heptane, and sublimed to give 0.2 g of *endo,endo*-3,5-diacetoxynortricyclene, mp 111–112° (glpc purity 98%). The diacetate was identical with that isolated from the oxymercuration of 7-acetoxynorbornadiene.

Registry No.—III, 17366-25-5; III (diacetoxy), 2979-27-3; IV, 17289-99-5; IV (diacetoxy), 17290-00-5; IV dinitrobenzoate, 17290-07-2; VI, 17290-01-6; VII, 17290-02-7; VII (diacetoxy), 17290-03-8; VII nitrobenzylidine derivative, 17290-04-9; IX, 17290-05-0 X, 4054-88-0.

Acknowledgment.—The authors appreciate useful discussions of these results with Professor H. C. Brown and with Dr. W. H. Mueller and Dr. G. A. Knudsen, Jr. The authors wish to thank Mr. J. H. Surridge for the experiments utilizing 7-norbornadienol.

Stereochemistry of the Bromination and Deuterobromination of *anti*-7-Bromobenzonorbornadiene

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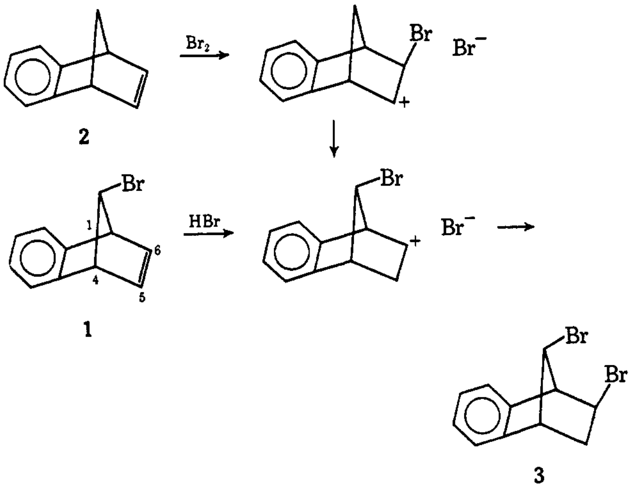
The polar addition of bromine and deuterium bromide to *anti*-7-bromobenzonorbornadiene (1) has been investigated. Even with the unfavorable steric factor *cis,exo* addition of both reagents is observed. Torsional strain effects are also ruled out as governing the "regiospecificity" of electrophilic attack on the double bond of this particular system. A stereoelectronic factor is felt to offer the best explanation and the possible origin of such a factor is discussed.

It has become increasingly apparent that steric,[1] torsional strain factors,[2,3] bridging or the rapid equilibration of classical ions,[4-6] and perhaps even subtle stereoelectronic effects[7] have the potential to influence the stereochemistry of electrophilic additions to the carbon–carbon double bond of norbornene and related bicycloheptene derivatives.[8] In either a concerted or stepwise addition all of these factors could play a role in determining the direction of approach of the electrophilic reagent. Bridging or the equivalent equilibrating classical ions must be considered as possibly controlling the direction of nucleophilic attack for a stepwise addition involving a cationic intermediate. The configuration of any rearranged product can be considered in similar terms.

In any given system more than one of these factors may be operating in a reinforcing manner. The question of the degree of delocalization in the transition state and its role in determining the direction of attack by the halide ion in a hydrohalogenation has been considered.[1,2,9] *exo* attack of halide can occur even when delocalization is probably not very significant.[2] The present work considers further the importance, if any, of steric and torsional strain effects in controlling the stereochemistry of electrophilic additions to norbornene systems.

