with diazomethane and was analyzed by vpc (EGIP column) and nmr which showed the sample to be pure and uncontaminated with acyclic esters.

Reduction of Sodium Cyclopropanecarboxylate.—A solution consisting of 80 mg (0.00348 g-atom) of sodium dissolved in 34 ml of ammonia was prepared in the usual manner; then 150 mg (0.00167 mol) of sodium cyclopropanecarboxylate was added; and the solution was stirred for 45 min. The reaction mixture was worked up in the usual manner to yield 0.087 g (73%) of the free acid. The acid was converted into the methyl ester by reaction with diazomethane, was analyzed by vpc (PEDS column) and nmr, and was shown to be pure and uncontaminated by methyl butyrate or methyl isobutyrate.

Reduction of 1-*n*-Pentyl-1-methyl-2,2-diphenylcyclopropane.—A solution consisting of 24 mg (0.00104 g-atom) of sodium in 35 ml of predried liquid ammonia was prepared in the usual manner, and then 0.0919 g (0.000331 mol) of crystalline 1-pentyl-1-methyl-2,2-diphenylcyclopropane was added. This material was seen to float on the surface of the solution and did not appear to dissolve. The solution was stirred for 3 hr near −33°; then dry hexane was added; and the ammonia was allowed to evaporate. The hexane solution was then filtered to remove the remaining sodium, and the solvent was then removed. The residue crystallized on standing, mp 55–56.5°. Recovered was 85 mg (94%) of the starting material.

A result similar to that above was obtained when the reduction was carried out in a much more concentrated sodium in liquid ammonia solution (3.78 g in 37 ml).

In one part of a modified U tube, made from thick-walled tubing, was placed 80.0 mg (2.9×10^{-4} mol) of the hydrocarbon, $[\alpha]^{30}_{546}$ −43.3°, and in the other part was placed 24 mg (9.6×10^{-4} g-atom) of sodium. The tube was then connected to the vacuum system and evacuated. Predried ammonia (25 ml) was distilled into the part of the tube containing the sodium, and the tube was then sealed and allowed to come to room temperature. The solid hydrocarbon was then tipped into the ammonia solution. The crystals did not dissolve but turned red at the surface. The mixture was allowed to remain at room temperature for about 15 hr. The reaction mixture was worked up in the usual manner. The residue was shown by vpc to consist of two components with the minor component being only 2–3% of the mixture. Since the residue was completely racemic, we did not attempt to isolate the components in the pure state. The nmr spectrum was consistent with the major components being 1,1-diphenyl-3-methyloctane: nmr (CCl_4) δ 7.05 (10 N, singlet), 3.95 (1 H, J = 8 cps), 2.35–0.75 (18.2 H, complex).

Registry No.—Sodium, 7440-23-5; ammonia, 7664-41-7; 1,2,2-triphenylpentane, 6393-07-3; 4,4-diphenylbutanoic acid, 14578-67-7; 4-phenylbutanoic acid, 1821-12-1; 4,4-diphenyl-2-methylbutanoic acid, 17413-46-6; 1,1-diphenyl-3-methyloctane, 17413-47-7; **1**, 17413-48-8.

Acknowledgment.—We wish to express our appreciation to Dr. B. Garrett for the esr spectra. Thanks are also due to Dr. G. Davis for repeating several experiments.

Oxymercuration–Demercuration of 7-Substituted Norbornenes and Norbornadienes

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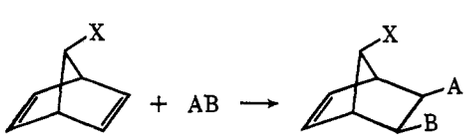
The oxymercuration–demercuration of *syn*- and *anti*-7-hydroxy- and -acetoxynorbornenes gave high yields of *exo,syn*- and *exo,anti*-2,7-dihydroxynorbornanes, respectively. 7-Acetoxynorbornadiene was converted into a mixture of *exo,syn*-2,7-dihydroxynorbornene-5 and *endo,endo*-3,5-dihydroxynortricyclene. 7-Hydroxynorbornadiene experienced an oxidative rearrangement to yield benzaldehyde as the sole reaction product. The synthetic utility and mechanistic implications of these reactions are discussed.

Recent papers from these[1,2] and other laboratories[3,4] have described the marked propensity for certain 7-substituted norbornenes and norbornadienes to react with electrophilic reagents through the *syn* double bond (eq 1). The stereochemistry of the resultant



(1)

X = OH, $OOCCH_3$, $OC(CH_3)_3$

syn adduct is generally *exo,cis* although in some cases concomitant *endo,cis* addition to the *syn* double bond has been noted.[3,4] The tendency of these mono- and diolefins to experience preferential reaction of the *syn* double bond in spite of the potentially adverse steric factors presented by the 7 substituent was unanticipated.[5] The observed selectivity for *syn* addition has been rationalized by the proposition that apparently adverse steric factors were overcome by a strong electronic effect.[1,3,4] While the nature of this electronic effect was vague, it seemed likely that stabilization of the *syn* transition state by coordination of the attacking electrophile by both the double bond and the oxygen-bearing 7 substituent was an important feature of these reactions.[1,6,7]

Brown and coworkers have recently described the oxymercuration–demercuration of olefins as a convenient synthetic route to Markovnikov-oriented alcohols.[8] Particularly pertinent results described by

(1) Diimide reduction: W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *J. Amer. Chem. Soc.*, **89**, 410 (1967).

(2) Silver nitrate complexation: B. Franzus, W. C. Baird, Jr., E. I. Snyder, and J. H. Surridge, *J. Org. Chem.*, **32**, 2845 (1967).

(3) Peroxidation, alkyllithium, carbene additions: G. W. Klumpp, A. H. Veefkind, W. L. deGraaf, and F. Bickelhaupt, *Ann.*, **706**, 47 (1967).

(4) Diazomethane addition: J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966).

(5) For example, calculations based on molecular models indicated that the diimide reduction of 7-acetoxy- or *t*-butoxynorbornadiene would favor the *anti* double bond by a factor of 24:1. See ref 1.

