(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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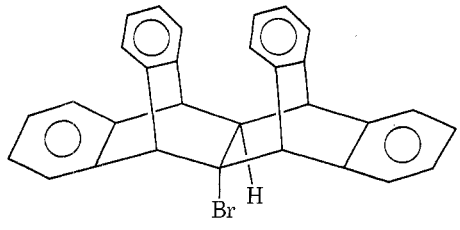
*Received September 8, 1975*

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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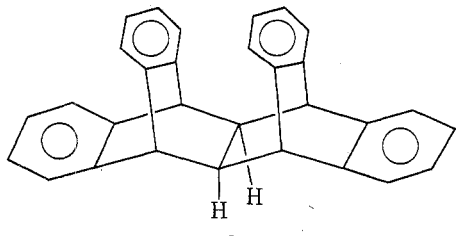
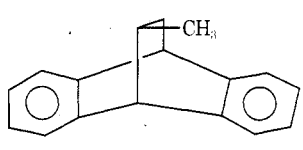


**2**

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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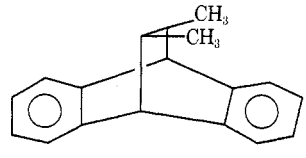

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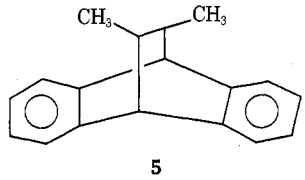

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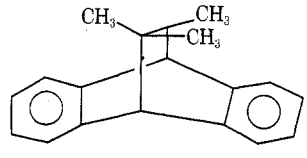

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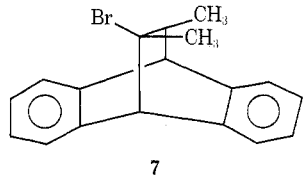

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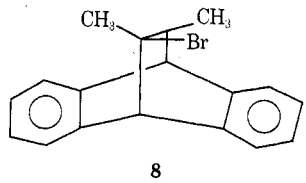

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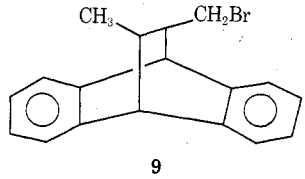

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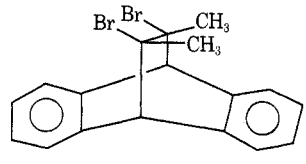

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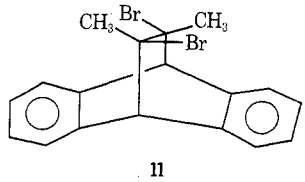

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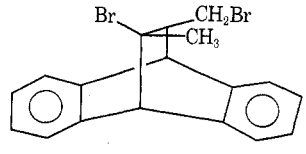

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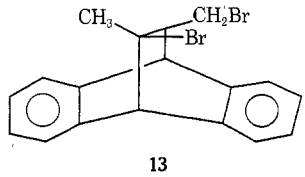

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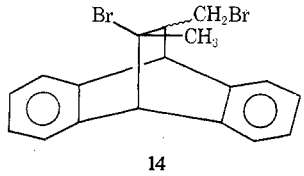
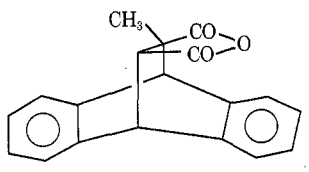


**14**

butene, respectively. When **4** was prepared in this fashion in a steel pressure autoclave, contamination with **5** was observed. This contamination, which was presumably the result of ferric ion catalyzed olefin isomerization, was eliminated by addition of small amounts of ethylenediaminetetraacetic acid and phthalonitrile to coordinate with the iron.

2-Methyl-2-butene could not be induced to react with anthracene to give **6**. Apparently the extra methyl group provides too much steric hindrance to allow reaction.[9] As **3**, **4**, and **5** had been prepared by lithium aluminum hydride reductive displacements on *p*-toluenesulfonate esters,[6-8] such a process appeared attractive for **6** as well. To this end, **16**, or its epimer, was required. Lithium aluminum hydride reduction of **15**[10] did not proceed well, but conversion of **15** to **17**,[10] followed by $LiAlH_4$ reduction, gave **16** readily

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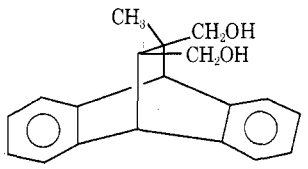


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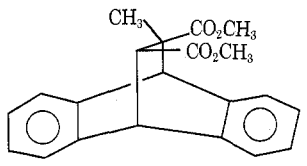


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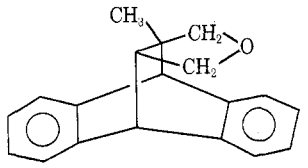


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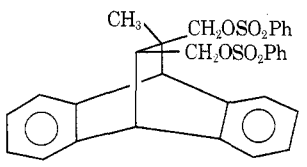


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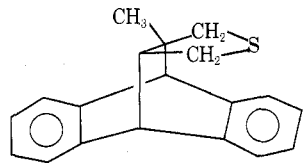


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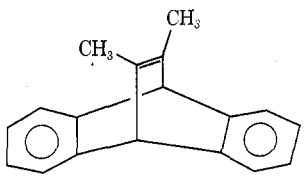


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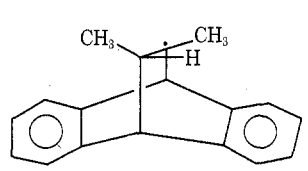



**22**

and in high purity. Attempts to convert the diol **16** to the bis-*p*-toluenesulfonate ester by standard procedures led instead to the tetrahydrofuran **18**, presumably by base-promoted reaction of the mono esters. The bisbenzenesulfonate ester **19** was prepared by oxidation of the readily prepared bisbenzenesulfinate ester.

Although the reduction of the analogue of **19** without the methyl group (and with *p*-toluenesulfonoxy groups) proceeds to give **4** in fair yield when special conditions are used, that of **19** led rather to the tetrahydrofuran **18**, presumably via attack at sulfur to give the monoester,[7] rather than at carbon to give the desired reduction product **6**. However, treatment of **19** with ethanolic sodium hydrosulfide gave the tetrahydrothiofuran **20**, which upon treatment with Raney nickel was readily converted to **6**.

The monobromo derivatives (**7** and **8**) of the dimethyl compounds were prepared by free-radical addition of hydrogen bromide to the olefin **21**. The trans isomer **8** predominated over the cis isomer **7** in a ratio of 7:1. Ionic addition of hydrogen bromide to **21** gave rearranged products with the dibenzobicyclo[3.2.1]octadiene skeleton, as well as [2.2.2] products. Attempts to prepare **7** and/or **8** by stereospecific syntheses failed. Although **7** and **8** were readily distinguished by $^1H$ NMR spectroscopy, the structures of these were not readily apparent from these data. X-Ray analysis of the major product (which was readily separated and purified) showed that it was the trans isomer **8**.

***trans*-7-Bromomethyl-8-methyldibenzobicyclo-[2.2.2]octadiene (9)** was prepared from the alcohol resulting from the reduction of the Diels–Alder adduct[12] of anthracene and methyl *trans*-crotonate. Treatment of this alcohol with triphenylphosphine dibromide gave **9**.

**Methods of Competitive Bromination and Results.** In order to measure the relative reactivities of the tertiary hydrogen atoms in the compounds of interest, we compared their rates of disappearance in paired sets[13] in photobromination reactions. Relative bromination rates will give relative hydrogen abstraction rates only if the reaction in eq 1

$$RH + Br\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R\cdot + HBr \quad (1)$$

$$R\cdot + Br_2 \xrightarrow{k_2} RBr + Br\cdot \quad (2)$$

is irreversible, that is, $k_2[Br_2] \gg k_{-1}[HBr]$, or if $k_{-1}/k_2$ is identical for all of the alkyl radicals under study, which seems highly unlikely. Furthermore, the reverse reaction in eq 1 may lead to epimerization of **4** and **5** and of **7** and **8**. Indeed such epimerization may be used as a measure of reversibility. Thus, the high reactivity of the radical **22** from **4** with hydrogen bromide compared with bromine may be noted from the fact that treatment of **4** with 1 mmol of bromine in 60 mol of carbon tetrachloride give a mixture of 54% of **7** and **8**, 8–11% of **4**, and 31–33% of the trans isomer **5**.[14] Isomerization of **4** to **5** was reduced substantially when 4–6% of solvent was replaced by a hydrogen bromide scavenger, 2,3-epoxy-2,3-dimethylbutane, and was almost completely eliminated when ratios of 1 mol of **4**, 1 of $Br_2$, 50 of $CCl_4$, and 21 of epoxide were used (at 50% bromination, the hydrocarbon mixture contained 97% of **4** and 3% of **5**).

