Registry No.—1, 58541-21-2; 1 oxime, 58541-22-3; 1 2,4-DNPH, 58541-23-4; 2, 58541-24-5; 2 oxime, 58541-25-6; 2 2,4-DNPH, 58541-26-7; 3, 31919-47-8; 4, 58541-27-8; 4 oxime, 58541-28-9; 4 2,4-DNPH, 58541-29-0; 5, 58541-30-3; 5 oxime, 58541-31-4; 5 2,4-DNPH, 58541-32-5; 6, 1015-14-1; 6 2,4-DNPH, 58541-33-6; 7, 938-16-9; 8, 98-86-2; homoadamantane-3-carboxylic acid, 21898-91-9; homoadamantane-1-carboxylic acid, 31061-65-1; 1-(α-hydroxybenzyl)homoadamantane, 58541-34-7; adamantane-1-carbonic acid chloride, 2094-72-6; bicyclo[2.2.2]octane-1-carboxylic acid, 699-55-8, bicyclo[2.2.2]octane-1-carboxylic acid chloride, 21891-38-3; 1-(α-hydroxybenzyl)bicyclo[2.2.2]octane, 5818-96-2; bicyclo[3.2.1]octane-1-carboxylic acid, 2534-83-0; bicyclo[3.2.1]octane-1-carboxylic acid chloride, 58541-35-8; 1-(α-hydroxybenzyl)bicyclo[3.2.1]octane, 58541-36-9; bicyclo[2.2.1]heptane-1-carboxylic acid, 18720-30-4; 1-(α-hydroxybenzyl)bicyclo[2.2.1]heptane, 5818-94-0; homoadamantane, 281-46-9.

References and Notes

(1) Part 8: Photochemical α-Cleavage of Ketones in Solution. Part 7: ref 5.
(2) (a) Camille and Henry Dreyfus Teacher–Scholar, 1973–1978, Alfred P. Sloan Fellow, 1975–1977; (b) PPG Industries Fellow, 1971–1972; National Science Foundation Trainee, 1972–1974.
(3) H.-G. Heine, W. Hartmann, D. R. Kory, J. G. Magyar, C. E. Hoyle, J. K. McVey, and F. D. Lewis, *J. Org. Chem.*, **39**, 691 (1974).
(4) F. D. Lewis, C. H. Hoyle, J. G. Magyar, H.-G. Heine, and W. Hartmann, *J. Org. Chem.*, **40**, 488 (1975).
(5) F. D. Lewis, R. T. Lauterbach, H.-G. Heine, W. Hartmann, and H. Rudolph, *J. Am. Chem. Soc.*, **97**, 1519 (1975).
(6) For a review see R. C. Fort, Jr., in "Carbonium Ions", Vol. IV, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N.Y., 1973, Chapter 32.
(7) C. Rüchardt, *Angew Chem., Int. Ed. Engl.*, **9**, 830 (1970).
(8) C. Rüchardt, "Mechanismen Radikalischer Reaktionen", Forschungsberichte des Landes Nordrhein-Westfalen, No. 247, Westdeutscher Verlag, Opladen, 1975, p 37 ff.
(9) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).
(10) F. D. Lewis and C. E. Hoyle, *Mol. Photochem.*, **6**, 235 (1974).
(11) D. I. Schuster and T. M. Weil, *Mol. Photochem.*, **4**, 447 (1972).
(12) F. D. Lewis and J. G. Magyar, *J. Org. Chem.*, **37**, 2102 (1972).
(13) F. D. Lewis and J. G. Magyar, *J. Am. Chem. Soc.*, **95**, 5973 (1973).
(14) (a) S. T. Koenig and H. Fischer, "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, p 157; (b) K. Herwig, P. Lorenz, and C. Rüchardt, *Chem. Ber.*, **108**, 1421 (1975).
(15) Dr. F. Gerhardt, University of Göttingen, private communication.
(16) R. C. Bingham and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93**, 3189 (1971).
(17) S. A. Godleski, W. D. Graham, T. W. Bentley, P. v. R. Schleyer, and G. Liang, *Chem. Ber.*, **107**, 1257 (1974).
(18) C. Rüchardt, private communication.
(19) H. Langhals and C. Rüchardt, *Chem. Ber.*, **108**, 2156 (1975).
(20) H. Langhals and C. Rüchardt, *Chem. Ber.*, **107**, 1245 (1974).
(21) L. F. Fieser and M. Fieser, "Reagents in Organic Chemistry", Vol. I, Wiley, New York, N.Y., 1967, p 410.
(22) H. Stetter and E. Rauscher, *Chem. Ber.*, **93**, 1161 (1960).
(23) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).
(24) A. W. Chow, D. R. Jakas, and J. R. E. Hoover, *Tetrahedron Lett.*, 5427 (1966).
(25) W. R. Boehme, *J. Am. Chem. Soc.*, **91**, 2762 (1959).
(26) D. B. Denney and R. R. DiLeone, *J. Am. Chem. Soc.*, **84**, 4737 (1962).
(27) H. Stetter, M. Schwarz, and A. Hirschhorn, *Chem. Ber.*, **92**, 1629 (1959).
(28) P. T. Lansbury and V. A. Pattison, *J. Org. Chem.*, **27**, 1933 (1962).

Bridged Polycyclic Compounds. 82. Multiple Mechanisms for Oxymercuration of Some Dibenzobicyclo[2.2.2]octatrienes[1]

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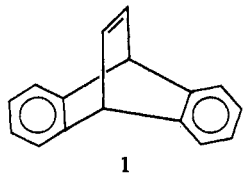
Received August 26, 1975

Addition of mercuric acetate to 1-methyldibenzobicyclo[2.2.2]octatriene, 1-methoxydibenzobicyclo[2.2.2]octatriene, and 1,4-dimethyldibenzobicyclo[2.2.2]octatriene has been carried out in a variety of solvent systems. With variation in substrate and in reaction conditions, cis addition, trans addition, and addition with rearrangement have been observed. The composition of the product mixtures have been rationalized in terms of these competing reaction paths for oxymercuration.

There has been much recent interest in oxymercuration reactions because of their usefulness in synthesis and their interesting mechanistic possibilities.[2] It has been suggested that oxymercuration proceeds via mercurinium ions, via concerted additions, and via β-mercuricarbocations, and a good deal of effort has been extended to prove or disprove the intervention of one or more of these intermediates or processes.

It seemed to us that a conservative viewpoint would assume that there are many mechanisms for oxymercuration reactions, just as for other electrophilic addition reactions. Our experience with dibenzobicyclo[2.2.2]octatriene (1) and related compounds suggested that this would be a useful system to investigate, as small modifications of structure or of reaction conditions often lead to mechanistic changes. The results of a portion of our studies are reported in this paper.



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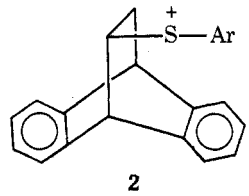
Although anti addition to 1 is quite rare, it does occur when onium ion intermediates intervene and are attacked directly by nucleophiles. Thus addition of arenesulfenyl chlorides proceeds via the sulfonium ions **2**, to give trans addition



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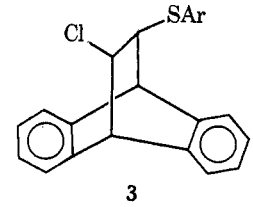

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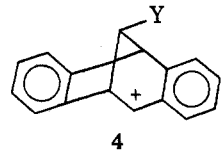

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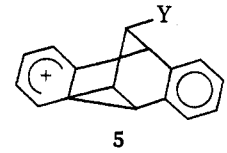

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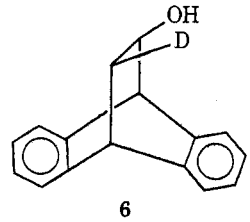

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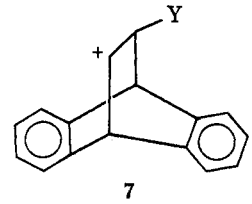

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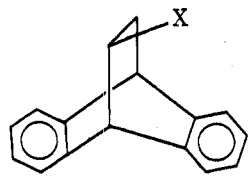
products **3**.[3] The fact that anti addition is generally not observed in these systems[4,5] suggests either that onium ions analogous to **2**, but with other heteroatoms, are often not involved[1] or that the reactivity toward displacements at the gunwale positions of the boat-form cyclohexane rings is small. Onium ions can then open with rearrangement to [3.2.1] cations, such as **4**, or to bridged cations **5**, which then give rearranged products. This has been noted even when sulfonium-ion intermediates are possible.[6]

Concerted bimolecular addition processes lead directly to syn products, exemplified by addition of deuteriodiborane to **1**, which gives *cis*-3-deuteriodibenzobicyclo[2.2.2]octadien-2-ol **6** upon oxidation of the intermediary organoborane.[7]

Open secondary cations of type **7** are of relatively high energy and are rarely observed,[7] while intermediates of type **4** or **5** are utilized in carbocationic pathways.[1] The solvolyses of **8** species invariably yield [3.2.1] products **9** through kinetic



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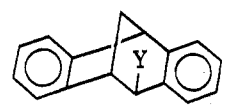

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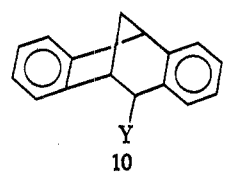

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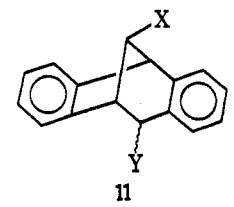

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control.[3,8,9] These are sometimes admixed with endo products **10**, and are rapidly converted to equilibrium mixtures with **10**. Such mixtures can generally be stereospecifically reisomerized to the [2.2.2] system. Additions follow similar paths, if carbocations are involved, giving [3.2.1] products. Thus additions to **1** of iodine and silver acetate, bromine in acetic acid, chlorine in carbon tetrachloride, and *tert*-butyl hypochlorite in acetic acid lead to the products **11** with the electrophile X at the syn-8 position, and the nucleophile Y at the benzylic position.

