was stirred at room temperature for 1 h with saturated sodium bicarbonate (4 mL) and ether (3 mL). The crude acetate **39** (R = Ac) (15 mg) was isolated by ether extraction as a light yellow oil: IR 1735, 1655, 1445, 1365, 1230, 1030, 880, and 800 cm^{-1}; NMR τ 9.15 (3 H, d, J = 6 Hz), 8.66 (6 H, s), 8.16 (3 H, br s), 7.96 (3 H, s), and 4.74 (1 H, m). TLC of the acetate **39** (R = Ac) on a silica gel plate impregnated with 20% silver nitrate, developed with petrol/ethyl acetate (13:1) or 0.5% glacial acetic acid in chloroform, gave a slight elongation of the spot. Analytical GLC using the usual columns was unsatisfactory. The above acetate **39** (R = Ac) had IR and NMR spectra in agreement with literature values.

Acknowledgment. We thank Professor J. A. Marshall for supplying spectra of authentic (±)-hinesol.

Registry No.—**11,** 65354-38-3; **12,** 23971-53-1; **13,** 65338-83-2; **13** alcohol, 65338-84-3; **14,** 65338-85-4; **15,** 58698-24-1; **15** acid, 65338-86-5; **16,** 58698-25-2; **19,** 58698-26-3; **20,** 58700-62-2; **21,** 58700-63-3; **22** isomer 1, 65378-09-8; **22** isomer 2, 65378-10-1; **23,** 65338-87-6; **23** alcohol, 65338-88-7; **24,** 58698-28-5; **25,** 65338-89-8; **25** diol, 65338-90-1; **26,** 65338-91-2; **27,** 65338-92-3; **28,** 65338-75-2; **28** mesylate, 65338-76-3; **29,** 65338-77-4; **30,** 65338-78-5; **30** 3-tosylate, 65366-44-1; **31,** 58698-29-6; **32,** 58698-30-9; **33,** 65338-79-6; **34,** 65338-80-9; (10*R*)-**35,** 65378-05-4; (10*S*)-**35,** 65378-06-5; **36,** 65338-81-0; **37,** 58700-60-0; **38a,** 58700-61-1; **387,** 65338-82-1; (+)-hinesol, 59331-07-6; 10-epihinesol, 59331-08-7; (+)-hinesol acetate, 65378-07-6; (+)-10-epihinesol acetate, 65378-08-7; *p*-toluenesulfonyl chloride, 98-59-9; acetic anhydride, 108-24-7; acetone, 67-64-1; methyllithium, 917-54-4; methyl phenyl sulfone, 3112-85-4; methyl iodide, 74-88-4.

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(2) Inquiries should be sent to the Evans Laboratory, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.
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(23) (+)-Hinesol is the mirror image of the natural isomer; see ref 8 for a discussion of the relevant stereochemical relationships.

Photochemical Transformations. 21. Photochemical and Thermal Methanolyses of Two Epimeric Bridged Polycyclic Bromides[1]

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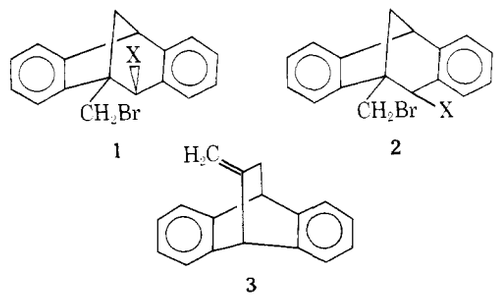
Addition of bromine to 7-methylenedibenzobicyclo[2.2.2]octadiene (**3**) gave a mixture of the epimeric 5-bromomethyl-4-bromodibenzobicyclo[3.2.1]octadienes (**1**-Br and **2**-Br). The dibromides suffer methanolysis in THF–methanol solutions in the dark at 60 °C and upon direct irradiation at room temperature to form the corresponding 4-methyl ethers (**1**-OCH_3 and **2**-OCH_3). The solvolyses are neither stereoselective nor stereoconvergent, although in all cases the exo ether (**1**-OCH_3) is the principal solvolysis product. Plausible rationalizations of the product differences are discussed.

Photoinduced solvolyses of a number of benzyl derivatives have been reported;[2] these have been shown to proceed through benzylic cation intermediates. It seemed to us that an interesting question is whether cationic intermediates, otherwise identical, but produced on the one hand from an electronically excited species and on the other hand from a ground-state species, would be different enough to note experimentally. Obviously, any differences could be noted only if bimolecular capture occurred more rapidly than unimolecular relaxation processes.