(6) A chelated structure has been suggested to account for the remarkable stability of the silver nitrate–*syn*-7-acetoxynorbornene complex.[2] This complex has been isolated from ethanolic solution as a stable, crystalline compound, mp 146–149° dec. W. C. Baird, Jr., and J. H. Surridge, unpublished results.

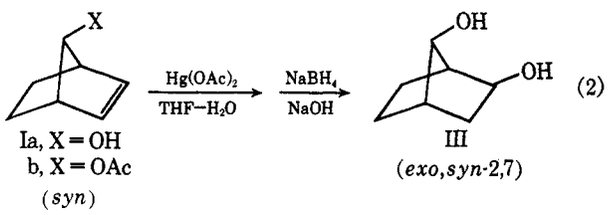
(7) W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **85**, 468 (1963), discuss the directive effects of the hydroxyl group on the Simmons–Smith reaction. See also ref 4.

(8) (a) H. C. Brown and P. Geoghegan, Jr., *ibid.*, **89**, 1522 (1967); (b) H. C. Brown and W. J. Hammar, *ibid.*, **89**, 1524 (1967); (c) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967).

Brown, and previously by Traylor and Baker,[9] are the facts that (1) oxymercuration of norbornene and of alkylnorbornenes occurs exclusively in an *exo,cis* manner,[8b,c,9] (2) no rearrangements of the norbornyl skeleton occur,[8c] and (3) the oxymercuration reaction occurs predominantly from the less hindered side of the molecule.[8b] Furthermore, Brown has noted that the time required for the discharge of the yellow color associated with the suspension of mercuric acetate in the aqueous tetrahydrofuran reaction solvent is a qualitative indicator of the rate of oxymercuration.[8a] For example, norbornene and 2-methylnorbornene experienced rapid oxymercuration, ~30 sec being required for the disappearance of the yellow color.[8c] 7,7-Dimethylnorbornene, on the other hand, required 15 min for the yellow color to vanish.[8c] While these three olefins all gave high yields (84–100%) of exclusively *exo* alcohols (>99.8% *exo*), the diminished rate in the latter case is attributed to steric inhibition presented by the 7-methyl group to reaction of the *syn* double bond.

These observations coupled with a continuing interest in the chemistry of 7-substituted norbornenes and norbornadienes prompted a study of the oxymercuration–demercuration reactions of these olefins utilizing Brown's techniques. The remainder of this paper describes the results of this study and the synthetic utility and mechanistic implications of these reactions.

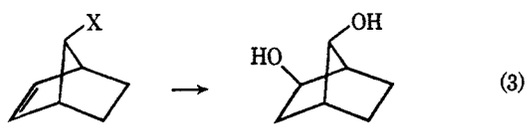
Equations 2 and 3 illustrate the oxymercuration–demercuration of various *syn*- and *anti*-7-substituted norbornenes and the products derived from them.



Ia, X = OH
b, X = OAc
(*syn*)

III
(*exo,syn*-2,7)

(2)



IIa, X = OH
b, X = OAc
(*anti*)

IV
(*exo,anti*-2,7)

(3)

Table I summarizes the experimental conditions and product yields. These reactions were performed according to Brown's procedure[8a] wherein the olefin was added to a suspension of mercuric acetate in aqueous tetrahydrofuran. Subsequent to the discharge of the yellow color the reaction mixture was stirred at the specified temperature for 0.5–10 min. The resultant oxymercuration adduct was decomposed by treatment with sodium hydroxide–sodium borohydride solution. The reaction was stirred for an additional 30–60 min to saponify any acetate functionality.

All of these oxymercuration reactions (eq 2 and 3) proceeded cleanly and in high yield to a single product. Both *syn*-7-hydroxy- (Ia) and -acetoxynorbornenes (Ib) were converted exclusively into *exo,syn*-2,7-dihydroxynorbornane (III). Similarly, the corresponding *anti*-7 alcohol (IIa) and -acetate (IIb) yielded only *exo,anti*-2,7-diol (IV). In all cases the reactions occurred with the introduction of the 2-hydroxyl group in an *exo* configuration; the diol products (III, IV) were not contaminated by any isomeric compounds that might have arisen through isomerization or carbon skeleton rearrangement reactions. In these respects these oxymercuration reactions are in complete accord with Brown's previous experience with norbornene and its alkyl derivatives.[8c] The reactions described here constitute unequivocal syntheses of the isomeric 2,7-norbornanediols (III, IV) and offer vastly improved routes to these compounds relative to previously published methods.[10]

TABLE I
OXYMERCURATION–DEMERCURATION OF 7-SUBSTITUTED NORBORNENES

Olefin	Temp, °C	Time, sec[a]	Product	Yield, %
Ia, X = OH	25	6	III	83
Ib, X = OAc	25	20	III	90
IIa, X = OH	25	13	IV	96
IIb, X = OAc	25	900	IV	92
Norbornene[b]	25	30	*exo*-Norborneol	100
7,7-Dimethylnorbornene[b]	25	900	Apoisoborneol	84

[a] Approximate time in seconds for disappearance of yellow color. [b] Reference 8c.

Inspection of the data of Table I reveals two interesting deviations from the oxymercurations of those norbornyl compounds previously studied.[8c] The first of these is the facile introduction of an *exo,syn*-hydroxyl group into Ia and Ib in spite of the apparent steric hindrance presented by the *syn*-7-hydroxyl and acetoxyl groups in these compounds. Brown has shown that the introduction of a *syn*-7-methyl group reduces the rate of oxymercuration by a factor of 30 relative to that of norbornene.[8c] Table I indicates that the presence of a *syn*-7-hydroxyl or -acetoxyl group has no such effect and, in fact, appears to slightly accelerate the oxymercuration reaction. The second noteworthy distinction is the slow reaction experienced by *anti*-7-acetoxynorbornene (IIb), which exhibits a reactivity comparable with that of 7,7-dimethylnorbornene (Table I) in spite of the total absence of any steric inhibition.