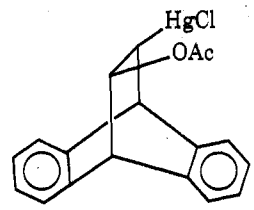
From such observations, it is clear that product studies may be used to determine addition reaction mechanisms. A reaction giving a cis-[2.2.2] product may be assumed to involve a cyclic mechanism, one giving a trans-[2.2.2] product must involve nucleophilic attack on an onium ion, and a [3.2.1] product establishes the intervention of a carbocation.

Much work has been reported supporting various mechanisms of oxymercuration. Lucas, Hepner, and Winstein[10] demonstrated reversible complex formation between mercuric ion and olefins. They proposed that the complexes were mercurinium ions and that they were intermediates in oxymercuration reactions, predicting correctly that the stereospecificity noted[11] in the methoxymercuration of cyclohexene would be that of anti addition. Many examples of anti addition have been since reported;[2] these seem clearly understandable as products of direct displacement (with inversion) on mercurinium ions.[2c] Bach and Richter[12] presented evidence supporting such a process in which ion formation is fast and reversible, and the rate-determining step is ligand or solvent attack.

While Kitching, Smith, and Wells[13] were unable to find ^{1}H NMR evidence for stable mercurinium ions, Olah and Clifford[14] did observe the ^{1}H NMR spectrum of the mercurinium ions formed in superacid solutions at −30 °C from 2-methoxyethylmercuric chloride and at −70 °C from *exo-cis*-3-hydroxy-2-norbornylmercuric chloride. Whitham[15] failed to find evidence for a mercurinium ion by a trapping experiment involving acid-catalyzed methanol–H_2O exchange. That experiment is consistent with a rapid equilibration between mercurinium ion and liganded mercuric ion and olefin, or with the nonexistence of mercurinium ions, as are the kinetic data of Halpern[16] and the experiment of Sokolov, Troitskaya, and Reutov.[17]

Traylor[18] noted that norbornene and substituted norbornenes add mercuric acetate or the elements of methoxymercuric acetate in a cis-exo fashion, even with large syn-7 substituents, and proposed a concerted cyclic mechanism. Brown and Kawakami[19] noted similar results, which they assume ruled out mercurinium ions in the syn-7-methyl case. As 2-methylnorbornene gave Markownikoff addition, they proposed that a mercuricarbenium ion must be involved rather than a cyclic process, although experience in Brown's laboratory with hydroboration reactions[20] seems to have been ignored in this interpretation.

Previous work with **1** indicates the occurrence of at least two mechanisms for oxymercuration. Sokolov[21] reported that, in acetic acid, oxymercuration of **1** gave only the cis product **12**,



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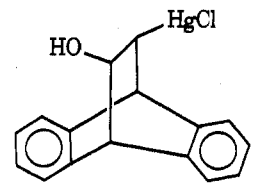

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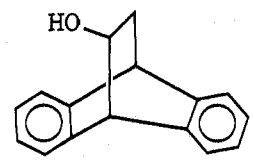
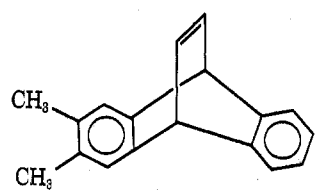


14

while in aqueous acetone both cis and trans addition occurred, giving the acetate **12** and the alcohol **13** in a 70:30 ratio. We have now confirmed these results and have shown that no rearrangement occurred in the reaction in aqueous acetone by reducing the mixture of mercurials with sodium borohydride to the alcohol **14**, without any 9-OH or 10-OH being produced. In acetic acid a cyclic process apparently obtains, while in aqueous acetone there is competition between a cyclic and a mercurinium ion process. The reaction of **15** with mercuric acetate in acetic acid, followed by hydrodemercuration with sodium borohydride, gave acetates **16** and **17** in equal amounts.[1] This result was similarly interpreted as evidence for cyclic processes involving molecular addition of mercuric acetate.



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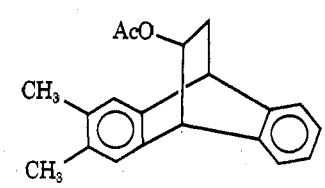

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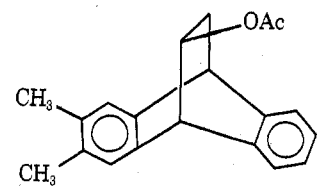

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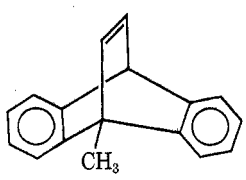
We have now examined the addition of mercuric acetate in

various solvents to 1-methyldibenzobicyclo[2.2.2]octatriene (18), 1-methoxydibenzobicyclo[2.2.2.]octatriene (19), and 1,4-dimethyldibenzobicyclo[2.2.2]octatriene (20).



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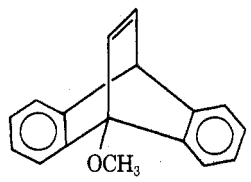

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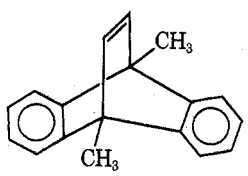

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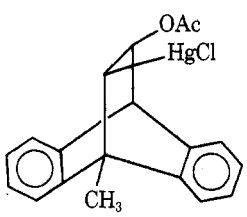
When addition of mercuric acetate to 18 was carried out in acetic acid and the products isolated as the chloromercurials, cis [2.2.2] addition products 21 and 22 were observed (^{1}H NMR) in a 3:2 ratio, respectively. This ratio was confirmed by hydrodemercuration of the product which gave a mixture of acetates 23 and 24 in which 23 predominated. Here, then, syn addition occurred, giving both of the anticipated products. We note that the electrophilic atom adds principally closer to the 9-methyl substituent, but offer no rationalization for this.



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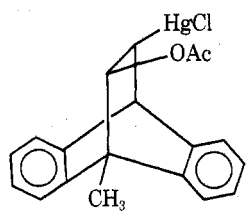

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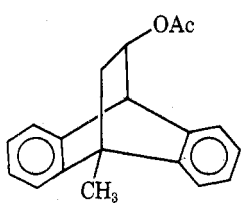

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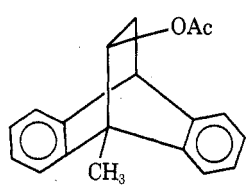

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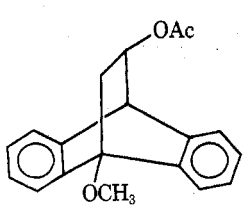
19 was treated with mercuric acetate in acetic acid, and the mixture subjected to hydrodemercuration. The principal (ca. 66%) product was 25, which again resulted from an addition



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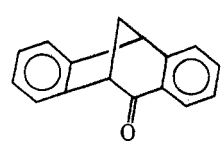

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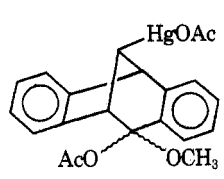

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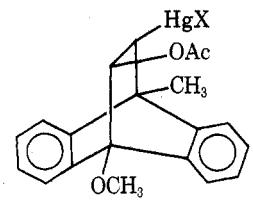
(presumably syn) process in which the electrophilic atom attacked the atom closer to the 9 substituent. The minor product was 26, which may be presumed to be formed via 27 in the work-up and reduction. With 19 we see the very interesting result that the consequence of attachment of electrophile to one end of a double bond is syn attachment of nucleophile, while the consequence of attachment of electrophile at the other end is a carbenium-ion rearrangement.

With 20, mercuric acetate in acetic acid gave two products, 28-OAc and 29-OAc, when the reaction time was short (1 h).