We have decided to investigate the bromination and deuterobromination of *anti*-7-bromobenzonorbornadiene (1) for several reasons. First of all it is known that the addition of bromine to benzonorbornadiene (2) proceeds with rearrangement to produce *exo*-5,*anti*-7-dibromobenzonorbornene (3).[10] This enables one to examine certain 1,2 additions to the double bond of *anti*-7-bromobenzonorbornadiene (1) without being directly concerned with rearranged adducts. Thus in the hydrobromination of this *anti*-7-bromide 1, one should obtain the same cationic intermediate, excluding differences in solvation, as the one giving rise to the *exo*-5,*anti*-7-dibromide 3 from the bromination of benzonorbornadiene (2). Furthermore the olefin 1 is weighted sterically in favor of *endo* attack at C-5 and C-6, the bulky bromine at C-7 competing with the π electron cloud at C-2 and C-3 for steric approach control. The torsional strain factor[11] is also diminished in this system since the vinyl hydrogens at C-5 and C-6 are more nearly eclipsed, *ca.* 10–15°, with the bridgehead hydrogens as compared with the analogous dihedral angle of *ca.* 20° for norbornene.[12]



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[1] H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **89**, 1525, 3898, 3900 (1967).

[2] R. Caple, H. W. Tan, and F. M. Hsu, *J. Org. Chem.*, **33**, 1542 (1968).

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[4] S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 2741 (1966).

[5] H. Kwart and J. L. Nyce, *J. Amer. Chem. Soc.*, **86**, 2601 (1964).

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[8] Hydride shifts can also affect product distribution. For example, see ref 6 and F. H. Dean, D. R. Marshall, E. W. Warnhoff, and F. L. M. Pattison, *Can. J. Chem.*, **45**, 2279 (1967).

[9] P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 3901 (1967).

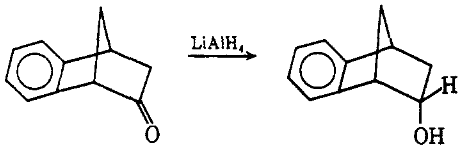
[10] S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3727 (1967).

[11] P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967).

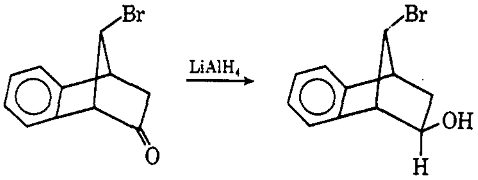
[12] These angles were estimated with aid of Dreiding stereomodels.

Results and Discussion

One piece of evidence that clearly indicates the bulky nature of the bromine in *anti*-7-bromobenzonorbornadiene (**1**) is the stereochemistry of the lithium aluminum hydride reduction of *anti*-7-bromo-5-benzonorbornenone (**4**). Whereas the reduction of 5-benzonorbornenone (**5**) selectively produced the *endo* alcohol (**6**),[13] the lithium aluminum hydride reduction of the bromo



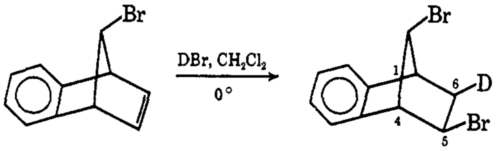
5 **6**



4 **7**

ketone **4** yielded the *exo* alcohol **7**. The bromo alcohol **7** was also obtained by the addition of the elements of hypobromous acid to benzonorbornadiene and has the characteristic nuclear magnetic resonance (nmr) spectrum for this type of disubstituted benzonorbornene[14] as discussed in the Experimental Section. A rearrangement is expected in the addition.[15-17]

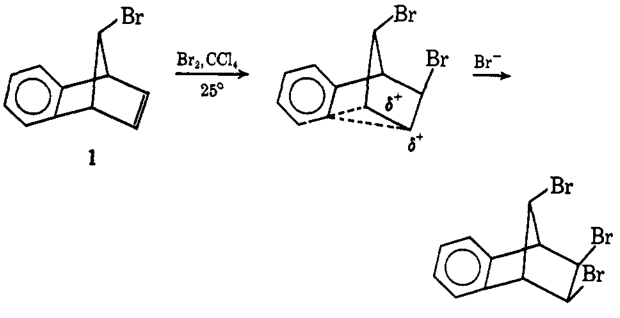
Analogous to some hydrochlorination results of Cristol and Nachtigall,[10] we have found that the addition of deuterium bromide to *anti*-7-bromobenzonorbornadiene (**1**) proceeded exclusively with *cis-exo* addition to produce *exo*-6-deuterio-*exo*-5,*anti*-7-dibromobenzonorbornene (**8**). The selective nature of this