The relative reactivities of the *syn*- and *anti*-7-substituted norbornenes toward oxymercuration would seem to be of diagnostic value with regard to the observed preference for reaction of the *syn* double bond.[1–4] Comparison of the relative reactivities of the *syn*- (Ib) and the *anti*-7-acetates (IIb), ~20 and ~900 sec, respectively, suggests that the oxymercuration reaction of these isomeric esters is sensitive to the same electronic and steric factors that influence the stabilities of the silver nitrate complexes of these olefins.[2,6,11–13] In the case of *anti*-7-acetoxynorbornene

(9) T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, **85**, 2746 (1963).

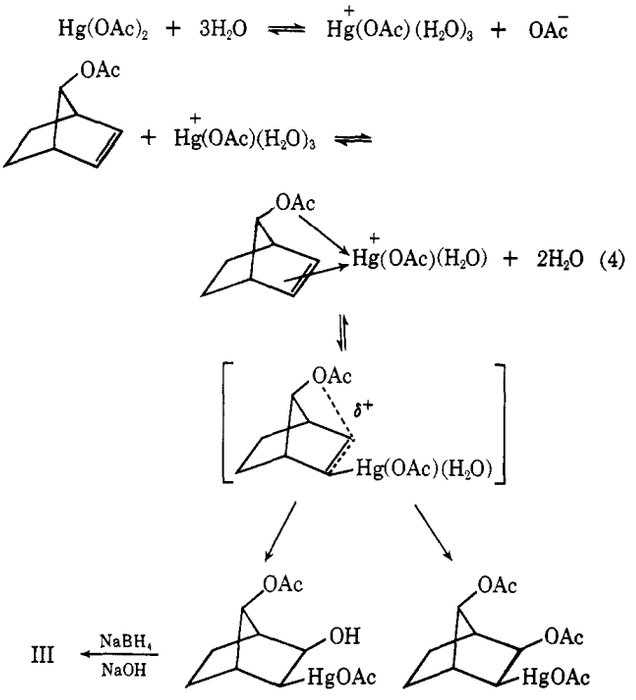
(10) (a) K. Alder, H. Wirtz, and H. Koppelberg, *Ann.*, **601**, 138 (1956); (b) S. B. Soloway and S. J. Cristol, *J. Org. Chem.*, **25**, 327 (1959). Both of these procedures gave diol mixtures containing ~50% *exo,syn*-2,7-, ~23% *exo,anti*-2,7-, and ~10% other isomeric diols (2,5- and 2,6-).

(11) Analogies among silver(I) and mercury(II) olefin complexes have previously been reviewed.[9,12]

(12) J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, **89**, 6427 (1967).

(13) Silver(I) and mercury(II) possess similar ionic and covalent radii. T. Moeller, "Inorganic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1952, pp 136–143.

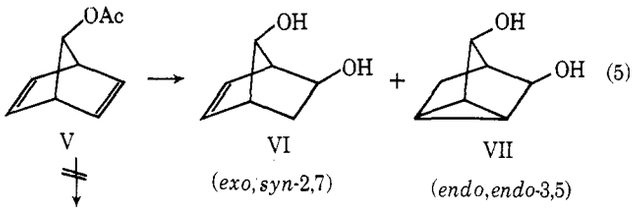
(IIb) withdrawal of the *anti* double-bond electrons by the 7-acetoxyl group quite obviously would diminish the reactivity of this olefin. In the case of the *syn*-7-acetate (Ib), however, inhibition by electron withdrawal and steric effects is more than compensated by stabilization of the mercury(II)–olefin complex through chelation of the mercury ion by the olefinic bond and the *syn*-7 oxygen (eq 4).[14] Oxymercuration of the *syn* isomer (Ib) is further abetted by the eventual stabilization of the partial positive charge that develops on carbon in the transition state (eq 4).[9,15–17]

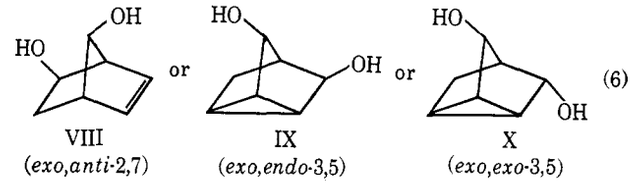


Precedence for such charge stabilization resides in the oxymercuration of certain unsaturated acyclic alcohols where enhanced reaction rates and the formation of cyclized products (ethers) have been attributed to stabilization of the mercurinium ion by the hydroxyl group.[12] Similar stabilization of the mercurinium ion derived from the *anti*-7-acetate is clearly not possible.

The reactivities of the *syn*- (Ia) and *anti*-7-hydroxynorbornenes (IIa) may be rationalized by a similar argument although distinctions here are not so apparent as in the case of the corresponding acetates. The *syn*-7-ol (Ia) exhibits a high degree of reactivity for the same reasons as discussed above for the oxymercuration of the *syn*-7-acetate, *i.e.*, chelation of the mercury(II) ion and subsequent stabilization of the mercurinium ion.[18] The high reactivity of the *anti*-7 alcohol (IIa) relative to that of the *anti*-7-acetate (IIb) is attributed to the inability of the *anti*-7-hydroxyl group to delocalize the olefinic electrons. Consequently, the *anti* alcohol assumes a reactivity comparable to that of the parent olefin, norbornene (Table I).

The oxymercuration–demercuration of 7-acetoxynorbornadiene (V) is illustrated by eq 5; the reaction





occurred at 20° and required ~9 sec for discharge of the yellow color. The combined yield of products VI and VII was 64%;[20] the selectivity to VI was 42% and to VII, 58%. The structure of VI (*exo,syn*-2,7-dihydroxynorbornene-5) was established by hydrogenation to the corresponding norbornanediol (III). The structure of VII (*endo,endo*-3,5-dihydroxynortricyclene) was established by comparison with an authentic sample.[21] The reaction of the acetoxydiene (V) was remarkably selective for the products shown. The formation of the isomeric *exo,anti*-2,7-norbornenediol (VIII) in an amount exceeding ~2–3% of the total product mixture was not detected (eq 6). Similarly, no evidence for the presence of the remaining two isomeric dihydroxynortricyclenes (IX, X) was apparent (eq 6). It is important to note that the formation of VI and VII occurred with the introduction of the hydroxyl group in an *exo* configuration and *syn* to the 7-acetoxyl group of the starting diene.