For preparative bromination reactions, we found that reversal and attendant isomerization could be lessened substantially by conducting the bromination in the presence of a water layer and using vigorous stirring. In this way the hydrogen bromide was extracted into the aqueous phase and its concentration in the organic solvent was low enough to cut down its competition with bromine for the intermediate radical.

Relative rates of disappearance were measured at 10–11 °C, using ratios of 0.5–1.0 mol of $Br_2$ to 1 of substrate mixture, 36 of $CCl_4$, and 21 of epoxide. After irradiation (tungsten lamp), solvents were removed by rotary evaporation, petroleum ether was added, and oxygen-containing substances were extracted with 85% phosphoric acid. Analysis was by $^1H$ NMR and/or GLC. Data and calculated relative reactivities are given in Table I and in Table II.

## Discussion

When the data in Table I are corrected for the number of tertiary hydrogen sites, it becomes evident that the monomethyl derivative **3** and the trans dimethyl derivative **5** have a reactivity ratio of about 2, and the cis dimethyl compound **4** and the trimethyl compound **6** have one of about 1.5. These pairs differ in having a methyl group which might provide interference with the attacking bromine atom; this effect is small. Presumably in its attack on a hydrogen atom, the bromine atom is not greatly interfered with by the hydrogens of the syn methyl group. On the other hand, the relative reactivities of each tertiary site in **4** to that of **3** of 16:1, and the corresponding ratio of that in **6** to those in **5** of 30:1, show the relatively large rate enhancement caused by the additional eclipsed methyl group remote from the site of attack. We see no simple rationaliza-

Table I. Data and Results on Photobrominations in a Carbon Tetrachloride–2,3-Dimethyl-2,3-epoxybutane Mixture

| Run | Mole ratios: Substrates | Mole ratios: $Br_2$ | Recovered substrates,[a] % of aromatic peaks | Rel reactivity |
|---|---|---|---|---|
| 1[b] | 5, 0.55; 3, 0.45 | 0.50 | 5, 45.0; 3, 35.6 | 3:5 = 1.2:1 |
| 2 | 5, 0.50; 3, 0.50 | 0.88 | 5, 24.0; 3, 24.0 | 3:5 = 1.0:1 |
| 3 | 4, 0.63; 5, 0.37 | 0.70 | 4, 6.4; 5, 34.6 | 4:5 = 34:1 |
| 4 | 4, 0.51; 5, 0.49 | 0.94 | 4, 2.6; 5, 45. | 4:5 = 35:1 |
| 5[b] | 5, 0.52; 6, 0.48 | 0.70 | 5, 48.2; 6, 16.1 | 5:6 = 14:1 |
| 6 | 4, 0.52; 6, 0.48 | 0.59 | 4, 14.3; 6, 32.4 | 4:6 = 3.3:1 |
| 7[b,c] | 7, 0.21; 8, 0.74 | 0.79 | 7, 18.5; 8, 23.0 | 8:7 = 9.2:1 |
| 8[c] | 7, 0.21; 8, 0.74 | 0.87 | 7, 13.5; 8, 5.0 | 8:7 = 6.1:1 |
| 9[d] | 8, 0.37; 6, 0.61 | 0.24 | 8, 14.0; 6, 44.0 | 8:6 = 3.0 |
| 10[e] | 8, 0.35; 6, 0.63 | 0.30 | 8, 13.0; 6, 46.0 | 8:6 = 3.2 |
| 11[e] | 8, 0.556; 9, 0.418 | 0.59 | 8, 8.2; 9, 41.0 | 8:9 = 100:1[f] |
| 12 | 3, 0.497; 9, 0.503 | 0.53 | 3, 33.0; 9, 46.5 | 3:9 = 5.0:1 |

[a] Mixtures of bromides and/or dibromides were also present. [b] Run stopped before all bromine was consumed. [c] This sample contained 5% of an unknown impurity. [d] This sample also contained 2% of 7. [e] This sample also contained 3% of 7. [f] Value probably has high error; not used for Table II computation.

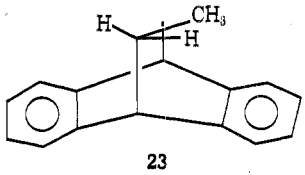
Table II. Relative Reactivities toward Bromine Atoms (Compound 5 ≡ 1.0)[a]

| Compd | Rel reactivity | Rel reactivity per tertiary H atom |
|---|---|---|
| 3 | 1.1 | 2.2 |
| 4 | 34. | 34. |
| 5 | 1.0 | 1.0 |
| 6 | 12. | 24. |
| 7 | 5. | 10. |
| 8 | 37. | 74. |
| 9 | 0.22 | 0.4[b] |

[a] Estimated reliabilities ±0.25. [b] Assuming that one of the tertiary hydrogens is preferentially attacked.

tion of these results other than steric acceleration due to back-strain relief.[2]

Rate enhancement might be anticipated[16,17] when two groups compressed in the initial state move farther apart in the radical formed. As it may be assumed that the angles between groups at the radical site in these radicals (e.g., **22**, **23**, and **24**) will be greater than tetrahedral, steric acceleration should be noted when the transition state is sufficiently advanced along the reaction coordinate. Thus, as observed, **4** should react more rapidly than **3**, and **6** more rapidly than **5**.

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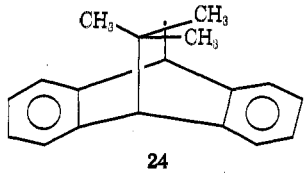


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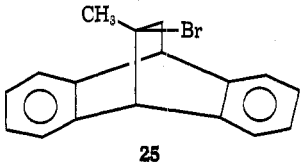


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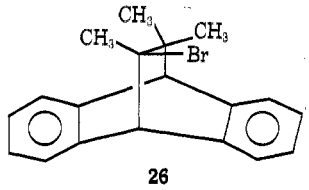



**26**

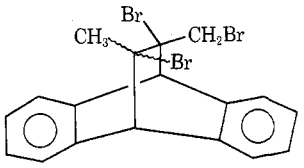
Steric acceleration of rate by back-strain relief has been noted by Simamura and Mayajima,[18] who observed that the tertiary equatorial hydrogen atom in 1,1,3,5-tetramethylcyclohexane reacts with alkylperoxy radicals 4.2 times as rapidly as the equivalent hydrogen atom in 1,3,5-trimethylcyclohexane, a result which was ascribed to relief of 1,3 interaction (methyl–methyl greater than methyl–hydrogen) in the hydrogen abstraction reaction. More recently, Abruscata and Tidwell[19] have ascribed the enhanced decomposition rate of *tert*-butyl di-*tert*-butylperoxyacetate over that of *tert*-butyl peroxyisobutyrate to back-strain relief. These cases, plus those discussed in this paper, put the steric acceleration phenomenon upon a solid base.