1 **8**

addition can readily be seen by comparing its nmr spectrum with that of authentic *exo*-5,*anti*-7-dibromobenzonorbornene (**3**).[14] The *endo* proton at C-6 in **3** occurs as an octet arising from J_{gem} = 13.1 cps, J_{cis} = 8.0 cps, and a long-range coupling with the proton at C-7 of about 1 cps. The *exo* proton at C-6 in **3** occurs as a doublet of triplets where, in addition to J_{gem}, J_{trans}, and $J_{1,6}$ = 4.1 cps. In the deuterated dibromide **8** the signal for the *exo* proton at C-6, δ 2.77,[18] clearly disappears, and the multiplet for the *endo* proton, δ 2.07, collapses to a doublet where the finer splitting is obscured and the peaks are broadened by the deuterium–hydrogen coupling, but where J_{gem} = 13.1 cps has distinctly vanished. These results are consistent with a stepwise[1,4,10] addition where the approach of the proton and bromide ion must be governed by factors other than those steric in origin.[10 19,20]

Somewhat more surprising is the *cis-exo* addition observed in the addition of bromine to *anti*-7-bromobenzonorbornadiene (**1**). The structure of the adduct, *anti*-7,*cis-exo*-5,6-tribromobenzonorbornene (**9**) is readily confirmed by its nmr spectrum. In addition



9

to the four aromatic protons only two narrow multiplets are observed.[21] A three-proton multiplet centered at δ 4.43 is observed with a width of 1.5 cps at the half-height for the isochronous protons on the carbons bearing bromine. The two chemically equivalent bridgehead protons produce a doublet, J = 1.2 cps, centered at δ 4.04.

Our experimental results do not enable us to distinguish a rearranged product from an unrearranged adduct, but it appears essential to us that to account for this stereoselective *exo* nucleophilic attack on an intermediate cation one must assume the intervention of carbon bridging or a "windshield wiper effect."[22]

Where delocalization or rearrangement is not important, *trans* addition of molecular bromine can occur.[23,24] Probably the best example of this effect is the *trans* addition of bromine to 7-norbornenone (**10**). Whereas deuterium bromide added primarily *cis-exo* to this system,[2] bromine added to yield almost exclusively *trans*-2,3-dibromo-7-norbornanone (**11**). Apparently, when the delocalization or rapid migration of the σ electrons is not important, the product is determined by a bridged bromonium ion intermediate. In this case the rearranged cation would involve a juxtaposition of positive charges. Presumably it is the initial electrophilic attack that leads to the *exo* bromine as this preference has been noted elsewhere.[10,15,25] The structure of the dibromide **11** is readily confirmed by nmr analysis[21] as noted in the Experimental Section. See Scheme I.

Torsional strain factors are probably not large enough to be significant here, especially in view of the weighted steric factor and the small dihedral angle between the bridgehead hydrogens and hydrogens on the

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(13) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **75**, 422 (1953).

(14) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3738 (1967).

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(19) J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *ibid.*, **32**, 893 (1967).

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(21) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

(22) H. C. Brown, Abstracts, the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961, p 2O; "Non-Classical Intermediates," Organic Reaction Mechanisms Conference, Brookhaven, N. Y., Sept 1962.

(23) J. A. Berson and R. Swidler, *J. Amer. Chem. Soc.*, **76**, 4060 (1953).