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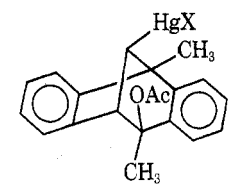

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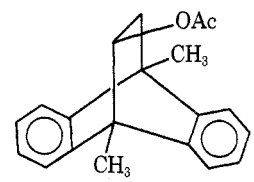

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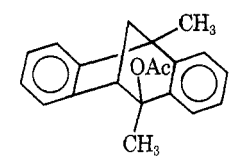

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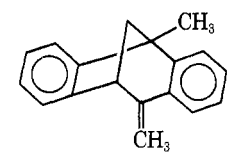

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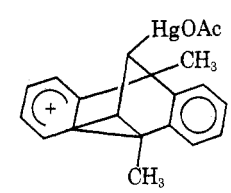
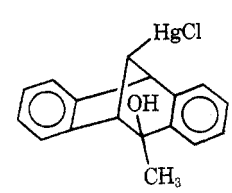
With longer times (1 day), the product was largely 28-OAc. The existence of both 28 and 29 was confirmed by reduction to 30 and 31, along with the olefin 32. The transformation of 20 to 29 as a substantial product of a short reaction time process indicates that in this system addition leads to a carbenium ion, which gives 29-OAc, about as fast as 20 reacts by a syn process to give 28-OAc. 29-OAc is unstable to reaction conditions and (see below) reverts to starting olefin and mercuric acetate which again distributes itself between 28 and 29, ultimately giving principally 28. It is also possible that some 28 arises via ion 33, in a process analogous to many such rearrangements.[22]



33

In view of the results in acetic acid, we decided to investigate additions in other solvents and in mixed solvents. With mercuric acetate in 50% aqueous acetone, 18 gave alcohol 34 as the predominant product. Hydrodemercuration of 34 gave the



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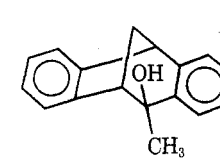

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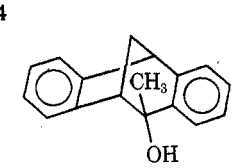
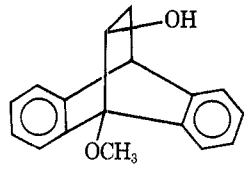
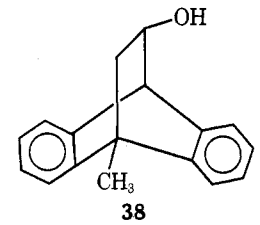


36

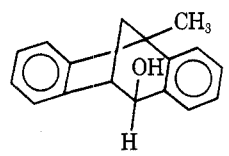
tertiary alcohol **35**. That the hydroxyl group was exo was concluded from the fact that addition of methylmagnesium iodide to **26** gave an epimeric product **36**. Hydrodemercuration of the product mixture from the addition gave a mixture of **35** (55%) and the [2.2.2] alcohols **37** and **38** (45%, ratio about 1:1).



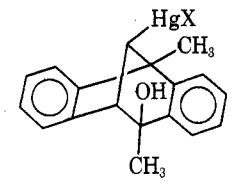
37



38



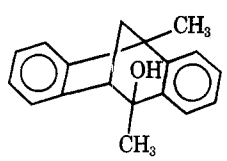
39



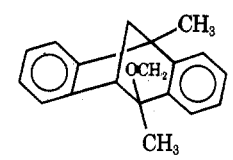
40

No alcohol **39** was present. The data do not indicate whether syn or anti addition occurred to give the progenitors of **37** and **38**, so that the processes competing with the carbenium ion rearrangement cannot be defined in this particular case, but clearly several mechanisms are operating.

Oxymercuration of **19** with mercuric acetate in 50% aqueous acetone, followed by hydrodemercuration gave **25** and **26** in about a 1:1 ratio. With **20**, only the rearranged alcohol **40**-Cl was formed, whose structure was confirmed by hydrodemercuration to **41**.



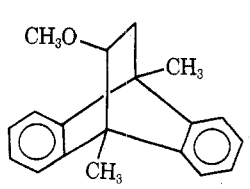
41



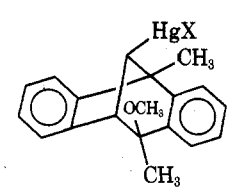
42

Addition of mercuric acetate to **18** and **20** was also carried out in 50% aqueous tetrahydrofuran. With **18**, the products identified after hydrodemercuration included alcohols **35**, **37**, and **38** along with acetates **23** and **24**. With **20** the sole product after hydrodemercuration was the [3.2.1] alcohol **41**, the result of a carbocation process.

Oxymercuration of **20** was carried out in a variety of other solvents. In 80% aqueous acetic acid, the only product after hydrodemercuration was the [3.2.1] alcohol **41**. In acetic acid–methanol (80:20), the only product after hydrodemercuration was the [3.2.1] ether **42**. When the reaction was carried out in acetic acid–methanol (95:5), the products isolated after reduction were the [3.2.1] ether **42**, the [2.2.2] acetate **30**, and olefin **32**. When the reaction was carried out in methanol, the products isolated after reduction were the [3.2.1] ether **42** and the [2.2.2] ether **43**. Isolation of **43** from the reduction does

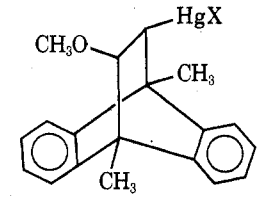


43

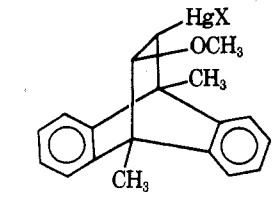


44

not tell whether the competition under these conditions is between the carbocation process which gives **44** and an anti process giving **45** or between the former and a syn process giving **46**. As noted above, anti processes are rare in these dibenzobicyclic systems, although Sokolov[21] did find such a process in the treatment of **1** with mercuric acetate in aqueous



45



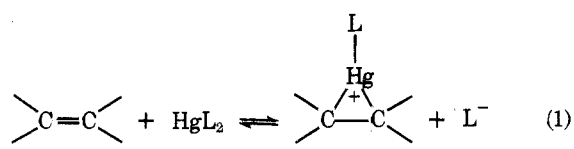
46

acetone mentioned above. That the anti process competes here as well was established by ^{1}H NMR analysis of the mixture of chloromercurial intermediates which clearly contained **44** and **45** and no detectable **46**. Hence the product is the result of an anti ring opening of a mercurinium ion intermediate and not that of a syn addition or of a rearrangement to **44** followed by the normal [3.2.1] → [2.2.2] rearrangement.[22]

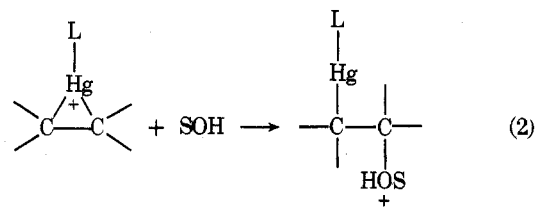
In order to verify the instability of **29**-OAc to oxymercuration conditions, addition of mercuric acetate to **20** in acetic acid was carried out and the **28**:**29** ratio was determined at various times. As **20** disappeared, **28** and **29** built up in amount at approximately the same rate (the **28**:**29** ratio being about 60:40) for about the first hour. After that, the **28**:**29** ratio increased until about 20 h and then remained relatively constant (**28**:**29** ratio being about 85:15). Since it was demonstrated that **28**-OAc was stable to reaction conditions, the **29**-OAc that was formed reverted to **20**, which then reacted again with mercuric acetate to form **28**-OA and **29**-OAc. For this reason, **28**-OAc was the predominant product observed in earlier experiments, which were carried out for long periods of time.