The products of bromination of **3** and **6** were, as anticipated, those of reaction at the tertiary site, **25** from **3** and **26** from **6**. Although one might anticipate that the product mixtures from **4** and **5** would be identical, as they both arise from the common radical **22**, this is not the case, for straightforward reasons. As is noted below and in Table II, bromides **7** and **8**, which have somewhat different reactivities (**8** > **7**), are both significantly more reactive than the trans-dimethyl compound **5**, and **8** is also more reactive than the cis-dimethyl compound **4**. This means that when bromination of **4** and **5** are conducted under conditions where substantial bromination occurs, the primary products **7** and **8** are further consumed to give dibromides **10** and **11** and the observed product ratio of **7**:**8** is the result of a complicated composition of formation and disappearance rates. Our data were not precise enough (nor did we conduct experiments of small enough reaction) to enable us to give relative rates of capture of **22** with any degree of precision. However, as may be anticipated from the data in Table II, when **5** was brominated extensively, the product mixture contained much dibromide, some **7**, and only traces of **8**.[20] On the other hand, when the more reactive **4** was brominated, much monobromide was observed in the product with ratios of **8**:**7** as high as 1.[20] This suggests that **22** is not highly discriminating in its reaction with bromine, and that in the transition state for its reaction to give **7**, the steric strain which results between the two eclipsing methyl groups and the hydrogen atom and the entering bromine atom is roughly equal to that in the transition state leading to **8**, resulting from eclipsing strains between methyl and hydrogen and methyl and the entering bromine atom. As no large dipoles are involved, and as bromine and methyl have approximately equal steric requirements,[21] this result appears reasonable. An amusing consequence of the difference between the sizes of hydrogen and bromine substituents is the large difference in the rates of formation of **22** from **4** and **5** and the small difference in the rates of reaction of **22** to give **7** and **8**, processes that appear, without consideration of steric interactions between leaving, entering, and remaining groups, to be almost alike. It would be

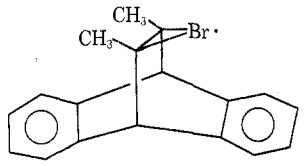
useful to check these ideas by bromine abstraction from **7** and **8** with a small radical reagent. These should have very similar reactivities.

**Bromination of Monobromo Compounds.** The bromination of **7** and **8**, or the bromination of **4** and **5**, led to mixtures of **10** and **11** in which one isomer predominated (7:1). The principal isomer was readily purified; x-ray analysis showed it to be the trans isomer **11**.

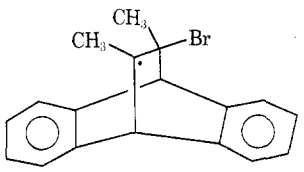
The product from photobromination of **9** was a mixture of the diastereoisomeric monobromination products **12** and **13** and of the dibromination products **27**. None of the



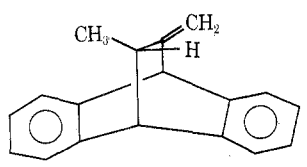
**27**



**28**



**29**



**30**

monobromination products **14** (which would result from attack on the tertiary hydrogen atom next to the bromomethyl group) was noted, although attempts to observe it (by $^1H$ NMR analysis, obviously an inprecise tool) in product mixtures were made. Whether this means that the **14** formed was so reactive that it led quantitatively to **27** or, as we feel more likely,[22] little was formed and **27** came largely from **12** and/or **13**, is not clear. Even if all of the **27** came from **14** it represented less than the amount of **12** and **13** and thus the other tertiary hydrogen was more reactive than that geminal to the bromomethyl group.

As described in the introduction to this paper, our studies were undertaken to see whether the rate enhancement noted with bromojanusene (**1**) over janusene (**2**) was a general phenomenon of syn-periplanar activation in the attack on hydrogen by bromine atom.[23] As the data in Tables I and II show, such expectations were not realized. Thus **7** is only one-third as reactive per hydrogen atom as **4**, rather than more reactive. If one, however, accepts the premise[24] that the inductive effect of a vicinal bromide should reduce reactivity by a factor of 7–9, it would appear that the net reduction is made of a slight increase of the sort apparent in **1** coupled with the inductive decrease. The effect of adding a bromine substituent in the trans-dimethyl compound **5** may be seen in the relative reactivities of **5**, **8**, and **9**. In comparing **8** and **5**, we see, rather than the anticipated[24] loss of reactivity by a factor of 7–9, an increase in reactivity by a factor of 74. We have noted above that the location of a methyl group in the position remote from the site of attack which eclipsed the methyl group in **5** (i.e., to give **6**) increases the reactivity by a factor of 34, and we have ascribed this rate enhancement to steric acceleration. As the effect of bromine–methyl eclipsing in **8** is probably similar to that of the two eclipsed methyl groups in **6** (or in **8**), a portion of the rate enhancement must be due to steric acceleration of rate. However, this cannot be the sole factor, as there still remains the fact that **8** is seven times as reactive as **7**.

It has been suggested[4] that there is anchimeric assistance by vicinal bromine in bromine atom attack on $\beta$-hydrogen atoms, and evidence favoring this idea continues to accumulate.[24,25] For this activation to operate most effectively, an anti-periplanar relationship between the activating bromine atom and the hydrogen atom is believed[24b] to be required. Under such conditions, activation of over 100 times is noted (and with correction for inductive effect, the activation may be computed[24b] to be about $10^3$). It is known[26] in ionic systems that anchimeric assistance is reduced or eliminated when the steric relationship between groups is changed from the antiperiplanar relation (dihedral angle of 180°) to that of trans groups in the bicyclo[2.2.2]octadiene system (dihedral angle of 120°), and a similar effect should[24b] be noted in radical reactions. Thus the relatively small factor of 7 between **8** and **7** seems consistent with a transition state leading to **28** rather than to the open radical **29** in the reaction of **8** with a bromine atom.[27]

While the steric acceleration component of the rate enhancements is a ground-state effect (in the sense that it is relief of ground-state strain that affects reactivities), the remaining effect, anchimeric assistance, is one arising in the transition state differences between **8** giving **28** (and **29**) and **7** giving **29**. The **28** $\rightleftarrows$ **29** equilibrium and their relative reaction rates with molecules (with hydrogen bromide to give **7** from **29** and **8** from **28** and **29**, and with bromine to give **10** from **29** and **11** from **28** and **29**) which pass over similar transition states might show similar phenomena. Indeed this is true. Thus the photobrominations of **7** and/or **8** give **11** and **10** in a ratio of about 7:1, quite similar to the ratio of reactivities of **8** and **7**. Free-radical addition of hydrogen bromide to **21**, which involves bromine atom addition to give the **28** $\rightleftarrows$ **29** mixture, then hydrogen transfer to give **7** and **8**, forms these two substances in a 1:7 ratio. These results may be compared with those involving the radical **22** where hydrogen removal to form **22** and bromine transfer to **22** differ considerably in selectivity.

The results with the trans methyl bromomethyl compound **9** (reactivity 40% of that of the trans dimethyl compound **5**, reaction largely geminal to methyl to give **12** and **13** rather than geminal to bromomethyl to give **14**, and substantial amounts of dibromination) are consistent with the concepts outlined above. The reactivity fits that[24b] of a hydrogen $\gamma$ to a bromine atom exactly (depression due to the inductive effect), and lack of the reaction at the tertiary proton geminal to the bromomethyl group indicates the extra depression of $\beta$-bromo substituent when no anchimeric assistance is seen. Presumable causes might be conformational difficulties, or deactivation by intramolecular complexing with the aromatic ring. The reactivities to be anticipated for **12**, **13**, or **14** compared with **9** (as judged by those of **7** and **8** compared with **5**) make understandable the fact that substantial amounts of dibromination are seen in the bromination of **9**.

Russell and Brown[28] have reported that a heterolytic dark reaction may occur with tertiary-alkyl halides. In order to show that such a reaction path did not compete in our systems, we held solutions of bromine, **7**, and **8** in carbon tetrachloride in the dark at reflux for 2 h or at room temperature for 1 day. No **10** or **11** was produced; instead partial rearrangements to bromo derivatives of dibenzobicyclo[3.2.1]octadiene were observed. An alternative path for bromination involving hydrogen bromide elimination–bromine addition[29] was also considered. However, addition of bromine to **21** (one of the possible elimination products from **7** or **8**) gave no **10** or **11**; again only [3.2.1] rearrangement–addition was observed.[20] Similarly **30** (anticipated elimination product from **9** or possibility from **7** or **8**) gave none of the products observed in the photobromination.[20] Hence the two paths may be disregarded.