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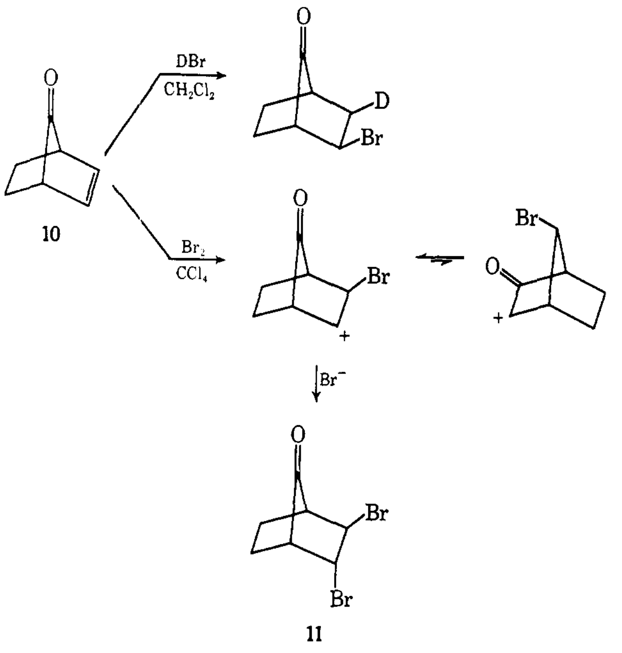
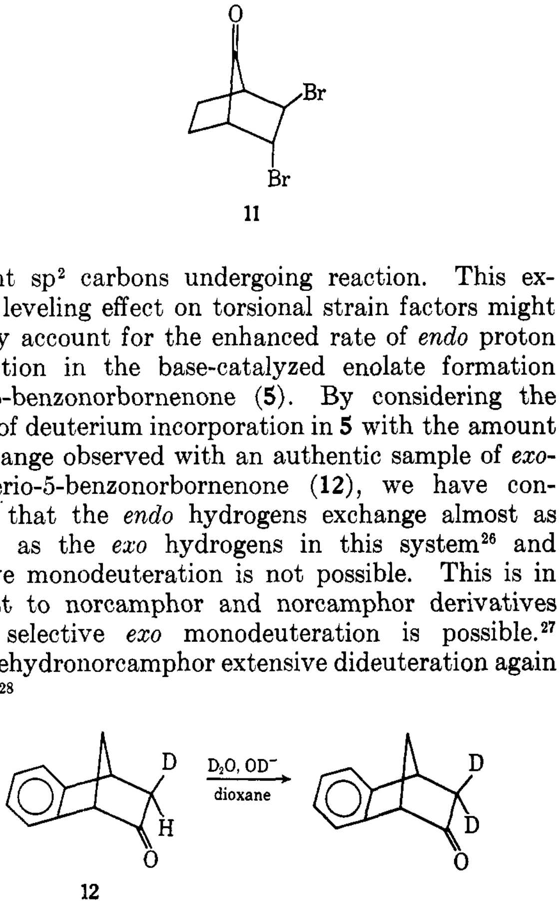
(25) M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 4293 (1965), and references cited therein.

SCHEME I



adjacent sp^2 carbons undergoing reaction. This expected leveling effect on torsional strain factors might possibly account for the enhanced rate of *endo* proton abstraction in the base-catalyzed enolate formation from 5-benzonorbornenone (**5**). By considering the extent of deuterium incorporation in **5** with the amount of exchange observed with an authentic sample of *exo*-6-deuterio-5-benzonorbornenone (**12**), we have concluded that the *endo* hydrogens exchange almost as rapidly as the *exo* hydrogens in this system[26] and selective monodeuteration is not possible. This is in contrast to norcamphor and norcamphor derivatives where selective *exo* monodeuteration is possible.[27] With dehydronorcamphor extensive dideuteration again occurs.[28]



We tend to believe that for the polar addition of bromine to **1** a significant stereoelectronic factor is operating, and this factor accounts for the kinetic preference for the "regiospecific"[29] *exo* approach of the electrophilic bromine in spite of the hindered transition state resulting from this attack. It is possible that the energy difference responsible for this stereoelectronic factor is related to the ease of *exo* capture of the norbornyl cation compared with *endo* capture.[30] The lower energy of activation for *exo* approach of electrophilic bromine may arise from the extent of delocalization in the transition state. If this energy difference approaches the order of magnitude observed for the norbornyl cation,[30] it certainly would have to be considered as one of the major factors controlling the initial *exo* approach. Electrophilic attack from the *endo* side on **1** cannot so readily involve delocalization in the transition state if the electrophile is being complexed with the π orbital in the rate-determining step.[31] See Scheme II.