As one test, we decided to investigate the epimeric 5-bromomethyl-4-bromo-2,3;6,7-dibenzobicyclo[3.2.1]octadienes (**1**-Br and **2**-Br). These offered the additional possibility that the two epimers might show differences among themselves, and in addition, we needed to have a system whose



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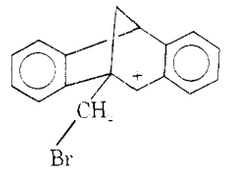
thermal solvolysis was not so fast as to overwhelm photosolvolysis. The 5-bromomethyl group was expected to provide enough electron attraction to accomplish the latter.

A mixture of exo dibromide (1-Br) and endo dibromide (2-Br) was produced in an almost equimolar ratio, when bromine was added in ethyl acetate to 7-methylenedibenzobicyclo[2.2.2]octadiene (3). No unrearranged (1,2) addition products were noted. The formation of both epimers suggests the intervention of benzylic ion 4 (as part of its several ion pairs with bromide ion), rather than of the phenonium ion 5 as the principal product precursor in the addition reaction. Obviously 5 intervenes in the rearrangement to 4, but it must



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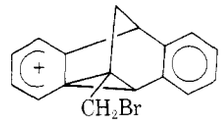

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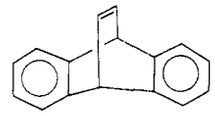

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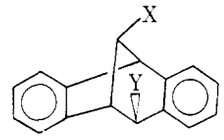

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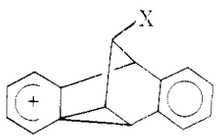
be transformed rapidly to 4. This is in marked contrast to additions to 6, where the formation of syn-exo products 7,[3] as well as other data,[4] suggests that phenonium ions 8, rather than benzylic ions, are principal product precursors in addition reactions. At equilibrium the *exo*-1-Br to *endo*-2-Br ratio is approximately 1:3.

The epimeric dibromides were separated by fractional crystallization. Reduction of 1-Br and 2-Br with tri-*n*-butyltin hydride gave 9, which has been previously described,[5] thus



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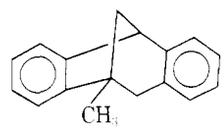

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confirming the carbon skeleton. The configurations of the two epimers were assigned on the basis of their ^{1}H NMR spectra, in particular the chemical shifts of the 4-proton (exo protons farther downfield than endo in dibenzobicyclo[3.2.1]octadiene systems,[6] as well as in others.[7])

Neither 1-Br nor 2-Br reacted measurably when allowed to stand in 50:50 methanol/tetrahydrofuran solution[8] at room temperature for 24 h. Reaction occurred slowly at 60 °C with each isomer to give a mixture of methyl ethers 1-OCH_3 and 2-OCH_3. The exo bromide was slightly more reactive than the endo (half-life ~3 h vs. ~18 h). Neither isomer reacted stereospecifically. The exo bromide (1-Br) gave *exo*-1-OCH_3 and *endo*-2-OCH_3 in a ratio of about 7 to 1, while the endo bromide (2-Br) gave these in a ratio of about 2.5 to 1.

Photosolvolysis of both bromides proceeded rapidly in a methanol–THF solution at room temperature upon direct irradiation with 254- and 300-nm light. Just as in the ground-state reaction, the principal product was the exo ether 1-OCH_3. With the exo bromide, (1-OCH_3) was produced in a ratio of approximately 9:1 over 2-OCH_3; the endo bromide gave a ratio of about 4:1. The photosolvolyses both proceed without apparent epimerization either of the bromides or of the ether products. Attempts to photosensitize the solvolyses with acetone, acetophenone, and benzophenone were unsuccessful, and the photosolvolyses were not quenched significantly by piperylene at concentrations at or below 0.5 M.

Discussion of Results

The results described above raise certain points for discussion. Among these are differences between product formation from the two epimers, differences between ground-state and excited-state reactions, questions of possible ion-pair return, and excited-state multiplicities.

As noted above, neither epimer gives stereospecific displacement, but the exo bromide 1-Br gives substantially more exo ether than does the endo bromide, in both ground-state and photochemical solvolyses. These solvolyses certainly involve cationic intermediates, and a plausible rationalization suggests the intervention of the phenonium ion 5 in the 1-Br reaction in competition with reaction via the benzylic ion 4. 5 cannot be formed directly in an inversion process from the endo epimer 2-Br. Our enthusiasm for this explanation is cooled markedly by the lack of stereospecificity in the 1-Br reaction and by the failure of 5 to intervene substantially as a product-determining intermediate in the addition of bromine to 3. We therefore propose an alternative explanation based upon consideration of possible conformations of the bromomethyl group at C-5.