## Experimental Section

***trans*-7,8-Dimethyldibenzobicyclo[2.2.2]octadiene (5).** A 0.5-l. steel autoclave was cooled with dry ice and charged with 35 g (0.21 mol) of anthracene, 0.5 g of 4-*tert*-butylcatechol, 200 g of dry

ice cooled *m*-xylene, and 100 ml (1.5 mol) of liquid *trans*-2-butene (Phillips). The autoclave was closed and allowed to warm to room temperature. It was then placed in a heating jacket and kept at 220–230 °C for 6 days. The vessel was then cooled to room temperature, the gases vented, and the *m*-xylene removed almost completely by rotary evaporation. The crude solids were then dissolved in petroleum ether (bp 60–70 °C), and shaken three times with concentrated sulfuric acid, one time each with water, aqueous sodium bicarbonate, and again with water. This sulfuric acid treatment makes unnecessary the usual method of removing unreacted anthracene by reacting it with maleic anhydride and dissolving that adduct by boiling in aqueous sodium hydroxide. The solution was dried, filtered, and concentrated. Recrystallization from petroleum ether gave 36 g (76%) of **5**: mp 93–94 °C (lit.[7,8] 89–92 °C); $^1$H NMR ($CCl_4$) $\delta$ 0.8 (d, $J$ = 6 Hz, 6 H, $CH_3$), 1.3 (m, 2 H, H-7 and -8), 3.82 (d, $J$ = 1.5 Hz, 2 H, H-1 and -4), 7.2 (m, 8 H, aromatic H).

***cis*-7,8-Dimethyldibenzobicyclo[2.2.2]octadiene (4)** was prepared in a similar fashion (on anthracene = 40 g scale) except that *cis*-2-butene was used and 2 g of ethylenediaminetetraacetic acid and 2 g of phthalonitrile were added to avoid ferric ion catalyzed olefin isomerization. Recrystallization from petroleum ether gave 31.7 g of **4** (60%): mp 172–173.5 °C (lit.[7] 173–174 °C); $^1$H NMR ($CCl_4$) $\delta$ 0.65 (d, $J$ = 6 Hz, 6 H, $CH_3$), 2.03 (m, 2 H, H-7 and -8), 3.82 (d, $J$ = 1.5 Hz, 2 H, H-1 and -4), 7.2 (m, 8 H, aromatic H).

***cis*-7,8-Bis(hydroxymethyl)-7-methyldibenzobicyclo[2.2.2]-octadiene (16).** A solution of 23.4 g (0.070 mol) of **17**[10] in 130 ml of dry tetrahydrofuran (THF) was added rapidly with stirring to a solution of 4.75 g (0.12 mol) of lithium aluminum hydride in 200 ml of THF. The reaction mixture was heated at reflux for 3 h, then cooled and poured onto ice. Workup by careful acidification, ether extraction, evaporation of solvent, and recrystallization from ethyl acetate gave 17.3 g (88%) of **16**: mp 146–148.5 °C; $^1$H NMR ($CDCl_3$–$D_2O$) $\delta$ 0.88 (s, 3 H, $CH_3$), 1.75 (m, $J$ = 9.3, 5, 2 Hz, 1 H, H-8), 3.05–3.72 (m, 5 H), 4.02 (d, $J$ = 2 Hz, 1 H, H-4), 7.16 (m, 8 H, aromatic H).

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.61; H, 7.20.

**7-Methyl-7,8-oxydimethyldibenzobicyclo[2.2.2]octadiene (18).** Treatment of **16** with *p*-toluenesulfonyl chloride and tri-*n*-butylamine under standard[30] conditions for the preparation of *p*-toluenesulfonate esters led instead to excellent yields of **18**: mp 133.5–135 °C; $^1$H NMR ($CCl_4$) $\delta$ 0.93 (s, 3 H, $CH_3$), 2.06 (m, $J$ = 5.1, 3, 1.5 Hz, 1 H, H-8), 3.02–3.98 (m, 6 H), 7.08 (m, 8 H, aromatic H).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 86.93; H, 6.99.

***cis*-7,8-Bis(benzenesulfonoxymethyl)-7-methyldibenzobicyclo[2.2.2]octadiene (19).** A saturated solution of 2 g (7.2 mmol) of **16** in anhydrous ether was prepared at 0 °C and 1.1 g (14 mmol) of pyridine was added. Benzenesulfinyl chloride[31] (2.8 g, 16 mmol) was added slowly at 0 °C, and the resulting mixture was kept in a refrigerator overnight. The solid (pyridine hydrochloride) was filtered, and the ethereal solution was washed with dilute acid, dilute base, and water. The solution was dried ($MgSO_4$) and then evaporated to dryness. The resulting mixture of diastereoisomers was oxidized to the sulfonate ester **19** with *m*-chloroperbenzoic acid using the general procedure of Wilt, Stein, and Wagner.[32] Recrystallization from ethyl acetate gave pure **19**: mp 147–148 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.8 (s, 3 H, $CH_3$), 1.27 (m, 1 H, H-8), 3.2–4.05 (m, 5 H), 4.16 (d, $J$ = 2 Hz, H-4), 7–8 (m, 18 H, aromatic H).

Anal. Calcd for $C_{31}H_{28}O_6S_2$: C, 66.41; H, 5.03. Found: C, 66.58; H, 4.96.

**7-Methyl-7,8-thiodimethyldibenzobicyclo[2.2.2]octadiene (20).** Small slivers of sodium (1.65 g, 7.1 mmol) were added to 100 ml of anhydrous ethanol in a 250-ml, two-neck, round-bottom flask. Anhydrous hydrogen sulfide was bubbled through this medium until saturation. About 3.8 g (7.2 mmol) of **19** (which was dried by evaporating the benzene from its benzene solution) was then washed into this reaction medium using a minimum of anhydrous ethanol. The solution was refluxed for 3 days, using a condenser fitted with a $CaSO_4$ drying tube. The solution was poured into ether and washed with portions of water, aqueous sodium carbonate, and water. The ether layer was dried ($MgSO_4$). Evaporation of the ether left **20**, possibly contaminated with traces of **18**. Recrystallization from absolute ethanol gave **20**: mp 154–155 °C; $^1$H NMR ($CCl_4$) $\delta$ 1.03 (s, 3 H, $CH_3$), 2–2.8 (m, 5 H, H-8, $-CH_2S$), 3.81 (s, 1 H, H-1), 3.90 (d, $J$ = 2 Hz, 1 H, H-4), 7.1 (m, 8 H, aromatic H).

Anal. Calcd for $C_{19}H_{18}S$: C, 81.97; H, 6.52. Found: C, 81.86; H, 6.52.

**7,7,8-Trimethyldibenzobicyclo[2.2.2]octadiene (6).** About 1.2 g of the crude thioether **20** was added under nitrogen to an excess of W-7 Raney nickel[33] in 100 ml of anhydrous ether. Stirring was continued at reflux under nitrogen for 3 h. The nickel (caution! pyrophoric) was removed by filtration through a fritted glass funnel. After the solvent was evaporated, the residue was dissolved in petroleum ether and washed twice with dilute HCl, once with dilute $NaHCO_3$, and then with water. Any cyclic ether **18** was removed by extraction with concentrated $H_2SO_4$ before the other extractions. Recrystallization by evaporation of the petroleum ether gave pure **6**: mp 89.5–90 °C; $^1$H NMR ($CCl_4$) $\delta$ 0.61 (s, 3 H, $CH_3$), 0.76 (d, $J$ = 7.3 Hz, 3 H, $CH_3$), 0.78 (s, 3 H, $CH_3$), 1.6 (m, $J$ = 7.3, 2 Hz, 1 H, H-8), 3.6 (s, 1 H, H-1), 3.79 (d, $J$ = 2 Hz, 1 H, H-4), 7.1 (m, 8 H, aromatic H).

Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.71; H, 8.08.