The high degree of reactivity demonstrated by 7-acetoxynorbornadiene toward oxymercuration and the exclusive introduction of an *exo,syn*-2-hydroxyl group is best rationalized by a reaction proceeding solely *via* the *syn* double bond. Mercury(II) complexation and charge stabilization identical with that previously discussed and illustrated by eq 4 led to the formation of the oxymercuration adduct XI (eq 7). This mercurial adduct (XI) subsequently experienced mercury-catalyzed rearrangement[22] involving carbon participation to generate the nortricyclic mercurial adduct (XII). Borohydride reduction of this mixture of adducts produced the isolated diol products, VI and VII. Precedence for the formation of the organomercurials, XI and XII, from the oxymercuration of 7-acetoxynorbornadiene is provided by the oxymercuration of norbornadiene itself (eq 8).[22] Both diene oxymercurations are completely analogous aside from the directive influence of the 7-acetate group in the reaction of V.

(14) A similar directive effect has been observed in the oxymercuration of certain 4-substituted cyclohexenes: H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 227 (1959).

(15) Discussion of the structure of mercury(II) olefin π complexes (mercurinium ions), the influence of substituents, neighboring-group effects, and the nature of the transition state may be found in ref 9, 12, and 16.

(16) (a) T. G. Traylor, *J. Amer. Chem. Soc.*, **86**, 244 (1964); (b) W. L. Waters and E. F. Kiefer, *ibid.*, **89**, 6261 (1967); (c) Y. Saito and M. Matsuo, *Chem. Commun.*, 961 (1967).

(17) The stabilization of the partial positive charge on carbon may involve a 1,3-acetoxyonium ion. The reaction conditions and the structure of the product neither confirm nor deny the participation of such an intermediate. R. J. Ouellette and R. D. Robins, *Tetrahedron Lett.*, 397 (1968).

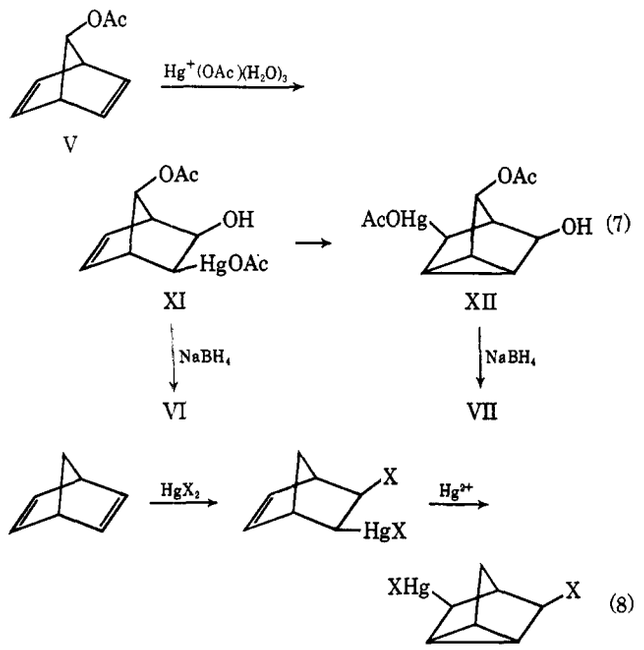
(18) The possibility that the reactivity of *syn*-7-hydroxynorbornene may be diminished by π bonding between the hydroxyl group and the double bond[19] is precluded by the experimental evidence.

(19) L. Joris, P. von R. Schleyer, and R. Gleiter, *J. Amer. Chem. Soc.*, **90**, 327 (1968).

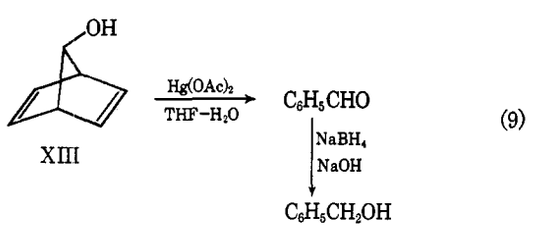
(20) The diminished yield is believed to be a reflection of the inherent instability of organomercurials derived from norbornadienes. The degree of spontaneous decomposition of these organomercury compounds is determined largely by the reaction conditions and by the nature of the mercury anion. See ref 9 and references cited therein.

(21) A. Ferretti and G. Tesi, *J. Chem. Soc.*, 5203 (1965).

(22) K. C. Pande and S. Winstein, *Tetrahedron Lett.*, 3393 (1964).



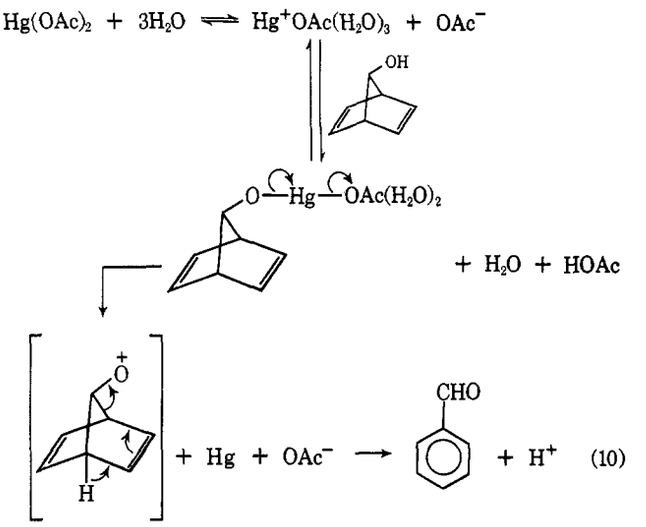
7-Hydroxynorbornadiene (XIII) failed to experience oxymercuration and instead underwent an oxidative rearrangement to yield benzaldehyde as the sole reaction product (eq 9). Addition of the dienol to a



suspension of mercuric acetate in aqueous tetrahydrofuran produced an instantaneous discharge of the yellow color and the precipitation of metallic mercury. Attempts to trap an oxymercuration adduct of XIII by performing the reaction at 0° and by treating the reaction mixture with sodium hydroxide–sodium borohydride immediately subsequent to the addition of dienol gave only benzyl alcohol in >80% yield. No trace of any of the potential diol products, VI–X, was found.