Models of 1-Br and of 2-Br suggest that the bromomethyl groups have considerably different conformations. Due to steric and electrostatic repulsions by the exo bromine atom in 1-Br, it seems likely that the bromine atom of the bromomethyl group is projected toward the adjacent aromatic ring. Evidence for this conformation is seen in the ^{1}H NMR spectrum, where the diastereotopic geminal protons have no chemical shift difference (both absorb at δ 4.11). On the other hand, the endo bromine in 2-Br does not interfere with the bromomethyl group, and a conformation with the bromine atom projected away from the adjacent aromatic ring is apparently favored. The ^{1}H NMR spectrum is consistent with this interpretation; the diastereotopic geminal protons are no longer in similar environments. One is over the shielding cone of the ring and is moved upfield to δ 3.73 and the other is in the deshielding plane and absorbs at δ 4.37. The coupling constant between the two protons is 10.5 Hz.

If we assume that these conformations are maintained in the heterolyses, the ion or ion pair from 1-Br will have a less internally crowded exo face than that from 2-Br. As a result the intermediate from 1-Br may be anticipated to coordinate with methanol from the exo face somewhat more readily than that from 2-Br. This explanation requires that coordination with solvent proceeds at a faster rate than relaxation of the intermediate by bond rotation. There are, by now, a number of cases[9] where otherwise identical ions from different sources behave differently, and conformational explanations have been given, with similar assumptions required.

The photomethanolyses of 1-Br and 2-Br follow the same trend as the ground-state reactions, although somewhat more *exo*-methyl ether (1-OCH_3) is produced in each case photochemically. The differences are not dramatic and may be caused, in part at least, by the higher temperature of the ground-state reaction. It would therefore appear that, in this work, the intermediates produced by normal heterolysis and by photoheterolysis do not differ markedly, at least at the time of coordination with nucleophile.

In neither the photomethanolysis nor the ground-state reaction was there any evidence for epimerization (1-Br $\rightleftarrows$ 2-Br) during the reaction. Thus this test for ion-pair return[2f] was negative. Perhaps use of a less nucleophilic solvent or of a more stable ion would provide positive evidence. We are presently looking for such examples.

The question of multiplicity in bond heterolysis of benzyl systems remains enigmatic. Upon direct irradiation in THF–methanol, both 1-Br and 2-Br solvolyze readily with a quantum yield near 0.01, and the reaction was not quenched

Table I. Photomethanolysis of 2-Br in 1:1 Tetrahydrofuran/Methanol

Irradiation wavelength, nm	Time of irradiation, min	Recovered bromide % 1-Br	Recovered bromide % 2-Br	Solvolysis products % 1-OCH_3	Solvolysis products % 2-OCH_3	*exo*-(1-OCH_3)/*endo*-(2-OCH_3)
254	0	0	100	0	0	
254	15	0	87	10.5	2.5	4.2
254	30	0	62	31	7	4.4
254	60	0	36	47	12	3.9
254	120	0	13	74	13	5.7
						Av 4.5
300	0	0	100	0	0	
300	140	0	65	30	5	6
300	235	0	43	46	11	4.2
300	360	0	32	52	16	3.3
						Av 4.5

Table II. Photomethanolysis of 1-Br in 1:1 Tetrahydrofuran/Methanol at 254 nm

Irradiation time, min	Recovered bromide % 1-Br	Recovered bromide % 2-Br	Solvolysis products % 1-OCH_3	Solvolysis products % 2-OCH_3	*exo*-(1-OCH_3)/*endo*-(2-OCH_3)
0	90	10			
15	47	10	38	5	7.6
30	32	9	54	5	10.8
60	10	10	72	8	9.0
90	0	5	85	10	8.5
120	0	0	80	10	8.0
					Av 8.8

Table III. Methanolysis of 1-Br and 2-Br in 1:1 Tetrahydrofuran/Methanol at 60 °C

Run no.	Time, h	Composition of mixture % 1-Br	% 2-Br	% 1-OCH_3	% 2-OCH_3	1-OCH_3/2-OCH_3
1	0.0	100	0			
	5.8	21	0	69.1	9.3	7.5
	18.0	0	0	88.6	11.4	7.7
						Av 7.6
2	0.0	0	100			
	5.8	0	83	11.7	5.3	2.2
	18.0	0	46	39.4	14.6	2.7
	26.3	0	31	48.1	20.8	2.3
	42.0	0	12	63.5	24.5	2.6
	91.0	0	0	75.6	24.4	3.1
						Av 2.6

with piperylene at concentrations up to 0.5 M. Chemical yields were 70–75%. Homolysis products were not observed.