***trans*-7-Bromomethyl-8-methyldibenzobicyclo[2.2.2]octadiene (9).** A solution of 40 g (0.16 mol) of *trans*-7-hydroxymethyl-8-methyldibenzobicyclo[2.2.2]octadiene[7] and 420 g (1.6 mol) of triphenylphosphine in 400 ml of dry dimethylformamide was placed in a three-necked flask covered with foil to prevent light from entering. After deaeration with nitrogen, 256 g (1.6 mol) of bromine was added dropwise, with the temperature controlled to below 100 °C. Stirring, nitrogen bubbling, and heating at 90 °C were continued for 5 days. The mixture was then cooled and poured into water. Ether extraction, solvent evaporation, partial dissolution in carbon tetrachloride, and filtration gave a solution of **9** and triphenylphosphine oxide and a solid residue of the oxide. The solution was dried ($CaSO_4$) and the solvent distilled off. The residue was chromatographed on silica gel (1 kg, 60–200 mesh) using petroleum ether–benzene mixtures to elute **9** and retain the oxide. **9** was contaminated with **21** and with 7-methylene-8-methyldibenzobicyclo[2.2.2]octadiene (**30**). Eluted fractions rich in **9** were dissolved in *n*-hexane, shaken with concentrated sulfuric acid, and recrystallized from *n*-hexane. The **9** had mp 88.5–89 °C; $^1$H NMR ($CCl_4$) $\delta$ 0.78 (d, $J$ = 6.5 Hz, 3 H, $CH_3$), 1.94 (m, 2 H, H-7 and -8), 3.15 (m, 2 H, $CH_2Br$), 3.82 (d, $J$ = 2 Hz, 1 H, H-4), 4.3 (d, $J$ = 2 Hz, 1 H, H-1), 7.13 (m, 8 H, aromatic H).

Anal. Calcd for $C_{18}H_{17}Br$: C, 69.02; H, 5.47. Found: C, 69.01; H, 5.60.

**7-Methylene-8-methyldibenzobicyclo[2.2.2]octadiene (30).** Compound **30**-enriched fractions of the chromatographed products obtained in the synthesis of **9** were fractionally recrystallized from absolute ethanol until pure **30** was obtained. An analytical sample of **30** had mp 98–98.5 °C; $^1$H NMR ($CCl_4$) $\delta$ 0.88 (d, $J$ = 7 Hz, 3 H, $CH_3$), 2.52 (m, 1 H, H-8), 4.6 (m, 2 H, $CH_2$), 3.98 (d, $J$ = 2.5 Hz, 1 H, H-4), 5.06 (d, $J$ = 2.3 Hz, 1 H, H-1), 7.08 (m, 8 H, aromatic H).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.13; H, 6.98.

***trans*-7,8-Dibromo-7,8-dimethyldibenzobicyclo[2.2.2]octadiene (11).** This compound was prepared by photobromination of either **4** or **5** of a mixture of these. The reaction proceeded badly when conducted in the normal fashion (addition of bromine to **4** or **5** in $CCl_4$), because of the presence of hydrogen bromide which interfered with the reaction of intervening radicals with bromine. The following technique, in which water was used to scavenge the hydrogen bromide, gave good yields of dibromides from which **11** was readily recovered.

A solution of 10 g (0.043 mol) of **5** (**4** may be used equally well) in 500 ml of $CCl_4$ and 1200 ml of water was placed in a 2-l. three-neck round-bottom flask fitted with a mechanical stirrer and a dropping funnel. The flask was cooled to 10 °C and irradiated with a 1000-W incandescent light bulb. Bromine (6.9 g, 0.043 mol) was added in three portions, with vigorous stirring of the two-phase system and changing the water before each addition, made after the bromine color had substantially faded. The product mixture was investigated by $^1$H NMR; if conversion to **11** and **10** was less than 95%, additional bromine was added. The $^1$H NMR spectrum indicated that the ratio of **11**:**10** was about 7:1, and initial fractional recrystallization from petroleum ether and final recrystallization by solvent evaporation from $CCl_4$ gave **11**: mp 153–154.5 °C; $^1$H NMR ($CCl_4$) $\delta$ 1.99 (s, 6 H, $CH_3$), 4.47 (s, 2 H, H-1 and 4), 7.18 (m, 8 H, aromatic H).

Anal. Calcd for $C_{18}H_{16}Br_2$: C, 55.13; H, 4.11. Found: C, 55.26; H, 4.24.

***cis*-7,8-Dibromo-7,8-dimethyldibenzobicyclo[2.2.2]octadiene (10)** was not isolated from the reaction mixture but its $^1$H NMR spectrum was inferred from those of enriched mixtures from

the preparation of the trans isomer: $^1$H NMR ($CCl_4$) $\delta$ 1.77 (s, 6 H, $CH_3$), 4.47 (s, 2 H, H-1 and 4), 7.18 (m, 8 H, aromatic H).

**7,8-Dimethyldibenzobicyclo[2.2.2]octatriene (21).** To a mixture of 2.6 g (0.042 mol) of zinc powder, 0.5 ml of glacial acetic acid, 2 g of ethylenediaminetetraacetic acid, and 300 ml of anhydrous ether in a 500-ml round-bottom flask equipped with a reflux condenser, 6.5 g (0.017 mol) of **10** and **11** (saturated solution in ether) was added with stirring at a rate which sustained gentle reflux. After addition was complete, stirring at reflux was continued for 2 h. The solids were removed by suction filtration, and the solution was washed with water and dried ($MgSO_4$). Evaporation of the ether left almost pure **21**, which after recrystallization from 95% ethanol had mp 189.5–190.5 °C; $^1$H NMR ($CCl_4$) $\delta$ 1.8 (s, 6 H, $CH_3$), 4.58 (s, 2 H, H-1 and -4), 6.99 (symmetrical m, 8 H, aromatic H).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.89; H, 7.13.

**7-Bromo-*trans*-7,8-dimethyldibenzobicyclo[2.2.2]octadiene (8).** A solution of 1 g (4.3 mmol) of **21** in purified *n*-hexane was cooled to 0 °C and placed in a quartz tube fitted with an inlet tube placed into the solution and a reflux condenser. The tube was irradiated with a GE H-100-A-4T lamp from which the glass envelope had been removed and 13 g (0.16 mol) of anhydrous hydrogen bromide was bubbled through the ice-cold solution over a 50-min period. After the addition, the excess hydrogen bromide was flushed out by air or nitrogen bubbling and the ultraviolet light then turned off. The hexane solution was washed with water and the solvent evaporated. A $^1$H NMR spectrum indicated that the residue was a mixture of **8** and **7** in a 7:1 ratio, respectively. Fractional recrystallization from petroleum ether, followed by solvent evaporation from carbon tetrachloride, gave **8**: mp 95–102 °C dec; $^1$H NMR ($CCl_4$) $\delta$ 1.03 (d, $J$ = 7 Hz, 3 H, $CH_3$-8), 1.65 (s, 3 H, $CH_3$-7), 1.72 (m, $J$ = 7, 2 Hz, 1 H, H-8), 3.85 (d, $J$ = 2 Hz, 1 H, H-4), 4.39 (s, 1 H, H-1), 7.1 (m, 8 H, aromatic H).

Anal. Calcd for $C_{18}H_{17}Br$: C, 69.02; H, 5.47. Found: C, 69.04; H, 5.35.

**7-Bromo-*cis*-7,8-dimethyldibenzobicyclo[2.2.2]octadiene (7).** Attempts to separate pure **7** from the **7–8** mixture described above were not successful. However, its $^1$H NMR spectrum was inferred from enriched mixtures: $^1$H NMR ($CCl_4$) $\delta$ 0.89 (d, $J$ = 7 Hz, 3 H, $CH_3$-8), 1.48 (s, 3 H, $CH_3$-7), 2.72 (m, $J$ = 7, 2 Hz, 1 H, H-8), 3.8 (d, $J$ = 2 Hz, 1 H, H-4, 4.35 (s, 1 H, H-1), 7.1 (m, 8 H, aromatic H).

**Photobromination of *trans*-8-Bromomethyl-7-methyldibenzobicyclo[2.2.2]octadiene (9).** In order to decipher the reaction path of the photobromination of **9**, we treated **9** with bromine at 20 °C on a small scale exactly as described for the competitive reactions. On a larger scale the two-phase method, with water as hydrogen bromide scavenger, described for the preparation of **25** and **26** proved quite useful. Difficulty in separation of products prompted us to rely entirely on $^1$H NMR spectroscopy for product identification and estimation. Only three groups of $^1$H NMR product peaks were noted, even when reactions were carried out to different extents or when enriched fractions were prepared by crystallizations. The chemical shifts, splitting patterns, and intensities of these groups of peaks allow the following assignments.