The formation of benzaldehyde from the attempted oxymercuration of 7-hydroxynorbornadiene is not readily rationalized. The dienol has been shown to be stable in aqueous perchloric acid,[23] and a ring-opening reaction catalyzed by aqueous acetic acid generated in the oxymercuration mixture may be reasonably precluded on this basis. Similarly, ring cleavage promoted by mercury(II) catalysis is equally unlikely. The available evidence implies that participation of a mercurinium ion in this reaction is not involved. This view is predicated on (1) the failure to detect any products of oxymercuration by a rapid borohydride quench at 0° and (2) the total absence of carbon skeleton rearrangements in other oxymercurations where such migrations might be reasonably anticipated.[8]

Consequently, the abnormal behavior of 7-norbornadienol (XIII) toward mercury(II) acetate in aqueous tetrahydrofuran demands an alternative explanation. Such a rationale may reside in an oxidative rearrangement to benzaldehyde similar to that experienced by norbornadienol when treated with manganese dioxide in chloroform.[24] Story has suggested that this reaction involves the initial formation of a manganese ester of 7-norbornadienol that subsequently experiences heterolytic oxygen–manganese bond cleavage. This electron transfer results in the reduction of manganese and the creation of a formally positively charged oxygen in the transition state. This mechanism has been extended to the oxidation of allylic and benzylic alcohols and has been employed to account for the insensitivity of the latter to different aryl substituents, the positive charge residing on oxygen rather than on the benzylic carbon. If this mechanism is applied to the present case, the transformation of the dienol to benzaldehyde may be depicted by eq 10.



While the oxidizing power of mercury(II) compounds is well known, it is equally true that the oxidation of normal alcohols by these reagents is not common. It may be that the reaction observed here is unique for 7-norbornadienol since the oxidation chemistry of this alcohol appears to be atypical.[24,25]

Experimental Section

Infrared spectra were recorded on a Beckman IR-5A spectrophotometer. Vapor phase chromatography (glpc) was performed using a Varian Aerograph Model 202 chromatograph and a Perkin-Elmer Model 226 capillary gas chromatograph. Preparative glpc was carried out using a Varian Aerograph Autoprep Model 700. Nmr spectra were recorded on a Varian Associates Model A-60 spectrometer using tetramethylsilane as an internal standard. Melting points and boiling points are not corrected.

The following compounds were prepared by published synthetic procedures: 7-acetoxynorbornadiene (V),[26] 7-hydroxynorbornadiene (XIII),[26] *syn*-(Ia)[27] and *anti*-7-hydroxynorbornenes (IIa),[28] and *syn*-(Ib)[28] and *anti*-7-acetoxynorbornenes (IIb).[28] All other reagents were obtained from commercial sources and used as received.

Oxymercuration of *syn*-7-Acetoxynorbornene (Ib).—A solution of 1.5 g (10 mmol) of *syn*-7-acetoxynorbornene in 5 ml of tetra-

(23) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **88**, 864 (1966).

(24) T. K. Hall and P. R. Story, *ibid.*, **89**, 6759 (1967).

(25) S. Yankelevich and B. Fuchs, *Tetrahedron Lett.*, 4945 (1967).

(26) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961); the ester may be purchased from Frinton Labs, Vineland, N.J.

(27) W. C. Baird, Jr., *ibid.*, **31**, 2411 (1966).

(28) E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, **86**, 1166 (1964).

hydrofuran was added at room temperature to a suspension of 3.2 g (10 mmol) of mercuric acetate in 10 ml of water containing 5 ml of tetrahydrofuran. The reaction was stirred vigorously for 5 min; decolorization of the reaction mixture was complete after ~20 sec. At the conclusion of the reaction period a sodium hydroxide test for mercury(II) was negative. To the reaction mixture was added 10 ml of 3 *M* sodium hydroxide and 10 ml of 0.5 *M* sodium borohydride in 3 *M* sodium hydroxide. The reaction was stirred at room temperature for 2 hr, and the reaction mixture was then saturated with sodium chloride and extracted with ethyl acetate (six 10-ml portions). The combined ethyl acetate extracts were washed once with 25 ml of saturated sodium chloride solution and dried over magnesium sulfate. The solvent was removed on a rotary evaporator at 60° (20 mm) to give 1.3 g of crystalline product. A small sample of the crude product was treated with excess acetyl chloride in pyridine, and the resultant acetate mixture was analyzed by glpc on a 5 ft × 1/4 in. 20% polypropylene glycol column at 190° and 65 ml/min helium flow.[29]

The crude product was shown to contain 11–12% *syn*-7-acetoxynorbornene (3.8 min) and 88–89% *exo,syn*-2,7-diacetoxynorbornane (21.6 min). The yield of *exo,syn*-2,7-dihydroxynorbornane was 1.15 g (90%). Recrystallization of the crude diol from 25 ml of cyclohexane and sublimation at 100° (0.2 mm) gave 0.8 g (63%) of pure diol, mp 179–181° (lit.[30] mp 180–181°). A diphenylurethan was prepared and recrystallized from benzene, mp 227–229° (lit.[30] mp 221–222°). The nmr spectrum of the *exo,syn*-2,7-diol in deuterium oxide had the following pattern: δ 3.90–4.23 (m, 2, >CH–O), 2.13–2.44 (m, 2, bridgehead), 0.91–2.12 (m, 6, *exo,endo* >CH_2).