Conclusions

Analysis of the data presented compels a path in which the first step is a fast, reversible formation of a mercurinium ion (eq 1);[23] if capture of this species by solvent (eq 2) is relatively

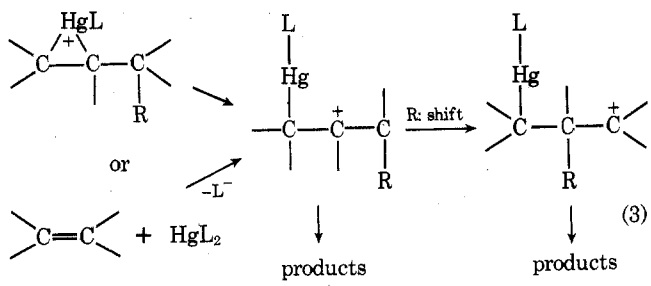


(1)

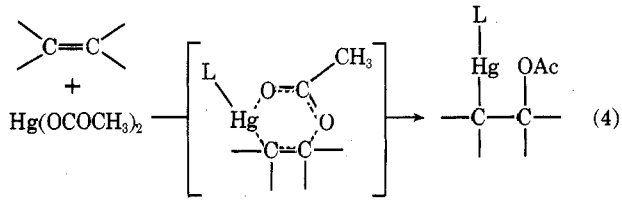


(2)

easy, the product isolated is the result of anti addition. If this step is very slow, then one or both of two additional reactions (eq 3 and 4) can occur. The pathways outlined in eq 3 may be



(3)



(4)

anticipated to occur in polar solvents, in particular when the solvent is relatively nonnucleophilic, and when a relatively stable carbocation is formed. It will be revealed when the product is that of a skeletal rearrangement and is stable under reaction conditions. It may also be occurring in cases where stereospecificity is not seen, although this may also be the result of a competition between the eq 2 and 4 pathways. The extra stability given to cation intermediates by the methyl or methoxy groups in **18**, **19**, and **20** thus favors carbenium ion intermediates and leads to rearranged products, while none are observed with **1** or with the "unsubstituted" ends of the double bonds in **18** and **19**. Finally, a syn-concerted[18] addition process (eq 4) intervenes when neither the process of eq 2 nor that of eq 3 occurs readily. Just as in all concerted electrophilic additions, it seems likely that in the transition state of eq 4, carbon–electrophile bonding is advanced over carbon–nucleophile bonding[24] but obviously no carbocationic intermediate is involved.[26] Thus the differences between the processes represented in eq 1, 3, and 4 are subtle in nature, particularly as the mercuric ion begins to approach the double bond, but it is clear that these differences have profound effects, leading finally to different products.

Our system is one of the few in which rearrangement of the carbon skeleton has been noted to occur during oxymercuration. Although other cases are reported in the literature, all are in strained systems.[27-31]

Experimental Section

^{1}H NMR spectra were taken on a Varian A-60A spectrometer in $CDCl_3$ solution, unless otherwise indicated, with tetramethylsilane as an internal standard.[32] Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

1-Methyl-*trans*-7,8-dichlorodibenzobicyclo[2.2.2]octadiene (47). A mixture of 10 g (52 mmol) of 9-methylanthracene, 30 ml (0.39 mol) of *trans*-1,2-dichloroethene, and about 1 g of 4-*tert*-butylpyrocatechol was heated for 2 days at 180 °C in a sealed thick-wall Pyrex tube. The contents of the tube were chromatographed on 425 g of activated alumina, followed by elution with Skellysolve B. The product was recrystallized from ethanol to give two crops of large, white needles in 73% yield: mp 104–105 °C; ^{1}H NMR δ 7.10–7.50 (m, 8, aromatic H), 4.19–4.42 (m, 2, H-4 and H-8), 3.93 (d, 1, J = 2.8 Hz, H-7) and 2.00 ppm (s, 3, CH_3).

Anal.[34] Calcd for $C_{17}H_{14}Cl_2$: C, 70.60; H, 4.88. Found: C, 70.68; H, 4.97.

1-Methyl-*cis*-7,8-dichlorodibenzobicyclo[2.2.2]octadiene (48). A similar reaction with *cis*-1,2-dichloroethene gave **48** in 78% yield: mp 187–188 °C; ^{1}H NMR δ 7.08–7.53 (m, 8, aromatic H), 4.40–4.61 (m, 2, H-4 and H-8), 4.12 (m, 1, H-7), and 2.03 ppm (s, 3, CH_3).

Anal. Calcd for $C_{17}H_{14}Cl_2$: C, 70.60; H, 4.88. Found: C, 70.56; H, 4.86.

1-Methyldibenzobicyclo[2.2.2]octatriene (18) was prepared by reduction of either **47** or **48** with zinc–copper couple in the usual fashion[33] for such reductions to give a 79% yield of **18**: mp 98–100 °C; ^{1}H NMR δ 6.8–7.4 (m, 9, aromatic H and H-8), 6.56 (d of d, 1, J = 7, 1.5 Hz, H-7), 5.04 (d of d, 1, J = 6 Hz, H-4), and 2.12 ppm (s, 3, CH_3).

Anal.[34] Calcd for $C_{17}H_{14}$: C, 93.94; H, 6.46. Found: C, 93.50; H, 6.41.

***trans*-7,8-Dichloro-1-methoxydibenzobicyclo[2.2.2]octadiene (50).** A mixture of 26.9 g (0.13 mol) of 9-methoxyanthracene (**49**), 1.0 g of hydroquinone, and 100 ml of *trans*-1,2-dichloroethane was heated in a sealed tube at 203° for 1 day. Workup as above for **47** gave 29 g (73%) of **50**: mp 134–135 °C; ^{1}H NMR δ 7.1–7.8 (m, 8, aromatic H), 4.2–4.4 (m, 3, H-4, H-7, and H-8), and 3.87 ppm (s, 3, CH_3).

Anal. Calcd for $C_{17}H_{14}Cl_2O$: C, 66.89; H, 4.57; Cl, 23.28. Found: C, 67.01; H, 4.60; Cl, 23.38.

***cis*-7,8-Dichloro-1-methoxydibenzobicyclo[2.2.2]octadiene (51).** A similar reaction with *cis*-1,2-dichloroethene gave **51**: mp 169–170 °C; ^{1}H NMR δ 7.0–7.8 (m, 8, aromatic H), 4.40 (broad s, 1, H-4), 4.57 (broad s, 1, H-7), 4.60 (broad s, 1, H-8), and 3.92 ppm (s, 3, CH_3).

Anal. Calcd for $C_{17}H_{14}Cl_2O$: C, 66.89; H, 4.57. Found: C, 66.73; H, 4.51.

1-Methoxydibenzobicyclo[2.2.2]octatriene (19). Reduction of **50** (or **51**) with zinc–copper couple[33] gave 80–85% of **19**: mp 174–175 °C; ^{1}H NMR δ 6.9–7.6 (m, 10, olefinic and aromatic H), 5.05 (d of d, 1, J = 5, 2 Hz, H-4), and 3.98 ppm (s, 3, CH_3).

Anal. Calcd for $C_{17}H_{14}O$: C, 87.18; H, 5.98. Found: C, 87.28; H, 5.83.

***trans*-7,8-Dichloro-1,4-dimethyldibenzobicyclo[2.2.2]octadiene (53).** A mixture of 32.0 g (0.155 mol) of 9,10-dimethylanthracene (**52**),[35] 170 ml (213 g, 2 mol) of *trans*-1,2-dichlorethene, and 0.5 g of hydroquinone was heated at about 155 °C in a sealed glass tube for 2 days. Workup as usual gave 43.8 g (93%) of **53**: mp 135–137 °C; ^{1}H NMR δ 7.0–7.5 (m, 8, aromatic H), 3.80 (s, 2, H-7 and H-8), and 2.20 ppm (s, 6, CH_3).

Anal. Calcd for $C_{18}H_{16}Cl_2$: C, 71.31; H, 5.28; Cl, 23.41. Found: C, 71.22; H, 5.35, Cl, 23.66.

***cis*-7,8-Dichloro-1,4-dimethyldibenzobicyclo[2.2.2]octadiene (54)** was prepared in a similar fashion from *cis*-1,2-dichloroethane: mp 176–177 °C; ^{1}H NMR δ 7.0–7.5 (m, 8, aromatic H), 4.13 (s, 2, H-7 and H-8), and 2.0 ppm (s, 6, CH_3).

Anal. Calcd for $C_{18}H_{16}Cl_2$: C, 71.31; H, 5.28; Cl, 23.41. Found: C, 71.49; H, 5.36; Cl, 23.46.

1,4-Dimethyldibenzobicyclo[2.2.2]octatriene (20) was prepared by reduction of **53** with zinc–copper couple:[33] mp 117–119 °C; ^{1}H NMR δ 6.9–7.4 (m, 8, aromatic H), 6.62 (s, 2, olefinic H), and 2.12 ppm (s, 6, CH_3).

Anal. Calcd for $C_{18}H_{16}$: C, 93.10; H, 6.90. Found: C, 93.21; H, 6.97.

Addition of Mercuric Acetate to 1-Methyldibenzobicyclo[2.2.2]octatriene (18) in Acetic Acid Solvent. A solution of 327 mg (1.5 mmol) of **18** and 463 mg (1.45 mmol) of mercuric acetate in 15 ml of glacial acetic acid was stirred at room temperature for 3 h. Approximately 360 mg of NaCl was added, and the mixture was stirred for an additional 1 h. Water (35 ml) was added, producing a heavy precipitate, which was filtered 1 h later. The precipitate was washed with water and dried in vacuo to give 677 mg (91%). The ^{1}H NMR spectrum of this mixture showed some **18** plus the two cis adducts **21** and **22**. Planimeter integration of enlarged peaks determined the ratio of **21**:**22** to be 73 ± 4:27 ± 4. Repeated recrystallization from acetone–water gave 4-methyl-*cis*-8-chloromercuri-7-dibenzobicyclo[2.2.2]octadienyl acetate (**21**): mp 189.5–191.5 °C; ^{1}H NMR δ 7.0–7.5 (m, 8, aromatic H), 5.38 (d of d, 0.8 H, J = 8.5, 3 Hz, H-7), 4.69 (d, 0.8 H, J = 3 Hz, H-1), 3.15 (d, 0.8 H, J = 8.5 Hz, H-8), 2.06 (s, 3, $OCOCH_3$), and 1.96 ppm (s, 3, CH_3).