**(*E*)-7-Bromo-8-bromomethyl-7-methyldibenzobicyclo[2.2.2]octadiene (12):** $^1$H NMR ($CCl_4$) $\delta$ 1.48 (s, 3 H, $CH_3$), 2.5–4 (m, 3 H, $CH_2Br$ and H-8), 4.3 (s, 1 H, H-1), 4.55 (d, $J$ = 2 Hz, 1 H, H-4), ~7.1 (m, 8 H, aromatic H).

**(*Z*)-7-Bromo-8-bromomethyl-7-methyldibenzobicyclo[2.2.2]octadiene (13):** $^1$H NMR ($CCl_4$) $\delta$ 1.65 (s, 3 H, $CH_3$), 2.5–4 (m, $CH_2Br$ and H-8), 4.4 (s, 1 H, H-1), 4.62 (d, $J$ = 2 Hz, 1 H, H-4), ~7.1 (m, 8 H, aromatic H).

**7,8-Dibromo-7-bromomethyl-8-methyldibenzobicyclo[2.2.2]octadiene (27):** $^1$H NMR ($CCl_4$) $\delta$ 2.0 (s, 3 H, $CH_3$), 3.3 (d, $J$ = 11.6 Hz, 1 H, $CH_2Br$), 3.9 (d, $J$ = 11.6 Hz, 1 H, $CH_2Br$), 4.5 (s, 1 H, H-4), 5.05 (s, 1 H, H-1), 7.25 (m, 8 H, aromatic H).

The *E–Z* assignment of **12** and **13** must be considered tentative at present. The chemical shifts of the 3 H singlets at 1.48 and 1.65 are strikingly similar to the methyl groups next to the bromines in **8** and **7**, respectively, and this forms the basis for the geometric assignment of **12** and **13**. The methyl group in compound **14** is expected to be a doublet at higher field. The structure of **12** and **13** is confirmed by the 1 H singlet in the bridgehead region with their chemical shifts being very close to the comparable ones of **7** and **8**. The required 1 H doublet bridgehead hydrogens are at surprisingly low fields when compared to the analogous hydrogens in **9**. The nonresolvable multiplets at $\delta$ 2.5–4 are to be expected for the single bridge hydrogen and two diastereotopic hydrogens ($CH_2Br$) which are coupled with each other. Compounds **14** would give rise to resolvable twin doublets for the diastereotopic hydrogens which could only be coupled with each other as in the case of **27**.

The product **27** has the expected two doublets which are characteristic of diastereotopic methylene hydrogens. The methyl group and bridgehead hydrogens should give rise to singlets as observed. The methyl singlet has the identical frequency as the methyl hydrogens in **11**.

The compounds **12, 13, 27,** and **9** accounted for more than 90% of the aromatic peaks for the scavenged reactions carried out to 50% completion at room temperature.

**Competitive Brominations.** Most of the necessary details are given in the discussion section and in Table I. The percentages of substrates which were recovered after reaction were determined by dividing the integration per hydrogen of their singlet or doublet bridgehead or methyl $^1$H NMR peaks (Varian A60-A) by the integration per hydrogen of the aromatic peak total. The product percentages were determined in like manner to serve as a check, and there was agreement within the normal experimental error (±3%) of such $^1$H NMR techniques. Although the total percent of remaining **4** and **5** was determined in this way, GLC (5 ft × 0.125 in. SE-30 column, 150 °C) had to be used in obtaining their ratio. As GLC did not separate **4** and **5** from their bromide products, the latter had to be removed prior to injection. This was accomplished by treatment of the entire reaction mixture with refluxing ethanolic silver nitrate, subsequent evaporation of the solvent, dissolution in petroleum ether and aqueous ammonia, and extraction of the organic layer with concentrated sulfuric acid. The ratio of **5** to **6** could similarily be determined by GLC and was used as a check on the ratio obtained directly from 60-MHz $^1$H NMR spectra. The ratio of **7** to **8** was not obtainable from 60-MHz $^1$H NMR spectra either. However, the doublet methyl as well as singlet bridgehead hydrogen peaks were completely separated in 100-MHz $^1$H NMR (Jeolco PFT-100) spectra. Integration by the cut-and-weigh method afforded the desired ratio.

**X-Ray Analyses.** As we were unable to prepare **7, 8, 10,** or **11** by stereospecific syntheses, and spectroscopic data were ambiguous, x-ray structure analysis was conducted on one of the isomers of each pair. In both cases the isomer used for the analysis was the one which predominated in the preparations and had methyl groups shifted downfield in its $^1$H NMR spectrum from those in the spectrum of the isomer that could not be isolated. The x-ray analysis showed that the major isomers were **8** and **11**.

**Crystal Data on 7-Bromo-*trans*-7,8-dimethyldibenzobicyclo[2.2.2]octadiene (8).** X-Ray crystal structure analysis of this compound was undertaken in order to determine whether the methyl groups were in the cis or trans configuration. The crystals were obtained from petroleum ether–carbon tetrachloride solution by evaporation. They grew as colorless, transparent needles.

The unit cell was found to be monoclinic with dimensions (standard deviations in parentheses) $a$ = 10.640 Å ($\sigma$ = 0.006 Å); $b$ = 9.401 Å ($\sigma$ = 0.003 Å); $c$ = 29.133 Å ($\sigma$ = 0.012 Å); $\beta$ = 95.84° ($\sigma$ = 0.04°). The observed density was 1.43 g/cm$^3$. Assuming eight molecules of $C_{18}H_{17}Br$ per unit cell gives a calculated density of 1.44 g/cm$^3$. Thus the cell contains eight molecules. Systematically absent spectra were ($h0l$) with $l$ odd and ($0k0$) with $k$ odd. The space group therefore is $P2_1/c$. Within the limiting sphere of Cu K$\alpha$ radiation there lie 6100 independent reflections. Measurements were made of the intensities of all reflections for which $2\theta \leq 118°$. Of the 4472 in this category only 2516 with intensities exceeding three times background were used in the analysis. The crystal used in the intensity measurements was 0.2 × 0.25 × 0.3 mm. No absorption correction was applied [$\mu$(Cu K$\alpha$) = 41.05 cm$^{-1}$]. The data were collected using a Syntex P$\bar{1}$ diffractometer in the $\theta$–$2\theta$ scan mode, with a scanning rate of 2 deg/min. The Cu K$\alpha$ line was selected using a graphite crystal monochromator.

**Structure Determination.** The space group $P2_1/c$ has a multiplicity of four and so the asymmetric unit contains two molecules of $C_{18}H_{17}Br$. The coordinates of the two bromine atoms were determined from an unsharpened three-dimensional Patterson synthesis. A three-dimensional electron density distribution, calculated using the bromine phases only, gave immediately the positions of the carbon atoms (reliability index, $R$ = 0.44). Fourier refinement of the structure converged at $R$ = 0.32. Further refinement was carried out by the block-diagonal least-squares procedure with unit weights and individual isotropic thermal parameters. The least-squares refinement converged at $R$ = 0.17. At this point it was clear that the two methyl groups were in the trans configuration and the analysis was terminated.

The atomic coordinates of the two crystallographically indepen-

**Table III. Fractional Coordinates (× $10^4$) and Isotropic Thermal Parameters (× $10^3$) Defining the Crystal Structure of 7-Bromo-*trans*-7,8-dimethyldibenzobicyclo[2.2.2]octadiene[a]**