The subsequent *exo* nucleophilic attack by bromide ion on the cationic intermediate can best be accounted for in terms of the delocalized bridged intermediate.[32]

If such stereoelectronic factors do operate, they might also account for the *cis-exo* addition of deuterium bromide to **1**. Steric hindrance to approach in this case is not so large, however, as when the electrophile is bromine. Torsional factors perhaps cannot be ruled out entirely when the electrophile is a deuteron (and, by implication, a proton), but we believe that the stereoelectronic factor best accounts for the stereoselective *exo* approach.[33]

Experimental Section

Analytical.—Nuclear magnetic resonance spectra were obtained using a Varian Associates Model A-60 spectrometer using tetramethylsilane as an internal standard. Gas chromatographic analyses were performed on an Aerograph A90-P3 instrument. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were obtained with a Thomas-Hoover Uni-Melt apparatus and are uncorrected (taken in capillaries).

***anti*-7-Bromo-*exo*-5-benzonorbornenol** (**7**).—Benzonorbornadiene (**2**), 15.6 g (110 mmol), and N-bromosuccinimide (Arapahoe Chemicals, Inc.), 23.0 g (129 mmol), were dissolved in 125 ml of *t*-butyl alcohol and 180 ml of 1 *N* sulfuric acid. The solution was stirred at room temperature for 12 hr. The reaction solution was then added to 750 ml of water and extracted with three 150 ml-portions of methylene chloride. The extract was washed several times with a 10% sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and evaporated under vacuum to yield 23 g of a white solid. A small second spot which was not starting material could be detected by thin layer chromatography (tlc) over silica gel. The solid was recrystallized three times from hexane to yield 17.5 g (67%) of the pure solid, mp 95–96°. The nmr spectrum of the alcohol **7** is as expected.[14] The signal for the proton at C-7 occurs as a narrow multiplet, 3.5-cps width at half-height, at δ 4.08. The *endo* proton at C-5 occurs as a broad, complex multiplet centered at δ 3.88. The rearranged configuration is further established by the nmr spectrum of the corresponding ketone **4**.

Anal. Calcd for $C_{11}H_{11}BrO$: C, 55.25; H, 4.64; Br, 33.42. Found: C, 55.04; H, 4.65; Br, 33.69.

***anti*-7-Bromo-5-benzonorbornenone** (**4**).—The oxidation of *anti*-7-bromo-*exo*-5-benzonorbornenol (**7**) to the corresponding ketone **4** was best accomplished using an Oppenauer oxidation. The alcohol **7**, 11.0 g (46 mmol), aluminum *t*-butoxide (Columbia Organic Chemicals Co., Inc.), 11 g, and *p*-benzoquinone, 12 g, were added to 300 ml of dry benzene. The black reaction mixture was refluxed with stirring for 12 hr; 5 g of additional aluminum *t*-butoxide was added; and the mixture was refluxed for another 3 hr. The cooled reaction mixture was then added to 500 ml of 3 *N* hydrochloric acid, and the reaction flask was washed thoroughly with benzene. The combined mixture was filtered with the aid of Celite. The benzene layer was removed and washed with three 250 ml-portions of 3 *N* hydrochloric acid,

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(26) C. P. Wick, unpublished results of this laboratory.

(27) A. F. Thomas, R. A. Schneider, and J. Meinwald, *J. Amer. Chem. Soc.*, **89**, 68 (1967).

(28) J. M. Jerkunica, S. Borčić, and D. E. Sunko, *Tetrahedron Lett.*, 4465 (1965). These authors offer an alternate explanation based on the relief of nonbonded repulsions to account for the *exo/endo* rates of exchange.