A 1.5-g sample of crude diol was acetylated with acetyl chloride–pyridine to give 1.85 g of acetate esters from which *exo,syn*-2,7-diacetoxynorbornane [n^{20}D 1.4642 (lit.[31] n^{20}D 1.4641); glpc purity 100%] was isolated by preparative glpc (12 ft × 3/8 in. 30% FFAP column, 190°, 180-ml/min helium flow). The diacetate had definitive ir absorptions (neat) at 1195, 1136, 1080, 1048, and 1016 cm^{-1}. The nmr spectrum ($CDCl_3$), had the following pattern: δ 4.53–4.83 (m, 2, >CH–OAc), 2.50 (m, 1, bridgehead), 2.30 (m, 1, bridgehead), 2.00 (d, 6, CH_3CO–), 1.00–1.96 (m, 6, *exo,endo* >CH_2).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.24; H, 7.60. Found: C, 61.94; H, 7.80.

Oxymercuration of *syn*-7-Hydroxynorbornene (Ia).—To 1.6 g (5 mmol) of mercuric acetate in 5 ml of water and 2.5 ml of tetrahydrofuran was added a solution of 0.55 g (5 mmol) of *syn*-7-hydroxynorbornene in 2.5 ml of tetrahydrofuran. The oxymercuration was complete in ~6 sec, and the reaction was stirred at room temperature for 10 min. The adduct was decomposed with 5 ml of 3 *M* sodium hydroxide and 5 ml of 0.5 *M* sodium borohydride. The reaction mixture was extracted as previously described to yield 0.6 g of crude *exo,syn*-2,7-dihydroxynorbornane. Glpc analysis (see above) of the diacetate indicated a sample purity of 89%; the yield of diol was 83%. The product was identical with that described above.

Oxymercuration of *anti*-7-Acetoxynorbornene (IIb).—The oxymercuration of *anti*-7-acetoxynorbornene was performed according to the procedure described for the oxymercuration of *syn*-7-acetoxynorbornene. Decolorization of the reaction mixture required 15 min. From the ethyl acetate extract was isolated 1.3 g of crystalline diol; acetylation and analysis of the diacetate by glpc (5 ft × 1/4 in. 20% polypropylene glycol, 190°, 65 ml/min) showed the product to consist of 9.1% *anti*-7-acetoxynorbornene (3.6 min) and 90.9% *exo,anti*-2,7-diacetoxynorbornane (20.9 min). The yield of diol was 1.18 g (92%). Recrystallization from benzene and sublimation at 100° (0.2 mm) gave a pure sample of *exo,anti*-2,7-diol, mp 196–198° (lit.[32] mp 196.5–197.5°). Reaction with *p*-nitrobenzoyl chloride afforded a dinitrobenzoate, mp 195–197° (recrystallized from benzene).

Anal. Calcd for $C_{21}H_8N_2O_8$: C, 59.43; H, 3.80; N, 6.60. Found: C, 59.45; H, 4.18; N, 6.64.

The nmr spectrum of the diol in deuterium oxide had the following pattern: δ 4.50 (m, 1, *J* = 3.8 cps, *anti*-7-HC–O), 4.0 (q, 1, *J* = 11 cps, *exo*-2-HC–O), 1.17–2.50 (m, 8, bridgehead, *exo,endo*-CH_2).

A 0.6-g sample of *exo,anti*-2,7-diol was acetylated with acetyl chloride–pyridine to give 0.9 g of diacetate, which was purified by preparative glpc (12 ft × 3/8 in. 30% FFAP column, 190°, 180 ml/min). The pure diacetate had a melting point of ~18–20° and n^{20}D 1.4644. The nmr spectrum of the diacetate ($CDCl_3$) had the following pattern: δ, 4.97 (m, 1, *J* = 3.5 cps, *anti*-7-H–C–OAc), 4.58 (q, 1, *J* = 11 cps, *exo*-2-H–C–OAc), 2.22–2.42 (m, 2, bridgehead), 2.03 (d, 6, CH_3CO), 0.91–2.02 (m, 6, *exo,endo*-CH_2). The ir spectrum (neat) had characteristic absorption bands at 1176, 1150, 1128, and 1075–1015 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.24; H, 7.60. Found: C, 61.95; H, 7.56.

Oxymercuration of *anti*-7-Hydroxynorbornene (IIa).—The reaction was performed using 2.2 g (20 mmol) of *anti*-7-hydroxynorbornene, 6.4 g (20 mmol) of mercuric acetate, 20 ml of tetrahydrofuran, and 20 ml of water. Decolorization of the reaction mixture required ~13 sec; the reaction was stirred at room temperature for 10 min prior to being decomposed with sodium borohydride solution. The ethyl acetate extract yielded 2.6 g of crude product which contained 94.6% *exo,anti*-2,7-dihydroxynorbornane by glpc analysis. The yield of diol was 2.46 g (96%); the diol was shown to be identical with that previously described.

Oxymercuration of 7-Acetoxynorbornadiene (V).—To a suspension of 6.4 g (20 mmol) of mercuric acetate in 20 ml of water and 10 ml of tetrahydrofuran was added a solution of 3 g (20 mmol) of 7-acetoxynorbornadiene in 10 ml of tetrahydrofuran. The reaction mixture decolorized in ~9 sec; stirring was continued for 10 min at 20°. The reaction mixture was decomposed with 20 ml of 3 *M* sodium hydroxide and 20 ml of 0.5 *M* sodium borohydride. The aqueous mixture was saturated with sodium chloride and extracted with ethyl acetate (five 25-ml portions). The extract was dried over magnesium sulfate, and the solvent was removed on a rotary evaporator to give 2.9 g of semicrystalline product. The crude diol was acetylated to yield 3.2 g of diacetate. The crude diacetate was dissolved in boiling *n*-heptane or cyclohexane, and the ester solution was decanted from intractable tars. Removal of the solvent gave 2.7 g (64%) of crystalline diacetate. The diacetate was analyzed by glpc, and the composition of the product is presented in Table II. The diacetate mixture (2.6 g) was triturated three times with 25-ml portions of pentane and separated into a pentane-soluble (1.35 g) and a pentane-insoluble fraction (1.2 g). The compositions of the two diacetate fractions are presented in Table II;

TABLE II

GLPC ANALYSIS OF DIACETATE FRACTIONS[a]

Compound	Retention time, min	Composition, % Reaction product	Pentane-soluble fraction	Pentane-insoluble fraction
exo,syn-2,7-Diacetoxynorbornene-5	17.6	42.4	90.5	6.8
endo,endo-3,5-Diacetoxynortricyclene	26.1	57.6	9.5	93.2