| Atom | x | y | z | u |
|---|---|---|---|---|
| Br1A | 422 (3) | 2649 (4) | 3501 (1) | 101 (1) |
| Br1B | 1623 (3) | 4118 (3) | 6268 (1) | 82 (1) |
| C1A | 3025 (20) | 1942 (22) | 3579 (7) | 41 (5) |
| C2A | 4203 (21) | 1842 (23) | 3321 (7) | 45 (6) |
| C3A | 4041 (22) | 886 (25) | 2945 (7) | 52 (6) |
| C4A | 2764 (22) | 190 (24) | 2887 (8) | 50 (6) |
| C5A | 2542 (20) | −456 (21) | 3348 (7) | 42 (6) |
| C6A | 2677 (20) | 495 (21) | 3714 (7) | 40 (5) |
| C7A | 2024 (23) | 2490 (26) | 3193 (8) | 59 (7) |
| C8A | 1876 (23) | 1471 (25) | 2775 (8) | 56 (6) |
| C9A | 5065 (23) | 663 (26) | 2679 (7) | 61 (7) |
| C10A | 6197 (25) | 1438 (27) | 2779 (9) | 70 (8) |
| C11A | 6314 (25) | 2366 (28) | 3139 (9) | 70 (7) |
| C12A | 5342 (23) | 2590 (25) | 3412 (8) | 56 (6) |
| C13A | 2466 (24) | 57 (27) | 4165 (8) | 65 (7) |
| C14A | 2120 (25) | −1394 (27) | 4211 (8) | 65 (7) |
| C15A | 1941 (25) | −2225 (28) | 3857 (9) | 71 (8) |
| C16A | 2148 (24) | −1868 (27) | 3398 (8) | 63 (7) |
| C17A | 2230 (20) | 4181 (23) | 3067 (7) | 42 (5) |
| C18A | 522 (30) | 924 (34) | 2622 (10) | 97 (9) |
| C1B | 1492 (20) | 1709 (22) | 5673 (7) | 45 (6) |
| C2B | 1996 (21) | 211 (23) | 5609 (7) | 45 (6) |
| C3B | 3295 (20) | 126 (22) | 5575 (7) | 41 (5) |
| C4B | 3926 (20) | 1530 (23) | 5650 (7) | 45 (6) |
| C5B | 3320 (20) | 2583 (22) | 5308 (7) | 45 (6) |
| C6B | 1990 (20) | 2684 (22) | 5328 (7) | 42 (5) |
| C7B | 2244 (22) | 2123 (24) | 6161 (8) | 55 (6) |
| C8B | 3725 (25) | 2071 (27) | 6166 (9) | 70 (7) |
| C9B | 3867 (21) | −1149 (23) | 5513 (7) | 48 (6) |
| C10B | 3124 (22) | −2386 (25) | 5478 (8) | 55 (8) |
| C11B | 1848 (22) | −2317 (25) | 5518 (8) | 56 (6) |
| C12B | 1249 (21) | −1046 (23) | 5575 (7) | 49 (6) |
| C13B | 1228 (23) | 3550 (25) | 5026 (8) | 54 (6) |
| C14B | 1843 (25) | 4357 (28) | 4705 (8) | 68 (7) |
| C15B | 3118 (23) | 4351 (26) | 4695 (8) | 59 (6) |
| C16B | 3837 (22) | 3472 (24) | 4981 (7) | 52 (6) |
| C17B | 1772 (24) | 1269 (26) | 6562 (8) | 64 (7) |
| C18B | 4447 (30) | 3568 (33) | 6265 (10) | 90 (9) |

[a] Standard deviations are given in parentheses. For the temperature factor the exponent has the form $8\pi^2(\sin\theta/\lambda)^2u$.

dent molecules are given in Table III. The fact that both molecules have the methyl groups in the trans configuration lends powerful support, if such be needed, to the results of the analysis.

**Crystal Data on *trans*-7,8-Dibromo-7,8-dimethyldibenzobicyclo[2.2.2]octadiene (11).** X-ray crystal structure analysis of this compound was undertaken to determine whether the bromine atoms were in a cis or trans configuration. The crystals were obtained from carbon tetrachloride solution by evaporation. They grew as colorless, transparent needles. The unit cell was found to be monoclinic with dimensions (standard deviations in parentheses) $a$ = 12.003 Å ($\sigma$ = 0.004 Å); $b$ = 8.043 Å ($\sigma$ = 0.002 Å); $c$ = 18.023 Å ($\sigma$ = 0.005 Å); $\beta$ = 116.84° ($\sigma$ = 0.02°). The observed density was 1.69 g/cm$^3$. Assuming four molecules of $C_{18}H_{16}Br_2$ per unit cell gives a calculated density of 1.68 g/cm$^3$. The cell therefore contains four molecules. The only systematic extinctions observed were in the class (0$k$0) which was absent with $k$ odd. The space group therefore is either $P2_1$ or $P2_1/m$.

Within the limiting sphere of Cu K$\alpha$ radiation there lie 3550 independent reflections. Measurements were made of the intensities of all reflections for which $2\theta \leq 100°$. Of the 1733 in this category only 1580 with intensities exceeding three times background were used in the analysis. The crystal used in the intensity measurements was 0.3 × 0.3 × 0.5 mm. No absorption correction was applied [$\mu$(Cu K$\alpha$) = 72.53 cm$^{-1}$]. The data were collected using a Syntex P$\bar{1}$ diffractometer in the $\theta$–$2\theta$ scan mode, with a scanning rate of 2 deg/min. The Cu K$\alpha$ line was selected by a graphite crystal monochromator.

**Table IV. Approximate Fractional Coordinates of the Bromine Atoms in Two Molecules of *trans*-7,8-Dibromo-7,8-dimethyldibenzobicyclo[2.2.2]octadiene (11)**

| Atom | x | y | z |
|---|---|---|---|
| Br1 | 0.5083 | 0.2292 | 0.4583 |
| Br2 | 0.8333 | 0.4375 | 0.4333 |
| Br3 | 0.4700 | −0.2292 | 0.1000 |
| Br4 | 0.1833 | 0.0208 | 0.0458 |

**Location of Bromine Atoms.** An unsharpened Patterson synthesis was computed using all 1580 observed intensities. From this synthesis, approximate coordinates were obtained for the four bromine atoms in one half of the unit cell. These are given in Table IV. The bromine atoms which are closest together are Br3 and Br4 and their separation is 4.0 Å. If the bromine atoms were to be in a cis configuration in molecules of this type, the distance between two bromine atoms on the same molecule could hardly exceed 3.4 Å.[34,35] Therefore it was concluded at this point that the bromine atoms were in the trans configuration. Since the trans configuration of the bromine atoms had been established the analysis was not pursued beyond this point.

**Acknowledgment.** The authors wish to acknowledge the generous support of this research by the National Science Foundation.

**Registry No.**—**3,** 32363-36-3; **4,** 5445-53-4; **5,** 5445-54-5; **6,** 51229-75-5; **7,** 58240-60-1; **8,** 58267-52-0; **9,** 58240-61-2; **10,** 58240-62-3; **11,** 58267-53-1; **12,** 58240-63-4; **13,** 58311-27-6; **16,** 58310-89-7; **17,** 5472-28-6; **18,** 58240-64-5; **19,** 58267-80-4; **20,** 58240-65-6; **21,** 58240-66-7; **27,** 58240-67-8; **30,** 58240-68-9; anthracene, 120-12-7; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; *trans*-7-hydroxymethyl-8-methyldibenzobicyclo[2.2.2]octadiene, 58240-69-0.