When the endo bromide (2-Br) was photosensitized with acetophenone in THF–methanol, the 2-Br disappeared with a yield of about 10–20% of ethers and 80% of unidentified material, the latter possibly the result of carbon–bromine bond homolysis. This is just opposite to results obtained with benzyl chloride,[2i,j] where the triplet sensitized reaction gives principally solvolysis and direct irradiation gives principally homolysis, but is similar to that of benzyltrimethylammonium ion.[2g,h] Experiments in our laboratory indicate that structural and leaving group modifications affect this dichotomy, but we still lack understanding of this phenomenon.[2i]

Experimental Section

^1H NMR data were obtained with a Varian Associates model A-60-A spectrometer, using $CDCl_3$ as solvent, with tetramethylsilane as an internal standard. Irradiations with 300- and 350-nm light were performed in a Rayonet photoreactor equipped with a merry-go-round while those at 254 nm were carried out with a Photochemical Quartz Product lamp. Melting points were determined on a Thomas-Hoover Unimelt apparatus. Elemental analyses were performed by Galbraith Laboratories. Mass spectra were recorded with a Varian MAT Model CH-5 single-beam mass spectrometer.

Methanol used in all cases was spectral grade. Tetrahydrofuran was freshly distilled from lithium aluminum hydride and stored over molecular sieves. 1,3-Pentadiene was redistilled and stored in a refrigerator until used.

***exo*- and *endo*-5-Bromomethyl-4-bromodibenzobicyclo[3.2.1]octadiene (1-Br and 2-Br).** A solution of 5 g (22 mmol) of 7-methylenedibenzobicyclo[2.2.2]octadiene (3)[5] in 25 mL of reagent-grade ethyl acetate was cooled in an ice bath. Bromine was added until the solution maintained an orange color for several minutes. The solvent was removed on a rotovac to give 8 g (97%) of an orange oil. ^1H NMR analysis of the oil indicated a mixture of 45% of 1-Br and 55% of 2-Br. The endo epimer (2-Br) was crystallized by pouring 100 mL of reagent-grade hexane on the oil. After 2 days the crystals were filtered off: mp 143–145.5 °C; UV (hexane) 300 (ϵ 180), 254 (ϵ 3170), max 221 nm (ϵ 26 000); ^1H NMR δ 7.67–7.0 (m, 8, aromatic), 6.11 (s, 1, H-4), 4.37 (d, 1, J = 10.5 Hz, CH_2Br), 3.95 (m, 1, H-1), 3.73 (d, 1, J = 10.5 Hz, CH_2Br), and 2.50 (m, 2, H-8). Anal. Calcd for $C_{17}H_{14}Br_2$: C, 54.00; H, 3.79; Br, 42.27. Found: C, 53.90; H, 3.69; Br, 42.01.

Successive fractional crystallizations from hexane gave pure needlelike crystals of 1-Br: mp 89–91 °C; UV (hexane) 300 (ϵ 200), 254 (ϵ 1420), max 210 nm (ϵ 23 400); ^1H NMR δ 7.83–7.08 (m, 8, aromatic), 5.56 (s, 1, H-4), 4.11 (s, 2, CH_2Br), 3.99 (m, 1, H-1), and 2.61 (m, 2, H-8). Anal. Calcd for $C_{17}H_{14}Br_2$: C, 54.00; H, 3.79; Br, 42.27. Found: C, 53.86; H, 3.72; Br, 42.26.

***exo*- and *endo*-5-Bromomethyl-4-methoxydibenzobicyclo[3.2.1]octadiene (1-OCH_3 and 2-OCH_3).** A solution of 3 g (8

mmols) of endo dibromide 2-Br in 30 mL of methanol was heated at reflux for 24 h and the solvent was removed in a rotovac. Thirty milliliters of reagent grade hexane was added to the colorless oil. After 24 h at room temperature colorless crystals began to form. The isolated crystals proved to be largely *exo*-methyl ether 1-OCH_3. These were recrystallized from hexane to give 567 mg (23%) of 1-OCH_3: mp 102.5–104.5 °C; ^1H NMR δ 7.07–7.76 (m, 8, aromatic), 4.31 (s, 1, H-4), 4.24 (d, 1, J = 10.5 Hz, CH_2Br), 4.00 (d, 1, J = 10.5 Hz, CH_2Br), 3.99 (m, 1, H-1), 3.68 (s, 3, OCH_3), and 2.49 (m, 2, H-8). Anal. Calcd for $C_{18}H_{17}OBr$: C, 65.67; H, 5.21. Found: C, 65.41; H, 5.12.