[a] On a 5 ft × 1/4 in. 20% polypropylene glycol column, 190°, 60 ml/min.

analysis by capillary glpc (200-ft 50:50 phenylnitrile–silicone column, 140°, 20 psig) gave identical results and did not further resolve the major peaks. The major product was separated from the pentane-soluble fraction by preparative glpc (12 ft × 3/8 in. 30% FFAP column, 190°, 180 ml/min) to give a sample of diacetate of 99% purity, mp ~30–35°. The nmr spectrum ($CDCl_3$) had the following pattern which was consistent with an *exo,syn*-2,7-diacetoxynorbornene-5 structure: δ 5.90–6.32 (m, 2, vinyl), 4.58–4.83 (m, 1, *J* = 12 cps, *endo*-H–C–OAc), 4.46–4.57 (m, 1, *J* = 4 cps, bridge H–C–OAc), 3.05–3.23 [m, 1, *J* = 7 cps, bridgehead (H_1)], 2.71–2.97 [m, 1, *J* = 6.5 cps, bridgehead (H_4)], 2.00 (d, 6, CH_3CO), 1.78–1.97 (m, 2, *exo,endo*-CH_2). Hydrogenation over 10% Pd–C in ethanol converted the unsaturated diacetate into *exo,syn*-2,7-diacetoxynorbornane which was shown to be identical with an authentic sample.

(29) Attempts to analyze the diol products directly by glpc on a variety of substrates were not successful owing to inadequate resolution of isomeric mixtures and sample decomposition on the column. These problems were successfully avoided by conversion of the products into acetate esters. Control analyses utilizing *t*-butylbenzene as an internal standard demonstrated that the analyses were quantitative.

(30) H. M. Walborsky and D. F. Loncrini, *J. Amer. Chem. Soc.*, **76**, 5936 (1954).

(31) K. Alder, F. H. Flock, and H. Wirtz, *Ber.*, **91**, 609 (1958).

(32) H. Krieger, *Suomen Kemistilehti*, **B35**, 127 (1962).

The pentane-insoluble fraction (1.2 g) was recrystallized from *n*-heptane or cyclohexane and sublimed [100° (0.2 mm)] to give 0.6 g of white crystalline product, mp 106–108°, glpc purity 97%. The nmr spectrum ($CDCl_3$) had the following pattern which was consistent with an *endo,endo*-3,5-diacetoxynortricyclene structure: δ 4.75–4.86 (m, 2, H-C-OAc), 2.34–2.50 (m, 1, bridgehead), 2.00 (d, 6, CH_3CO), 1.25–1.83 (m, 5, cyclopropyl, bridge).

Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.50; H, 6.80.

A sample of *endo,endo*-3,5-diacetoxynortricyclene (1.8 g) was refluxed in 15 ml of methanol containing 0.2 g of sodium methoxide for 1 hr; the methanol was removed by distillation until the total volume was reduced to ~3 ml. Saturated sodium chloride solution (15 ml) was added, and the product was extracted with ethyl acetate (five 10-ml portions). From the dried extract 1.1 g of semicrystalline diol was isolated. A sample was acetylated and analyzed by glpc to demonstrate that no degradation or rearrangement had occurred. The crude product was sublimed twice at 100° (0.3 mm) to give 0.5 g of waxy, hygroscopic diol, mp 152–154° (sealed capillary). The nmr spectrum of the diol in deuterium oxide had the following pattern: δ 4.40–4.54 (m, 2, H-C-O), 2.13–2.34 (m, 1, bridgehead), 1.50–1.97 (m, 5, bridge, cyclopropyl).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.72; H, 8.15.

A sample of diol was converted into its *p*-nitrobenzylidene derivative; recrystallization from cyclohexane and sublimation gave a white crystalline product, mp 161–163°. The ir spectrum (CCl_4) of the benzylidene derivative revealed the total absence of hydroxyl and carbonyl functionality. The formation of a benzylidene derivative can only be accommodated by *endo,endo*-3,5-dihydroxynortricyclene.

Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.89; H, 5.05; N, 5.40. Found: C, 65.10; H, 5.46; N, 5.97.

A sample of the diol was converted into its dibenzoate; recrystallization from *n*-heptane gave white platelets, mp 115.5–117° (lit.[21] mp 116.5–117). The nmr and ir spectra of the dibenzoate were identical with the nmr and ir spectra of the dibenzoate of an authentic sample of *endo,endo*-3,5-dihydroxynortricyclene.[21]

Oxymercuration of 7-Hydroxynorbornadiene (XIII).—To a solution of 3.2 g (10 mmol) of mercuric acetate in 10 ml of water was added 10 ml of tetrahydrofuran and 1.1 g (10 mmol) of 7-hydroxynorbornadiene. The yellow suspension became white instantaneously, and within 10 sec a gray precipitate had separated. The reaction was quenched by the addition of 10 ml of 3 *M* sodium hydroxide; the reaction mixture was stirred at room temperature for 1 hr. The reaction was saturated with salt and extracted with ethyl acetate (five 25-ml portions). From the extract 1.0 g of crude product was isolated. Distillation gave 0.6 g (57%), bp 72° (14 mm), of benzaldehyde, which was identified by comparison of its ir spectrum with that of an authentic sample.

The reaction was repeated at 0° using the same quantities of reagents. The reaction mixture decolorized immediately, and a gray precipitate formed gradually during the subsequent 10 min. The reaction was decomposed with 10 ml of 3 *M* sodium hydroxide and 10 ml of 0.5 *M* sodium borohydride. The reaction mixture was stirred at 0° for 30 min and then at room temperature for 30 min. The standard work-up gave 1.1 g of oil which was acetylated with acetyl chloride–pyridine. The acetate product (1.6 g) was shown by glpc analysis to contain >80% benzyl acetate. The structure of the ester was confirmed by comparison of its nmr and ir spectra with those of an authentic sample.