Anal. Calcd for $C_{19}H_{17}CLHgO_2$: C, 44.45; H, 3.34. Found: C, 44.43 H, 3.32.

Sodium Borohydride Reduction of the Acetoxymercuration Adducts of 18. To a mixture of 257 mg (0.5 mmol) of a product mixture similar to that described in the previous paragraph and of 12 mg (0.3 mmol) of sodium borohydride was added 2.0 ml of THF and 2.0 ml of 2 M NaOH. A rapid reaction occurred; the mixture was stirred for 20 min. Some chloroform and water were added, and the product was decanted from 89 mg (89%) of metallic mercury into 20 ml of water. The product was extracted with three 25-ml portions of chloroform. The chloroform extracts were washed with 25 ml of water and 25 ml of saturated aqueous NaCl and dried ($MgSO_4$). Evaporation of the chloroform gave 150 mg of an oil. The product was separated on a preparative TLC plate (silica gel G, 20 × 20 × 0.25 cm, developed with 10% ether in benzene), and the entire band of acetate products was collected (120 mg, 86%). ^{1}H NMR integration showed it to contain **23** and **24** in a ratio of 71:29, in good agreement with the ratios for **21** and **22**.

Oxymercuration of 20 in Acetic Acid for 1 h. Hydrodemercuration of 28-Cl and 29-Cl with Sodium Borohydride. A solution of 0.70 g (3 mmol) of **20** and 1.45 g (4.5 mmol) of mercuric acetate in 15 ml of glacial acetic acid was stirred for 55 min before 1.0 g (17 mmol) of NaCl was added. The solution was stirred for 5 min before 100 ml of water was added. The precipitate was collected, washed with water, and dried in vacuo over P_2O_5 for 1 day, to give 1.50 g (95%). The ^{1}H NMR spectrum of this product, in Me_2SO-d_6, showed the ratio of **28**:**29** to be 55:45 [from multiple integration of the absorptions of δ 5.34 (d, J = 9 Hz, H-7 of **28**) and 4.48 ppm (d, J = 5 Hz, H-1 of **29**)]. Approximately 15% of unreacted **20** remained. The product mixture (1.45 g, 2.85 mmol) was reduced with 0.20 g (5.3 mmol) of sodium borohydride in 15 ml of tetrahydrofuran and 15 ml of 2 M NaOH for 20 min. After the usual workup procedure, 0.85 g (about 100%) of an oil was obtained and the ratio of **30**:**31** was found to be 61:39 [multiple integrations of the absorptions at δ 4.88 (d of d, J = 9, 3 Hz, H-7 of **30**) with that at 4.37 ppm (d, J = 5 Hz, H-1 of **31**)]. Approximately 12% of the mixture was unreacted **20**.

Oxymercuration of 20 in Acetic Acid for Long Period of Time. Preparation of 28-Cl. A solution of 2.1 g (9 mmol) of **20** and 4.35 g (14.5 mmol) of mercuric acetate in 30 ml of glacial acetic acid was stirred for 19 h before 2.0 g (33 mmol) of NaCl was added. Workup as above, followed by recrystallization from aqueous acetone, gave 3.52 g (74%) of 1,4-dimethyl-*cis*-8-chloromercuri-7-dibenzobicy-

clo[2.2.2]octadienyl acetate (**28**): mp 204–205 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 7.18–7.58 (m, 8, aromatic H), 5.34 (d, 0.65 H, J = 9 Hz, H-7), 3.24 (d, 0.65 H, J = 9 Hz, H-8), 2.13 [s, 3, C(1) CH_3], 2.02 (s, 3, acetate CH_3), and 1.93 ppm [s, 3, C(4) CH_3].

1,4-Dimethyl-7-dibenzobicyclo[2.2.2]octadienyl Acetate (30). To 0.53 g (1 mmol) of **28**-Cl in 10 ml of tetrahydrofuran and 10 ml of 2 M NaOH, 0.04 g (1 mmol) of sodium borohydride was added and the reaction mixture was stirred for 20 min. Usual workup gave 250 mg of an oil, whose ^{1}H NMR spectrum indicated that it was largely **30**, with small amounts of **32** and **20** also present. Crystallization and recrystallization from aqueous ethanol gave **30**: mp 96–97 °C; ^{1}H NMR δ 7.15–7.50 (m, 8, aromatic H), 4.92 (d of d, 1, J = 9, 3 Hz, H-7), 2.33 (d of d, 1, J = 14, 9 Hz, H-8 anti), 1.85–2.0 (m, 9, bridgehead and acetoxy CH_3), and 1.37 ppm (d of d, 1, J = 14, 3 Hz, H-8 syn).

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.19; H, 6.85. Found: C, 83.25; H, 6.65.

Oxymercuration–Hydrodemercuration of 1-Methoxydibenzobicyclo[2.2.2]octatriene (19) in Acetic Acid. A solution of 10.0 g (43 mmol) of **19** and 27.3 g (86 mmol) of mercuric acetate in 200 ml of glacial acetic acid was stirred for 2 days before 10.0 g of NaCl and 100 ml of water were added. Workup as above was followed by reduction with sodium borohydride in the normal fashion to give 14.3 g of an oil whose ^{1}H NMR spectrum showed **25** and **26** in a ratio of 2:1.

Oxymercuration of 18 in Acetone–Water. A 550-mg (2.30 mmol) sample of **18** was dissolved in 10 ml of acetone and, with stirring, 10.0 ml of distilled water and 0.5 ml of acetic acid were added. To this mixture was added 829 mg (2.6 mmol) of mercuric acetate. After 23 h, 600 mg of sodium chloride was added. The mixture was stirred for 15 min, and the turbid solution poured into 100 ml of water and extracted with three 75-ml portions of chloroform. Appropriate workup followed by recrystallization from chloroform–carbon tetrachloride gave *syn*-8-chloromercuri-*endo*-2-methyl-*exo*-2-dibenzobicyclo[3.2.1]octadienol (**34**): mp 220.2–221.8 °C dec; ^{1}H NMR δ 6.9–7.5 (m, 8, aromatic H), 4.10 (d, 0.8 H, J = 4 Hz, H-1), 3.48 (d, 0.8 H, J = 4.5 Hz, H-5), 3.22 (t, 0.8 H, J = 4.2 Hz, H-8 anti), 2.52 (s, 1, OH), and 1.55 ppm (s, 3, CH_3).

Anal. Calcd for $C_{17}H_{15}ClHgO$: C, 43.32; H, 3.21. Found: C, 43.10; H, 3.14.

Hydrodemercuration of 34 with Sodium Borohydride. Treatment of **34** with sodium borohydride by the general treatment described above gave *endo*-2-methyl-*exo*-2-dibenzobicyclo[3.2.1]octadienol (**35**): mp 122–122.5 °C; ^{1}H NMR δ 6.9–7.5 (m, 8, aromatic H), 3.90 (m, 1, $W_{1/2}$ = 7 Hz, H-1), 3.29 (m, 1, $W_{1/2}$ = 7 Hz, H-5), 2.53 (m, 2, H-8), 2.15 (s, 1, OH), and 1.50 ppm (s, 3, CH_3).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.85. Found: C, 86.19; H, 7.09.

Hydrodemercuration of Products from Oxymercuration of 18 in Acetone–Water with Sodium Borohydride. After a mixture of 291 mg (1.0 mmol) of **18** and 319 mg (1.0 mmol) of mercuric acetate in 4 ml of acetone and 4 ml of water was stirred for 24 h, 2.0 ml of acetone and 2.0 ml of 6 M NaOH (aqueous) were added, followed by 38 mg (1.0 mmol) of sodium borohydride. The usual treatment and workup gave an oil (272 mg) from which 44 mg of **35** crystallized and was removed. Multiple integrations of the ^{1}H NMR spectrum (CCl_4) over the regions δ 3.3–4.2 (2 protons for both **37** and **38** and 1 proton for **35**) and 2.9–3.2 ppm (1 proton for **35**) allowed calculation of the ratio of **37** + **38**:**35**. The mixture consisted of 16% **18**, 46% **35**, and 38% **37** + **38**. The ratio of **37**:**38** could not be determined exactly, but was estimated at about 50:50. Addition of these data indicates that the original oxymercuration mixture showed an 85% reaction of **18** to give a 60:40 mixture of **34**:unrearranged hydroxy mercurials. Approximately 80% of the mercury added to the 8 carbon of **18**.