The mother liquors from the first crystallization were stripped on a rotovac to yield a colorless oil. Enough hexane was added to dissolve the oil. The pure *endo*-methyl ether (2-OCH_3) was isolated as an oil by HPLC collection from a silica gel column, eluting with 10% ether in hexane. ^1H NMR δ 7.01–7.20 (m, aromatic, 8), 4.97 (s, 1, H-4), 4.34 (d, 1, J = 10.5 Hz, CH_2Br), 3.90 (m, 1, H-1), 3.79 (s, 3, OCH_3), 3.78 (d, 1, CH_2Br, J = 10.5 Hz), and 2.46 (m, 2).

General Procedure for Photosolvolysis. All tubes used for photosolvolyses were 1.2 by 25 cm. Five milliliters of solution was added to each tube. The tubes were sealed with rubber septa and cooled to −30 °C. Dry nitrogen was bubbled through the solution for 30–40 min. After being warmed to room temperature, each tube was taped above the solution line to remove the possibility of gas-phase reaction. Usually one tube was completely taped for a dark reaction. Analysis was by ^1H NMR, using the geminal proton peaks.

Direct Irradiation of the Endo Dibromide 2-Br. A 0.043 M solution of 2-Br in 1:1 tetrahydrofuran/methanol was placed in six quartz tubes, prepared in the usual fashion. Each tube was irradiated with 254-nm or 300-nm light. Tubes were withdrawn from time to time, and immediately following irradiation, solvent was removed on a rotovac at room temperature. Methanolysis to 1-OCH_3 and 2-OCH_3 was monitored. Data are reported in Table I. No reaction occurred in the dark (taped) tubes.

Sensitized Irradiation of 2-Br Using 350-nm Light. A solution 0.042 M in 2-Br and 0.05 M in acetophenone was prepared in 1:1 tetrahydrofuran/methanol as solvent. Under these conditions the acetophenone absorbs 99.5% of the light. Five uranium glass tubes were prepared in the usual fashion and deaerated with nitrogen. A control tube was irradiated in the absence of sensitizer for 24 h. The tubes were irradiated for periods from 45 min to 24 h. Solvents were removed in a rotovac and analysis was by ^1H NMR. Approximately 10% solvolysis and 90% loss of starting material was observed after 24 h of irradiation in the sensitized tubes. The control tubes demonstrated a 5% loss of 2-Br to solvolysis products.

Direct Irradiation of 1-Br. A 0.041 M solution of a mixture of 9:1 1-Br/2-Br in 1:1 tetrahydrofuran/methanol was placed in six quartz tubes and treated as described for the endo isomer. Solvolysis to the methyl ethers 1-OCH_3 and 2-OCH_3 was monitored. Results are given in Table II.

Control Reactions Using Sodium Bicarbonate. When similar irradiations of dibromide epimers were performed in the presence of 0.1 g of solid sodium bicarbonate, similar results were obtained.

Direct Irradiation of the Methyl Ether in Methanol Using 254-nm Light. An approximately 0.04 M solution of the methyl ether 1-OCH_3 in 1:1 tetrahydrofuran/methanol showed no reaction or epimerization after 6 h of irradiation. The quartz tubes were prepared in the usual fashion and each contained a trace of acid.

Quenching Study of the Methyl Ether Formation by 1,3-Pentadiene. A standard solution of 2-Br in 1:1 tetrahydrofuran/methanol was prepared. Five quartz tubes were prepared by the standard method with an additional 25, 50, 250, and 1000 μL of 1,3-pentadiene injected into four tubes, respectively, before irradiation. The fifth tube was the control. After irradiation with 254-nm light for 1 h, the tubes were stripped of solvent and analyzed. There was 20% methanolysis in the control tube and similar reaction in the first three tubes with quencher concentrations at 0.05, 0,1, and 0.5 M. The fourth tube with a 2 M quencher concentration showed between 30 and 40% reduction in solvolysis.

Ground-State Methanolysis of 1-Br. A solution containing 511 mg (1.4 mmol) of 1-Br in 50 mL of 1:1 tetrahydrofuran/MeOH was divided equally into six preconstricted thick-walled Pyrex tubes. The tubes were cooled in a dry ice–acetone bath and sealed. After being warmed to room temperature, the tubes were heated at 60 °C. At various intervals tubes were cooled and opened and the contents were examined by ^1H NMR (see Table III).

Ground-State Methanolysis of 2-Br. A similar experiment was carried out with 520 mg (1.4 mmol) of 2-Br. Results are given in Table III.

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Registry No.—1-Br, 64771-42-2; 1-OMe, 64771-43-3; 2-Br, 64812-29-9; 2-OMe, 64812-30-2; 3, 19978-14-4.

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