The reaction was repeated at 0° using the same quantities of reagents. In this case the reaction mixture was treated with sodium hydroxide–sodium borohydride solution immediately subsequent to the addition of the dienol. The reaction was stirred at 0° for 15 min and then worked up as previously described. The reaction yielded 0.85 g (79%) of benzyl alcohol; acetylation gave 1.15 g (97%) of benzyl acetate.

Isolation of the Isomeric 3,5-Dihydroxynortricyclenes from the Peroxidation of Norbornadiene.—Norbornadiene underwent reaction with performic acid in ethyl acetate solution according to the literature procedure.[21,33] Carbonyl-containing impurities were removed from the diol mixture by extracting an aqueous solution of the diols with carbon tetrachloride. From the aqueous phase was recovered 17 g of crude hygroscopic diols, mp 139–149°. A 1.2-g sample of the diol mixture was acetylated and analyzed by glpc; the results are summarized in Table III. The remaining 15.6 g of diols were recrystallized four times from acetonitrile; the composition of the crystal crops was followed by glpc and is presented in Table III. The quantities of acetonitrile employed and the material balances are summarized in Table IV.

TABLE III

GLPC ANALYSIS OF ISOMERIC 3,5-DIHYDROXYNORTRICYCLENES[a]

Compound	Retention time, min	Composition, % Crude product	Acetonitrile recrystallization 1st	2nd	3rd	4th
2,7-*exo,syn*	14.9	10.6	1.7			
3,5-*exo,endo*	18.5	19.4	21.6	15.0	5.6	
3,5-*exo,exo*	20.2	62.3	75.6	85.0	94.4	99.4
3,5-*endo,endo*	23.6	5.6				

[a] On a 5 ft × 1/4 in. 20% polypropylene glycol column, 190°, 75 ml/min.

TABLE IV

RECRYSTALLIZATION OF 3,5-DIHYDROXYNORTRICYCLENES

Recrystallization	CH_3CN, ml	Charge, g	Yield, g	Filtrate, g
1	40	15.6	9.3	6.5
2	30	9.3	7.4	1.8
3	40	7.4	5.6	1.6
4	25	5.6	4.4	0.9

This procedure yielded 4.4 g of *exo,exo*-3,5-dihydroxynortricyclene (purity by glpc 99%), mp 157–158° (lit.[21] mp 158–159°). The dibenzoate (recrystallized from *n*-heptane) had mp 113–114° (lit.[21] mp 110.5–111.5°). The nmr and ir spectra of the *exo,exo*-3,5-dibenzoate were identical with those previously reported.[21]

The 6.5 g of isomeric diols recovered from the filtrate of the first acetonitrile recrystallization (Table IV) was recrystallized from benzene (75 ml)–acetonitrile (4 ml) to give 3.5 g of crystalline material; the filtrate yielded 2.9 g of oily solids. These crystalline diols were combined with the residues recovered from the remaining acetonitrile filtrates (Table IV, 2–4) to give 7.1 g of mixed diols. This mixture was recrystallized from benzene (200 ml)–acetonitrile (10 ml) to give 5.6 g of hygroscopic diols. Acetylation gave 7 g of isomeric diacetates; the composition as shown by glpc analysis was 2.0% *exo,syn*-2,7-diacetoxynorbornene, 47.6% *exo,endo*-3,5-diacetoxynortricyclene, and 47.3% *exo,exo*-3,5-diacetoxynortricyclene. The diacetates were separated by preparative glpc (12 ft × 3/8 in. 30% FFAP column, 190°, 165 ml/min) to give 2.8 g of *exo,endo* isomer (71% pure). A second preparative glpc separation gave 1.1 g of *exo,endo*-diacetate of 92% purity. Saponification of the diacetate with sodium methoxide in methanol gave 0.6 g of diol; after sublimation at 120° (0.2 mm) the diol melted at 166–168° (lit.[21] mp 175–176°). The dibenzoate was prepared and recrystallized from ethanol–water: mp 86–88° (lit.[21] mp 87.5–88°). The nmr and ir spectra of the *exo,endo* dibenzoate were identical with those previously reported.

The 2.9 g of oily solids recovered from the first benzene–acetonitrile recrystallization were combined with 2.5 g of crude diols recovered from the carbon tetrachloride extraction of the original reaction mixture. Acetylation gave 7.4 g of diacetates which contained 9.5% *endo,endo*-3,5-diacetoxynortricyclene by glpc. The diacetate mixture was transferred to a centrifuge tube and stored at 0° to crystallize the *endo,endo* isomer. After 3 weeks the crystalline deposit was separated from the supernatant liquid by centrifugation. The *endo,endo* isomer content of the liquid phase had decreased to 4%. The crystalline solids (0.4 g) were washed with pentane, recrystallized twice from *n*-

(33) J. P. Schaefer, *J. Amer. Chem. Soc.*, **82**, 4091 (1960).

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.

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

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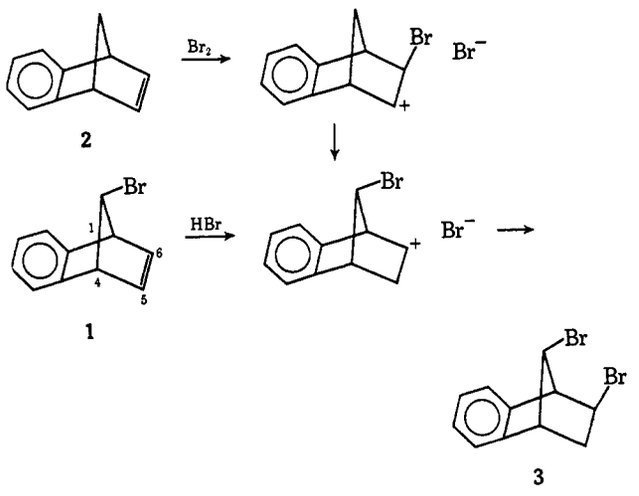
The polar addition of bromine and deuterium bromide to *anti*-7-bromobenzonorbornadiene (1) has been investigated. Even with the unfavorable steric factor *cis,exo* addition of both reagents is observed. Torsional strain effects are also ruled out as governing the "regiospecificity" of electrophilic 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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