(29) A. Hassner and F. Boerwinkle, *J. Amer. Chem. Soc.*, **90**, 216 (1968).

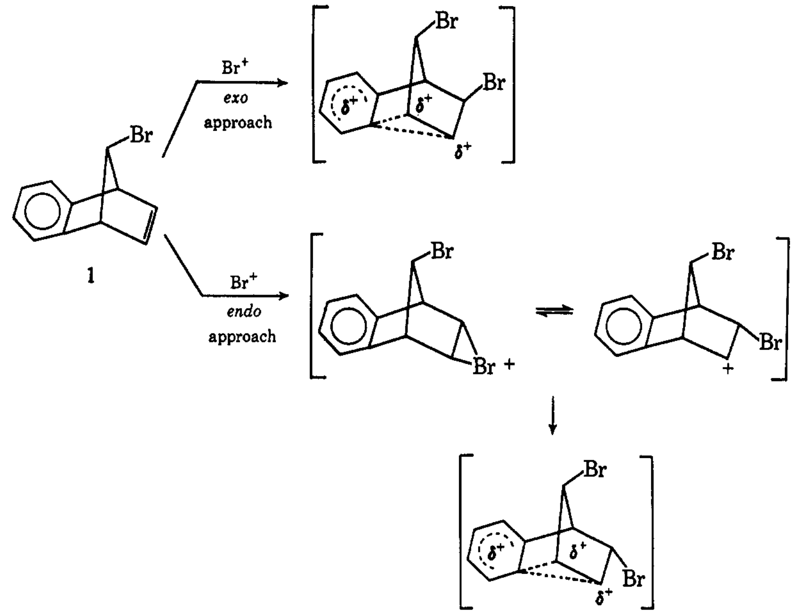
(30) H. L. Goering and C. B. Schewene, *ibid.*, **87**, 3516 (1965).

(31) J. E. Dubois and F. Garnier, *Chem. Commun.*, 241 (1968).

(32) (a) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *J. Amer. Chem. Soc.* **90**, 1901 (1968); (b) H. Tanida, H. Ishitobi, and T. Irie, *ibid.*, **90**, 2688 (1968); (c) H. C. Brown and G. L. Tritle, *ibid.*, **90**, 2689 (1968).

(33) For recent reviews on electrophilic additions, see P. B. D. de la Mare and R. Boulton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966, and B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms," John Wiley & Sons Ltd., London, 1965 and 1966.

Scheme II



then with three 200 ml-portions of a 5% sodium hydroxide solution, and finally with water. The benzene extract was dried over anhydrous magnesium sulfate and removed under vacuum. A viscous yellow liquid remained which showed only one spot by tlc. Distillation under reduced pressure, bp 94–96° (0.02 mm), yielded 7.2 g (65%) of a colorless liquid. The distillate solidified upon standing to a crystalline mass. Recrystallization from cyclohexane yielded white crystals, mp 54.5–55.5°. The nmr spectrum of the ketone 4 is quite distinct. The signal for the proton at C-7 occurs as a narrow multiplet at δ 4.37. The *exo* proton at C-6 exists as a quartet, $J_{gem} = 17.0$ cps and $J_{1,6} = 3.8$ cps, centered at δ 2.77. The *endo* proton at C-6 occurs as a quartet, $J_{gem} = 17.0$ cps and $J_{6,7} = 2.4$ cps, centered at δ 1.83.

Anal. Calcd for $C_{11}H_9BrO$: C, 55.72; H, 3.83; Br, 33.70. Found: C, 55.51; H, 3.69; Br, 33.90.

Lithium Aluminum Hydride Reduction of 4.—A small sample of *anti*-7-bromo-5-benzonorbornenone (4) was reduced with lithium aluminum hydride in ethyl ether in a manner similar to that used for the reduction of 5-benzonorbornenone (5).[13] A near-quantitative yield of an alcohol was obtained that was identical in spectral and physical properties with those of an authentic sample of *anti*-7-bromo-*exo*-5-benzonorbornenol (7).

