 (1 H, d, C-1 H), $J_{15} = 6.5$, 6.58 (3 H, s, methoxy H), and 6.60 (1 H, m, C-5 H), $J_{45} = 3.5$, $J_{15} = 6.5$. Extraneous peaks appeared, possibly due to methanolysis products of **9**. For example, there was an additional methoxy peak at τ 6.56. To show this was not due to a *syn*-4-methoxy group, the product mixture was dissolved in 100 ml of anhydrous ether and heated at reflux in a N_2 atmosphere with 243 mg (10 mg-atoms) of magnesium turnings for 3 hr. The reaction mixture was filtered and extracted with 100 ml of 1% hydrochloric acid. The organic phase was extracted with 100 ml of 10% sodium bicarbonate solution and dried ($MgSO_4$). The ether was evaporated (aspirator). Elution of the residue from an alumina column with petroleum ether gave 177 mg (50%) of the *anti*-methoxy ether (**10**) as determined by pmr comparison with an authentic sample. None of the *syn*-methoxy ether (**11**) was eluted. Elution with ether gave 150 mg of other substances which gave proton resonances.

Addition of Hydrogen Bromide to Dibenzotricyclo[3.3.0.$0^{2,8}$]-octadiene (4). Equilibration of *anti*- (12)- and *syn*-4-Bromodibenzobicyclo[3.3.0]octadiene (13). Hydrogen bromide was added to a solution of **4** (204 mg; 1 mmol) in 75 ml of dichloromethane at a rate of about 100 ml/min at 630 Torr for 5 min. The solvent was removed (aspirator). Pmr analysis of the residue indicated 10% of addition product, all *syn* epimer **13**, and 90% of **4**. The residue was dissolved in 75 ml of dichloromethane and more hydrogen bromide introduced for 220 min. Similar analysis showed only addition products in a ratio 57:43 for **13** and **12**, respectively. Reaction was continued with hydrogen bromide bubbling for 5 min and the solution was allowed to stand for 12 hr. Pmr analysis revealed a 21:79 ratio of **13** to **12**. This ratio did not change after 12 hr in dichloromethane saturated with hydrogen bromide.

Addition of Hydrogen Bromide to 2,8-Dideuteriobenzotricyclo-[3.3.0.$0^{2,8}$]octadiene (15). Hydrogen bromide was added to a solution of 220 mg (1.1 mmol) of **15** in 75 ml of dichloromethane at a rate of about 50 ml/min at 630 Torr for 200 min. The solution was allowed to stand for 12 hr. The dichloromethane was evaporated (aspirator) at 25–30°. Pmr analyses revealed a 79:21 ratio of *anti*-4-bromo-*syn*-4,*anti*-6-dideuteriodibenzobicyclo[3.3.0]-octadiene (**18**) and *syn*-4-bromo-*anti*-4,*anti*-6-dideuteriodibenzobicyclo[3.3.0]octadiene (**17**), respectively.

Pmr analysis ($CDCl_3$) for **18** showed: τ 5.18 (1 H, d, C-1 H), 6.25 (1 H, t, C-5 H), 7.28 (1 H, broad d, C-6 H); $J_{15} = 7.5$, $J_{56} = 6$; pmr ($CDCl_3$) for **17**: τ 5.42 (1 H, C-1 H), 6.25 (1 H, t, C-5 H), 6.88 (1 H, broad d, C-6 H); $J_{15} = 7$, $J_{56} = 6$. Confirmation of these results was obtained from pmr spectra on a 100-MHz instrument. Spin decoupling of the C-5 proton resonances resulted in singlets at τ 5.20 and 7.28 (broad) for **18** and τ 5.42 and 6.88 (broad) for **17**. We estimate the limit of detection of protons on C-4 or of *syn* proton on C-6 to be 5–10% (pmr analysis). No such protons were detected.

Structural Analysis of 17 and 18. For the analysis of **17** and **18**, it is necessary to assign the pmr absorbance for the undeuterated compounds **12** and **13**, in particular, those for the protons at C-6. In compound **12** the C-6 *syn*-H and C-6 *anti*-H have different chemical shifts. One absorbs at τ 7.40 with $J_{56} = 6.5$ Hz, and the other absorbs at τ 6.82 with $J_{56} = 8.5$ Hz. The geminal splitting, $J_{6_{syn}6_{anti}}$, is 15 Hz. On the basis of coupling with the C-5 H, the proton absorbing at τ 7.40 would be assigned to the *syn* proton, as such protons in other compounds[11c] have shown smaller couplings than epimeric *anti* protons. This conclusion can also be reached on the basis of bond angles measured in models. In compound **13**, the C-6 *syn* and C-6 *anti* protons both absorb at about τ 6.87, and no geminal splitting is observed. Thus, the *syn* proton at C-6 is shifted downfield from its normal position at around τ 7.40 by a *syn* bromine which has a deshielding effect. This shift has also been observed in the epimeric dibromides (**6** and **7**). In **7** the C-4 and C-6 protons absorb at τ 4.67 and we may take this as the normal chemical shift for a *syn* proton where an *anti* bromine is bonded to the same carbon atom. In compound **6** the *syn* proton (C-4 proton) absorbs at τ 4.22; $J_{45} = 3$. The assignment of this proton is certainly indicated by the small coupling constant (the *anti* proton at C-6 absorbs at τ 4.28; $J_{56} = 8$). Thus, in this pair of epimers we also see the deshielding effect of a *syn* bromine on a *syn* proton. This deshielding amounts to 0.45–0.58 ppm for these compounds. The phenomenon of deshielding by bromine is observed in other systems. Thus, in 2-bromopropene, the vinylic proton *cis* to the bromine absorbs at τ 4.48, while that *trans* absorbs at 4.67.[27] In *cis*- and *trans*-1,3-dichlorocyclopentane a similar shift is found, as the protons α to the chlorine atoms absorb at τ 5.93 and 5.62, respectively, for these epimers.[28]

In compound **18**, the absorbance at τ 6.8 is absent and that with the smaller coupling constant remains. It is clear then that the proton in this compound (and in **17**) is the *syn* proton at C-6 and the *anti* position at C-6 is occupied by a deuterion.

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