***exo*-2-Methyl-*endo*-2-dibenzobicyclo[3.2.1]octadienol (36).** A solution of 3.69 g (18 mmol) of dibenzobicyclo[3.2.1]octadien-4-one (**26**) in 70 ml of anhydrous ether was added to excess methylmagnesium iodide in ether and allowed to stand overnight at room temperature. Normal workup of Grignard reactions led to **36**, which after recrystallization from aqueous ethanol melted at 64–67°: ^{1}H NMR δ 6.9–7.5 (m, 8, aromatic H), 3.84 (d, J = 4.1 Hz, H-1), 3.35 (d, 1, J = 4.8 Hz, H-5), 2.63 (d of d of d, 1, J = 12.2, 4.8 Hz, 4.1 Hz, H-8 anti), 2.74 (d of t, 1, J = 11.2, 1 Hz, H-8 syn), and 1.74 ppm (s, 4, CH_3 and OH).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.85. Found: 86.62; H, 6.91.

Oxymercuration of 20 in Acetone–Water. Synthesis of *endo*-2,5-Dimethyl-*syn*-8-chloromercuri-*exo*-2-dibenzobicyclo[3.2.1]octadienol (40-Cl). A solution of 2.1 g (9 mmol) of **20** and 4.35 g (14.5 mmol) of mercuric acetate in 30 ml of acetone, 20 ml of water, and 0.5 ml of glacial acetic acid was stirred for 18 h. NaCl (2.0 g, 34 mmol) was added and stirred for 1 h. Workup gave, after recrystallization from chloroform–carbon tetrachloride, 3.60 g (82%) of **40**: mp 214–215 °C dec; ^{1}H NMR δ 6.7–7.7 (m, 8, aromatic H), 6.2 (s, 1, OH), 3.47 (d, 1, J = 5 Hz, H-1), 3.05 (d, 1, J = 5 Hz, H-8 anti), 1.83 [s, 3, C(2) CH_3], and 1.5 ppm (s, 3, bridgehead CH_3).

Anal. Calcd for $C_{18}H_{17}ClHgO$: C, 44.54; H, 3.50. Found: C, 44.35; H, 3.52.

***endo*-2,5-Dimethyl-*exo*-2-dibenzobicyclo[3.2.1]octadienol (41)** was prepared by hydrodemercuration of **40** in the usual fashion: mp 100–102 °C; ^{1}H NMR δ 6.7–7.6 (m, 8, aromatic H), 3.26 (d, 1, J = 4.5 Hz, H-1), 2.58 (d, 1, J = 11 Hz, H-8 syn), 2.25 (d of d, 1, J = 11, 4.5 Hz, H-8 anti), 1.17 (s, 3, bridgehead CH_3), and 1.46 ppm [s, 3, C(2) CH_3].

Oxymercuration of 19 in Acetone–Water. A solution of 0.70 g (3 mmol) of **19** and 2.87 g (9 mmol) of mercuric acetate in 50 ml of acetone–water (4:1) and 1.5 ml of glacial acetic acid was heated at reflux for 1 day. Addition of 1.0 g (47 mmol) of NaCl in 120 ml of water and extraction with chloroform was followed by the usual workup. The ^{1}H NMR spectrum showed a mixture of **25** and **26** in a 1:1 ratio.

Oxymercuration of 18 in Tetrahydrofuran–Water. A solution of 0.319 g (1 mmol) of mercuric acetate in 1.0 ml of water was added to a solution of 0.218 g (1 mmol) of **18** in 1.0 ml of tetrahydrofuran and the reaction mixture was stirred for 21.5 h. Reduction with sodium borohydride, followed by the usual workup, gave a mixture whose ^{1}H NMR spectrum showed about 17% **35** and 21% acetate **33**, with the remainder being alcohols **37** and **38**.

Oxymercuration of 20 in Aqueous Tetrahydrofuran. A solution of 0.70 g (3 mmol) of **20** and 1.45 g (4.5 mmol) of mercuric acetate in 30 ml of 50% aqueous tetrahydrofuran to which 1 ml of glacial acetic acid had been added was stirred for 2 h. NaOH (0.5 g) and excess sodium borohydride were added. After the usual workup, the ^{1}H NMR spectrum of the product showed only **20** and **41** in approximately a 1:1 ratio. No **30**, **31**, or **32** was observed.

Oxymercuration of 1 in Acetic Acid for a Short Time. A solution of 0.20 g (1 mmol) of **1** and 0.67 g (2 mmol) of mercuric acetate in 20 ml of glacial acetic acid was stirred for about 19 min before 1.0 g of NaCl was added. The solution was stirred for about 2 min before 100 ml of water was added. Sodium borohydride reduction gave a mixture whose ^{1}H NMR spectrum showed that approximately 30% of **1** had been converted to the acetate of **14**. No rearranged products were observed.

Oxymercuration of 20 in Acetic Acid–Water (4:1). A solution of 1.00 g (4.3 mmol) of **20** and 1.75 g (5.5 mmol) of mercuric acetate in 50 ml of glacial acetic acid–water (4:1) was stirred for 1 day before 2.0 g of NaCl was added. The precipitate was reduced with sodium borohydride. After the usual workup, a ^{1}H NMR spectrum of the product showed it to be exclusively the [3.2.1] alcohol **41**.

Oxymercuration of 20 in Acetic Acid–Methanol (4:1). A solution of 5.0 g (21.6 mmol) of **20** and 10.3 g (32.3 mmol) of mercuric acetate in 70 ml of an acetic acid–methanol (4:1) mixture was stirred for 15 h before 5.0 g (85 mmol) of NaCl was added. Workup as usual gave 7.7 g (70%) of *syn*-8-chloromercuri-*endo*-2,5-dimethyl-*exo*-2-dibenzobicyclo[3.2.1]octadienyl methyl ether (**44**), which, after recrystallization from chloroform–carbon tetrachloride, had mp 185–186°; ^{1}H NMR (Me_2SO-d_6) δ 6.7–7.0 (m, 8 H, aromatic H), 3.85 (d, 0.8 H, J = 4.5 Hz, H-1), 3.48 (s, 3 H, OCH_3), 3.05 (d, 0.7 H, J = 4.5 Hz, H-8 anti), 1.87 [s, 3 H, C(2) CH_3], and 1.95 ppm (s, 3 H, bridgehead CH_3).

Anal. Calcd for $C_{19}H_{19}OHgCl$: C, 45.69; H, 3.81. Found: C, 45.59; H, 3.73.

***endo*-2,5-Dimethyl-*exo*-2-dibenzobicyclo[3.2.1]octadienyl methyl ether (42)** was prepared by sodium borohydride reduction of **44**-Cl, oil: ^{1}H NMR δ 6.9–7.5 (m, 8, aromatic H), 3.51 (m, 1 H, J = 5 Hz, H-1), 3.38 (s, 3, OCH_3), 2.69 (d, 1, J = 11 Hz, H-8 syn), 2.20 (d of d, 1, J = 11, 5 Hz, H-8 anti), 1.75 [s, 3, C(2) CH_3], and 1.42 ppm (s, 3, bridgehead CH_3).

Oxymercuration of 20 in Acetic Acid–Methanol (19:1). A solution of 1.00 g (4.3 mmol) of **20** and 1.75 g (5.5 mmol) of mercuric acetate in 50 ml of acetic acid–methanol (19:1) was stirred for 1 day before 1.0 g of NaCl was added. Workup and sodium borohydride reduction gave a product whose ^{1}H NMR spectrum showed **42** (67%), **30** (22%), and **32** (11%).

Oxymercuration of 20 in Methanol. A solution of 2.1 g (9 mmol) of **20** and 4.35 g (13.5 mmol) of mercuric acetate in 35 ml of methanol was stirred for 17 h before 1.0 g (20 mmol) of NaCl and 75 ml of water were added. The precipitate was collected and dried in vacuo over P_2O_5, yielding 4.1 g of solid product. The ^{1}H NMR spectrum (Me_2SO-d_6) of the product mixture indicated that the [2.2.2] addition product had trans stereochemistry[32b] for the Hg–X and OCH_3 substituents [δ 4.27 ppm (J = 3 Hz, H-8)]. The ^{1}H NMR spectrum also indicated that the acetoxymercurials had been isolated, not the chloromercurials. To 4.0 g (7.6 mmol) of the product dissolved in 20

Table I. Oxymercuration of 1,4-Dimethyldibenzobicyclo[2.2.2]octatriene in Acetic Acid. Effect of Time on Product Composition

	Composition, %			
Time, h	20	28	29	28:29
0.25	56.4	24.9	18.7	57:43
0.50	47.2	28.2	24.6	53:47
1.0	27.9	38.9	33.3	54:46
2.0	22.7	48.8	28.5	63:37
4.5	14.7	54.2	31.1	64:36
9.0	11.8	65.5	24.7	72:28
21.0	12.5	72.3	15.2	83:17
32.5	9.7	77.0	13.3	85:15
44.5	10.8	75.6	13.6	85:15
66.5	9.9	80.1	10.0	89:11

ml of tetrahydrofuran and 20 ml of 2 M NaOH, 0.50 g (13.2 mmol) of sodium borohydride was added and the solution was stirred for 15 min. The solution was decanted from 1.49 g (92%) of metallic mercury and the usual workup gave 2.11 g (99%) of an oil. The ^{1}H NMR spectrum of the product mixture indicated that ethers **42** and **43** were present in approximately equal amounts. The ethers were separated by high-pressure liquid chromatography on silica gel with 4% ether in hexanes as elutant. The ^{1}H NMR spectrum of the second ether eluted corresponded with that of **42**. Recrystallization of the first fractions from hexane gave 1,4-dimethyl-7-dibenzobicyclo[2.2.2]octadienyl methyl ether (**43**): mp 107–108 °C; ^{1}H NMR δ 7.0–7.5 (m, 8, aromatic H), 3.38 (d of d, 1, J = 9, 3 Hz, H-7), 3.20 (s, 3, OCH_3), 2.07 (d of d, 1, J = 11, 9 Hz, H-8 anti), 2.00 [s, 3, C(1) CH_3], 1.93 [s, 3, C(4) CH_3], and 1.47 ppm (d of d, 1, J = 11, 3 Hz, H-8 syn).