Hydrobromination of *anti*-7-Bromobenzonorbornadiene (1).—*anti*-7-Bromobenzonorbornadiene (1),[10] 1.0 g (4.5 mmol), was dissolved in 150 ml of reagent methylene chloride, and the solution was saturated with anhydrous hydrogen bromide at 0°. The reaction flask was tightly stoppered and allowed to stand at 0° in the dark for 25 hr. The excess hydrogen bromide and methylene chloride were removed by gentle warming and then under aspirator vacuum. Fresh methylene chloride was added, and the solution was dried over anhydrous magnesium sulfate. The solvent was removed under vacuum and produced a near-quantitative yield of the dibromide 3. Only one spot could be detected by tlc; its nmr spectrum was identical with that of an authentic sample of 3.[10] Treatment with activated charcoal and recrystallization from ethanol produced white crystals, mp 78–79° (lit. mp 78–79.5[10] and 77–77.5°[15]).

Deuterobromination of *anti*-7-Bromobenzonorbornadiene (1). The addition of deuterium bromide was carried out as with the corresponding hydrobromination. The deuterium bromide was generated by the addition of deuterium oxide, 99.8% (Columbia Organic Chemicals Co., Inc.) to Eastman phosphorous tribromide. The deuterium bromide was trapped and distilled from a Dry Ice–acetone trap into a methylene chloride solution of 1.

***anti*-7,*cis*-*exo*-5,6-Tribromobenzonorbornene (9).**—*anti*-7-Bromobenzonorbornadiene (1), 1.0 g (4.5 mmol), was dissolved in 5 ml of carbon tetrachloride, and the reaction flask was wrapped in aluminum foil. A 10% solution of bromine in carbon tetrachloride was added dropwise until the bromine color was maintained. The adduct immediately started to crystallize from the carbon tetrachloride solution. Removal of the solvent under vacuum gave a quantitative yield of a slightly yellow solid. Only one spot could be detected by tlc for this crude crystalline product. The adduct was recrystallized from benzene, mp 192–192.5°.

Anal. Calcd for $C_{11}H_9Br_3$: C, 34.68; H, 2.38; Br, 62.94. Found: C, 34.79; H, 2.38; Br, 62.73.

***trans*-2,3-Dibromo-7-norbornanone (11).**—7-Norbornenone (10),[34] 5.0 g (46 mmol), was dissolved in 11 ml of carbon tetrachloride and cooled in a salt–ice bath. To this solution was added dropwise a 40% solution of bromine in carbon tetrachloride at such a rate as to maintain the temperature below 0°. The addition of bromine was continued until a faint bromine color persisted. The solvent was removed under vacuum and the crude product examined by nmr spectroscopy. A very small amount of an unidentified product(s) was observable. A vpc analysis indicated about 10% of some impurity. The crude product was distilled, bp 140° (2 mm), and then the resulting low-melting solid "sublimed" six times at 100° (0.2 mm) to yield a clear solid, mp 52–54°. The nmr spectrum is quite conclusive.[21] The *exo* proton at C-2 occurs as broad multiplet centered at δ 4.73, whereas the *endo* hydrogen at C-3 occurs as a sharp doublet, $J_{2,3} = 2.6$ cps, at δ 4.21.

Anal. Calcd for $C_7H_8Br_2O$: C, 31.37; H, 3.01; Br, 59.65. Found: C, 31.14; H, 2.81; Br, 59.44.

Registry No.—1, 7605-10-9; 4, 17497-60-8; 7, 17497-61-9; 9, 17497-62-0; 11, 17519-24-3.

Acknowledgments.—We are indebted to the Petroleum Research Fund of the American Chemical Society, Grant No. 1100-G1, and the Graduate School of the University of Minnesota for support of this work. One of us (C. S. I.) as a National Science Foundation Undergraduate Research Participant would like to thank the National Science Foundation.

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