## References and Notes

(1) Part 82: S. J. Cristol, J. S. Perry, Jr., and R. S. Beckley, *J. Org. Chem.*, preceding paper in this issue.
(2) A portion of this work was published as a preliminary communication: S. J. Cristol and H. W. Mueller, *J. Am. Chem. Soc.*, **95,** 8489 (1973).
(3) S. J. Cristol, M. A. Imhoff, and D. C. Lewis, *J. Org. Chem.*, **35,** 1722 (1970).
(4) (a) W. A. Thaler, *J. Am. Chem. Soc.*, **85,** 2607 (1963); (b) P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85,** 2849 (1963); (c) P. S. Skell and P. D. Readio, *ibid.*, **86,** 3334 (1964); (d) J. Traynham and W. Hines, *ibid.*, **90,** 5208 (1968).
(5) S. J. Cristol and D. C. Lewis, *J. Am. Chem. Soc.*, **89,** 1476 (1967).
(6) E. I. Snyder and R. A. Clement, *J. Am. Chem. Soc.*, **82,** 1424 (1960).
(7) H. M. Walborsky, *Helv. Chim. Acta*, **36,** 1251 (1953).
(8) H. Nozaki, H. Kato, and R. Nozori, *Tetrahedron*, **25,** 1661 (1969).
(9) The steric inhibition by methyl groups as well as bromine in the cycloaddition of maleic anhydride to anthracene has been noted.[10,11]
(10) W. E. Bachmann and L. B. Scott, *J. Am. Chem. Soc.*, **70,** 1458 (1948).
(11) W. R. Vaughan and K. M. Milton, *J. Org. Chem.*, **16,** 1748 (1951).
(12) J. P. Kochansky, Ph.D. Thesis, University of Colorado, 1971.
(13) W. A. Thaler, *Methods Free-Radical Chem.*, **2,** 121 (1969).
(14) The relative reactivities of free radicals with different atom-transfer reagents is apparently not well studied or understood. Thus our result with the radical **22** is clearly different from that with the 1-bromo-2-methyl-2-butyl radical, which is reported[15] to react with bromine much faster than with hydrogen bromide.
(15) K. J. Shea and P. S. Skell, *J. Am. Chem. Soc.*, **95,** 283 (1973).
(16) H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, *J. Am. Chem. Soc.*, **66,** 435 (1944).
(17) G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77,** 4031 (1955).
(18) (a) O. Simamura, *Top. Stereochem.*, **4,** 1 (1969); (b) S. Mayajima, D.Sc. Thesis, Tokyo University, Tokyo, Japan, 1967, reported in ref 18a.
(19) G. J. Abruscata and T. I. Tidwell, *J. Am. Chem. Soc.*, **94,** 672 (1972).
(20) Data are given in detail in the Ph.D. Thesis of Hans W. Mueller, University of Colorado, 1974.
(21) L. Pauling, "Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1940, p 189.
(22) Our experience suggests that **14** should not be significantly more reactive than **12** or **13** and that some should accumulate in the course of the bromination reaction.
(23) The earlier data[3] were obtained in the absence of hydrogen bromide scavenger, and might therefore be questionable. We have now reinvestigated the photobromination of **2,** both with and without 2,3-epoxy-2,3-dimethylbutane scavenger, and note that the presence of the scavenger has only minimal effect upon the relative reactivities of **1** and **2.** Thus the original basis upon which this work was begun was confirmed.
(24) (a) P. S. Skell and K. J. Shea, *J. Am. Chem. Soc.*, **94,** 6550 (1972); (b) K. J. Shea, D. C. Lewis, and P. S. Skell, *ibid.*, **95,** 7768 (1973).

(25) (a) J. G. Traynham, E. E. Green, Y.-S. Lee, F. Schweinsberg, and C.-E. Low, J. Am. Chem. Soc., 94, 6552 (1972); (b) P. S. Skell, R. R. Pavlis, D. C. Lewis, and K. J. Shea, ibid., 95, 6735 (1973).
(26) S. J. Cristol and R. P. Arganbright, J. Am. Chem. Soc., 79, 3441 (1957).
(27) Skell and his co-workers[24,25] have discussed the question of unsymmetrical and symmetrical bridging and the barrier between bridged and open radicals.
(28) G. A. Russell and H. C. Brown, J. Am. Chem. Soc., 77, 4025 (1955).
(29) M. S. Kharasch, W. Hered, and F. R. Mayo, J. Org. Chem., 6, 818 (1941).
(30) C. S. Marvel and V. C. Sekera, "Organic Syntheses", Collect. Vol. III, E. C. Horning, Ed., Wiley, New York, N.Y., 1955, p 366.
(31) F. Kurzer, "Organic Syntheses", Collect. Vol. IV, N. Rabjohn, Ed., Wiley, New York, N.Y., 1963, p 937.
(32) J. W. Wilt, R. G. Stein, and W. J. Wagner, J. Org. Chem., 32, 2097 (1967).
(33) H. R. Billica and H. Adkins, Org. Synth., 29, 24 (1949).
(34) I. L. Karle, J. Karle, and K. Britts, J. Am. Chem. Soc., 88, 2918 (1966).
(35) G. L. Hardgrove, L. K. Templeton, and D. H. Templeton, J. Phys. Chem., 72, 668 (1968).

# Lanthanide-Induced Chemical Shifts and the Relative Stereochemistry of Multistriatin, 2,4-Dimethyl-5-ethyl-6,8-dioxabicyclo[3.2.1]octane

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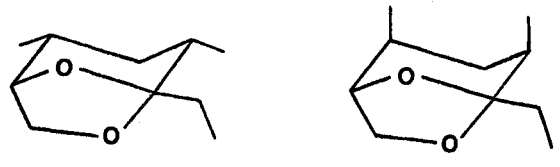
*Received August 28, 1975*

The $^1H$ NMR spectra of the four diastereomers of multistriatin, 2,4-dimethyl-5-ethyl-6,8-dioxabicyclo[3.2.1]octane (1α–δ), and of frontalin, 1,5-dimethyl-6,8-dioxabicyclo[3.2.1]octane (2), were recorded in the presence of the europium paramagnetic shift reagent $d_{27}$-tris(2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato)europium(III) [(Eu(fod)$_3$]. The binding of Eu(fod)$_3$ to each substrate was investigated by comparing observed shift ratios with those calculated for lanthanide atom positions about each of the oxygen atoms in 1α–δ and in 2. The calculations indicated that for each of these dioxabicyclo[3.2.1]octanes, substrate binding occurred preferentially at one oxygen atom, and that the location of the lanthanide atom was related to steric hindrance about the two potential binding sites. Comparisons of the observed shift ratios for each isomer of 1 with the calculated shift ratios of all isomers of 1 verified the relative stereochemical assignments for these isomers. A correlation between the shift reagent binding site and the biological activity of 1α–δ was observed.

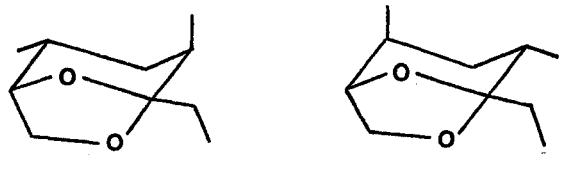
α-Multistriatin (1α), a component of the aggregating pheromone of the European elm bark beetle, *Scolytus multistriatus*, was identified as 2,4-dimethyl-5-ethyl-6,8-dioxabicyclo[3.2.1]octane by spectrometric and synthetic methods.[2] The previously reported synthesis yielded the four possible diastereomers (1α–δ), and these isomers were separated by GLC and were characterized by NMR, ir, and MS.[3] The spectrometric data in combination with a stereospecific synthesis provided evidence for the assignment of the relative stereochemistry of each of the four diastereomers.



1α



1β



1γ



1δ

Lanthanide-induced shift (LIS) experiments represented a potential and possibly unique method for testing structural assignments for 1α–δ. The objective of this study was to first evaluate the binding of the shift reagent to 1α–δ and to 1,5-dimethyl-6,8-dioxabicyclo[3.2.1]octane, frontalin (2), and then to compare any definitive evidence relating the structure of the 6,8-dioxabicyclo[3.2.1]octanes to the previous stereochemical assignments for 1α–δ.

The use of LIS data to test proposed configurations or conformations has been recently reviewed.[4-7] In the case of monofunctional substrates, bonding occurs between donor atom (X) on the substrate (S) and the lanthanide metal atom (L), and a set of equilibria exists for L, S, LS, $LS_2$, and perhaps additional species. This bonding situation is essentially the same for a multifunctional substrate if L binds preferentially to one functional group.

Competitive complexing with multiple donor atoms on the substrate molecule has also been reviewed[8] and is of particular importance in this study of bicyclic ketal structures. Similar donor atoms with identical environments should experience identical L–X bonding, and this expectation has been verified by experiment. However, the lanthanide bonding properties of like functional groups with dissimilar environments can differ. Functional groups usually bond preferentially (OH > ketones ≥ esters > ethers); however, this bonding trend can be altered as a consequence of steric hindrance. Such was the case in a computer-assisted LIS study by Farid et al., who described preferential bonding of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium(III) to an unhindered ether in the presence of a hindered alcohol group.[9] Selective binding in substrates that contain two dissimilar ether groups has also been reported.[8]

The lanthanide-induced change in chemical shift for proton $H_n$ ($\Delta\delta_n$) can be calculated from the pseudocontact term of the McConnell–Robertson equation[10]

$$\Delta\delta_n = K\,(3\cos^2\theta_n - 1)r_n^{-3} \qquad (1)$$

where $\theta_n$ is the $XLH_n$ angle and $r$ is the $LH_n$ distance.[5-7] Direct application of this equation to the evaluation of the paramagnetic shifts assumes the absence of a contact contribution to the observed chemical shifts and that the LS complex has effective axial symmetry about the L–X bond. Both