Anal. Calcd for $C_{19}H_{20}O$: C, 86.36; H, 7.57. Found: C, 86.53; H, 7.66.

Stability of 29-OAc to Oxymercuration Conditions in Acetic Acid. Olefin **20** (2.32 g, 10 mmol) in 25 ml of glacial acetic acid was added to 3.18 g (10 mmol) of mercuric acetate in 25 ml of glacial acetic acid at room temperature. Aliquots (5.0 ml) were removed from time to time. NaCl (0.5 g) was added to each aliquot and 50 ml of water was added after 1–5 min of stirring. For the shorter reaction times, the time between NaCl addition and water addition was less. The solid product was then collected, washed with water, and dried on a suction filter. The ^{1}H NMR spectra (Me_2SO-d_6) of the resulting product mixtures were obtained and the product ratios were determined by comparing multiple integrations of the peaks at δ 6.52 (H-7 and H-8 of **20**) with those at 5.34 (d, J = 9 Hz, H-7 of **28**) and those at 4.48 ppm (d, J = 5 Hz, H-1 of **29**). Results are summarized in Table I.

Stability of 28-OAc to Oxymercuration Conditions in Acetic Acid. A solution of 1.40 g (6 mmol) of **20** and 3.83 g (12 mmol) of mercuric acetate in 25 ml of glacial acetic acid was stirred for 24 h and poured into 200 ml of water. The aqueous solution was decanted from the solid product and approximately 0.3 g of the product was dried in vacuo over P_2O_5. The remainder of the product was redissolved in 20 ml of glacial acetic acid and stirred for 17 h before 2.0 g (34 mmol) of NaCl was added. The solution was stirred for another 15 min, 100 ml of water was added, and the product was collected, washed with water, and dried. The ^{1}H NMR spectrum (Me_2SO-d_6) of the product (**28**-OAc) before its reaction with acetic acid indicated that no **20** or **29**-OAc were present. The ^{1}H NMR spectrum (Me_2SO-d_6) of the product after reaction in acetic acid also indicated no **20** or **29**-Cl.

1,4-Dimethyl-7-dibenzobicyclo[2.2.2]octadienol (55). To a solution of 10.0 g (43 mmol) of **20** and 7.45 g (197 mmol) of sodium borohydride in 110 ml of dry bis(2-methoxyethyl) ether (diglyme) at 0 °C, a solution of 10.5 ml (85 mmol) of boron trifluoride etherate in 40 ml of dry diglyme was added over a 2-h period under a nitrogen atmosphere. The reaction mixture was stirred for another 4 h during which the reaction was allowed to warm to room temperature. Water (25 ml) was *cautiously* added over 45 min, followed by 40 ml of 10% aqueous NaOH while the solution was cooled to 0 °C. To the solution, 40 ml of 30% hydrogen peroxide was added over a 30-min period and the reaction mixture warmed to room temperature and stirred for 13 h. Normal workup gave 10.6 g (98%) of **55**. Recrystallization from ethanol–water (1:1) gave 9.4 g (87%) of **55**: mp 144–145 °C; ^{1}H NMR δ 7.0–7.5 (m, 8, aromatic H), 3.75 (d of d, 1, J = 9, 3 Hz, H-7), 2.18 (d of d, 1, J = 13, 9 Hz, H-8 anti), 1.95 (s, 3, bridgehead CH_3), 1.88 (s, 3, bridgehead CH_3), and 1.22 ppm (d of d, 1, J = 13, 3 Hz, H-8 syn).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.40; H, 7.20. Found: C, 86.57; H, 7.29.

1,4-Dimethyl-7-dibenzobicyclo[2.2.2]octadienyl *p*-toluenesulfonate (56) was prepared from **55** and *p*-toluenesulfonyl chloride in dry pyridine at 0 °C. Workup and recrystallization from ether–petroleum ether (bp 60–70°) gave **56**: mp 89–91 °C dec; ^{1}H NMR δ 7.1–7.8 (m, 12, aromatic H), 4.62 (d of d, 1, J = 8, 3 Hz, H-7), 2.42 (s, 3, bridgehead CH_3), 2.12 (d of d, 1, J = 14, 8 Hz, H-8 anti), 1.87 (s, 6, bridgehead CH_3 and tosylate CH_3), and 1.53 ppm (d of d, 1, J = 14, 3 Hz, H-8 syn).

Anal. Calcd for $C_{25}H_{24}O_3S$: C, 74.26; H, 5.94. Found: C, 74.11; H, 6.06.

Solvolysis of 56 in Acetic Acid with Sodium Acetate. Isolation of 2-Methylene-5-methyldibenzobicyclo[3.2.1]octadiene (32). A solution of 3.14 g (7.8 mmol) of **56** and 0.70 g (8.5 mmol) of sodium acetate in 60 ml of glacial acetic acid was heated at reflux for 12 h. The mixture was poured into 100 ml of benzene and 200 ml of water. Normal workup gave 1.8 g (100%) of olefin **32**, which after recrystallization from ethanol had mp 119–120°; ^{1}H NMR δ 6.9–7.75 (m, 8, aromatic H), 5.45 (s, 1 H, vinyl H cis to aromatic ring), 5.15 (s, 1 H, trans vinyl H), 4.00 (t, 1 H, J = 2 Hz, H-5), 2.37 (d, 2 H, J = 2 Hz, H-8), and 1.8 ppm (s, 3, CH_3).

Anal. Calcd for $C_{18}H_{16}$: C, 93.10; H, 6.90. Found: C, 93.22; H, 6.93.

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Registry No.—**1**, 2734-13-6; **18**, 58426-49-6; **19**, 58426-50-9; **20**, 58426-51-0; **21**, 58426-52-1; **26**, 2198-06-3; **28**-Cl, 58426-53-2; **28**-OAc, 58426-54-3; **29**-Cl, 58426-55-4; **29**-OAc, 58426-56-5; **30**, 58426-57-6; **32**, 58426-58-7; **34**, 58426-59-8; **35**, 58426-60-1; **36**, 58462-42-3; **40**-Cl, 58426-61-2; **41**, 58426-62-3; **42**, 58426-63-4; **43**, 58426-64-5; **44**, 58426-65-6; **47**, 58426-66-7; **48**, 58426-67-8; **49**, 2395-96-2; **50**, 58426-68-9; **51**, 58426-69-0; **52**, 781-43-1; **53**, 58426-70-3; **54**, 58426-71-4; **55**, 58426-72-5; **56**, 58426-73-6; *trans*-1,2-dichloroethene, 156-60-5; *cis*-1,2-dichloroethene, 156-59-2; mercuric acetate, 10507-39-8; 9-methylanthracene, 779-02-2.

References and Notes

(1) Part 81: S. J. Cristol and M. C. Kochansky, *J. Org. Chem.*, **40**, 2171 (1975).
(2) For reviews, see (a) W. Kitching, *Organomet. Chem. Rev.*, **3**, 61 (1968); (b) C. Chandra, M. S. Muthana, and D. Devaprabhakara, *J. Sci. Ind. Res.*, **30**, 333 (1971); (c) D. J. Pasto and J. A. Gontarz, *J. Am. Chem. Soc.*, **93**, 6902 (1971).
(3) S. J. Cristol, R. P. Arganbright, G. D. Brindell, and R. M. Heitz, *J. Am. Chem. Soc.*, **79**, 6035 (1957).
(4) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, **28**, 1374 (1963).
(5) S. J. Cristol, F. P. Parungo, and D. E. Plorde, *J. Am. Chem. Soc.*, **87**, 2870 (1965).
(6) (a) S. J. Cristol, R. Caple, R. M. Sequeira, and L. O. Smith, Jr., *J. Am. Chem. Soc.*, **87**, 5679 (1965); (b) S. J. Cristol and B. B. Jarvis, *ibid.*, **88**, 3091 (1966).
(7) (a) S. J. Cristol, R. J. Bopp, and A. E. Johnson, *J. Org. Chem.*, **34**, 3574 (1969); (b) S. J. Cristol and R. J. Bopp, *ibid.*, **39**, 1336 (1974).
(8) W. R. Vaughan and A. C. Schoenthaler, *J. Am. Chem. Soc.*, **80**, 1956 (1958).
(9) (a) S. J. Cristol and R. K. Bly, *J. Am. Chem. Soc.*, **82**, 6155 (1960); (b) S. J. Cristol and D. D. Tanner, *ibid.*, **86**, 3122 (1964); (c) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **87**, 2879 (1965); (d) S. J. Cristol, J. R. Mohrig, and G. T. Tiedeman, *J. Org. Chem.*, **37**, 3239 (1972).
(10) H. J. Lucas, F. R. Hepner, and S. Winstein, *J. Am. Chem. Soc.*, **61**, 3102 (1939).
(11) G. F. Wright, *J. Am. Chem. Soc.*, **57**, 1993 (1935).
(12) R. D. Bach and R. F. Richter, *J. Am. Chem. Soc.*, **94**, 4747 (1972).
(13) W. Kitching, A. J. Smith, and P. R. Wells, *Aust. J. Chem.*, **21**, 2395 (1968).
(14) G. A. Olah and P. R. Clifford, *J. Am. Chem. Soc.*, **93**, 1261 (1971).
(15) S. Bentham, P. Chamberlain, and G. H. Whitham, *J. Chem. Soc. D*, 1528 (1970).
(16) J. Halpern and H. B. Tinker, *J. Am. Chem. Soc.*, **89**, 6427 (1967).
(17) V. I. Sokolov, L. L. Troitskaya, and O. A. Reutov, *J. Organomet. Chem.*, **17**, 323 (1969).
(18) (a) T. G. Traylor and A. W. Baker, *Tetrahedron Lett.*, 14 (1959); (b) T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963); (c) T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, **33**, 2614 (1968).
(19) H. C. Brown and J. H. Kawakami, *J. Am. Chem. Soc.*, **95**, 8665 (1973), and references cited therein.
(20) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972, p 265 ff.
(21) V. I. Sokolov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1285 (1968).
(22) Reference 5, and other work in this laboratory.
(23) In this discussion, we have no information regarding the numbers of ligands attached to mercuric ion, or the steps in which they are lost, and simply assume at least that one acetate ligand is attached in the whole process.
(24) Evidence for the electrophilic nature of the oxymercuration of norbornene is summarized by Traylor.[25]
(25) T. G. Traylor, *Acc. Chem. Res.*, **2**, 152 (1969).
(26) A concerted molecular addition such as proposed in eq 4 and a cis ligand migration,[25] which may sometimes be considered as an alternative, are, in reality not significantly different as they have identical transition states.

(27) H.-P. Löffler and G. Schröder, *Tetrahedron Lett.*, 2119 (1970).
(28) E. J. Corey and R. S. Glass, *J. Am. Chem. Soc.*, **89**, 2600 (1967).
(29) K. B. Wiberg and Wan-fang Chen, *J. Org. Chem.*, **37**, 3235 (1972).
(30) M. S. Newman and M. C. Vander Zwan, *J. Org. Chem.*, **39**, 1186 (1974).
(31) G. R. Krow and J. Reilly, *J. Org. Chem.*, **40**, 136 (1975).
(32) Structural interpretations of NMR data were made according to (a) S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **30**, 1956 (1965); (b) S. J. Cristol, T. W. Russell, J. R. Mohrig, and D. E. Plorde, *ibid.*, **31**, 581 (1966).
(33) S. J. Cristol and W. Y. Lim, *J. Org. Chem.*, **34**, 1 (1969).
(34) Sample prepared by Dr. G. O. Mayo.
(35) S. J. Cristol and J. S. Perry, Jr., *Tetrahedron Lett.*, 1921 (1974).

Bridged Polycyclic Compounds. 83. Steric and Bromine Substituent Acceleration in Bromination Reactions[1,2]

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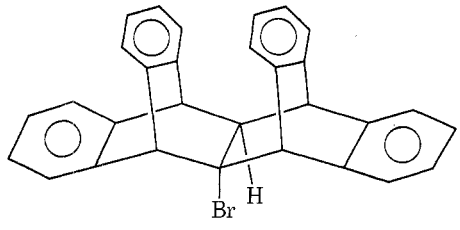
Free-radical brominations of a number of bridged compounds (compounds **3–9**) have been carried out, with attention paid both to product compositions and to relative reactivities. Each of the compounds had at least one tertiary hydrogen atom at a nonbridgehead position, and reaction occurred exclusively at such positions. A solvent system was devised which scavenged hydrogen bromide rapidly, and competitive brominations were conducted with pairs of compounds. The relative reactivities of the compounds have been rationalized in terms of structural features, and the product compositions have also been discussed.

Some time ago it was reported[3] that 5a-bromojanusene (**1**) was more reactive toward free-radical bromination than



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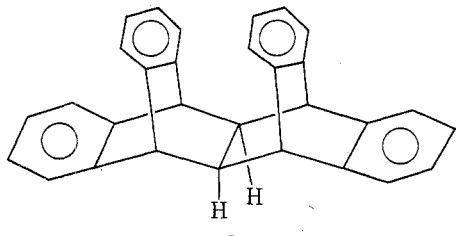

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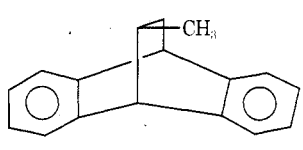
janusene (**2**) itself. This seemed to us to be an interesting result, as the usual explanation[4] for β-activation by bromine, that is, anti-neighboring group participation by bromine in the transition state for hydrogen abstraction, cannot be invoked in this case for obvious geometric reasons. Rather some syn activation process might be inferred, or the ring system itself, which is not without other unusual properties,[5] might be responsible for the rate enhancement. We therefore undertook the study reported in this paper to see whether or not such syn periplanar activation is a general phenomenon in the abstraction of tertiary hydrogen atoms by bromine atoms.

To this end, we determined to study the relative rates of free-radical bromination of compounds **3–9**. With these compounds we would be in a position not only to study the effect of bromine substituents upon the reactivities of vicinal hydrogen atoms, but also the effects of neighboring methyl groups.

Preparation of Reagents. 7-Methyldibenzobicyclo[2.2.2]octadiene (**3**)[6] and *cis*- (**4**)[7] and *trans*-7,8-dimethyldibenzobicyclo[2.2.2]octadiene (**5**)[7,8] had already been described. We found it convenient to prepare **4** and **5** by diene syntheses at 225 °C from anthracene and *cis*- and *trans*-2-



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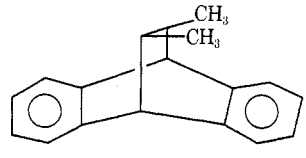

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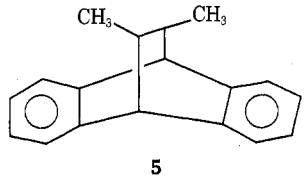

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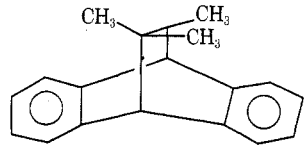

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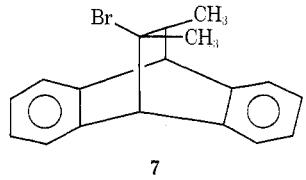

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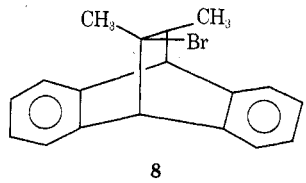

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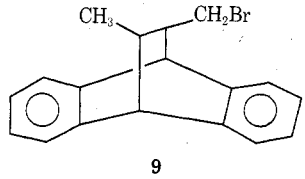

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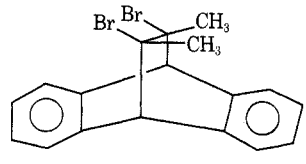

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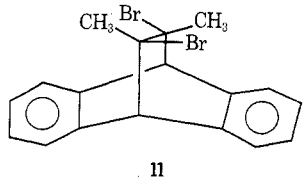

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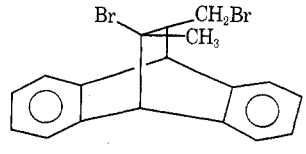

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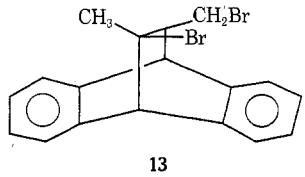

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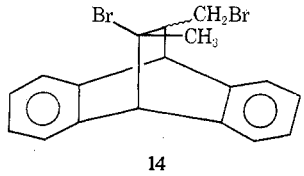

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