

ml of acetone for 10 min at room temperature. After filtration and drying, 5.8 g (87% yield) of white crystalline product was obtained, mp 228–229°.

For analysis, see Table IV.

5-(Dimethylcarbamoyloxy)-1,3-phenylenebis(trimethylammonium iodide) (IV).—A solution of 3.95 g of 3,5-dinitrophenol (I), 2.33 g of dimethylcarbamoyl chloride, and 4 ml of triethylamine in 100 ml of benzene was refluxed for 4 hr. Triethylamine hydrochloride was removed by filtration and the filtrate washed with 0.1 N sodium hydroxide and dried (Na₂SO₄). Addition of 20 ml of ethanol precipitated crude 3,5-dinitrophenyl dimethylcarbamate (II). Recrystallization from ethanol–water gave 2.83 g (52%) of yellow crystals, mp 78–79°.

Anal. Calcd for C₉H₉N₃O₆: C, 42.4; H, 3.5; N, 16.5. Found: C, 42.7; H, 3.5; N, 16.3.

A mixture of 510 mg of 3,5-dinitrophenyl dimethylcarbamate (II) and 200 mg of platinum oxide in 20 ml of absolute ethanol was hydrogenated in a Parr apparatus (Parr Instrument Co., Inc., Moline, Ill.). Absorption of 6 mol of hydrogen was com-

plete in 20 min. The catalyst was removed by filtration and the filtrate was evaporated to give 3,5-diaminophenyl dimethylcarbamate (III) as a residue. The residue was dissolved in 5 ml of N,N-dimethylformamide. 2,6-Lutidine (0.9 ml) and methyl iodide (3 g) were added and the solution was allowed to stand at room temperature for 12 hr. The precipitate that formed was collected on a filter. Recrystallization from methanol–ether gave 670 mg (63%) of 5-(dimethylcarbamoyloxy)-1,3-phenylenebis(trimethylammonium iodide) (IV).

For analysis, see Table IV.

Registry No.—Trimethylphenylammonium iodide, 98-04-4; II, 15925-97-0; IV, 23649-61-8.

Acknowledgment.—The authors are indebted to Mr. Ronald D. Deibel for his valuable assistance in the experimental work.

Studies of Benzonorbornene and Derivatives. II. The *ac*-Bromobenzonorbornenes and -dienes¹

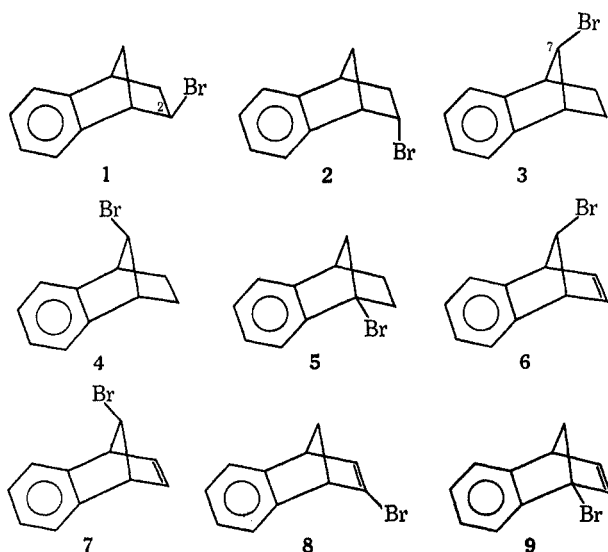
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Received July 14, 1969

The synthesis and properties of the nine *ac*-bromobenzonorbornenes and -dienes are described. Addition of hydrobromic acid to benzonorbornadiene (10) produced the *exo*-2 bromide 1. Its *endo* epimer 2 was prepared by diimide reduction of the vinylic bromide 8. The *anti*-7 bromide 3 was obtained most simply by hydrogenolysis of the *exo*-2,*anti*-7 dibromide 13, itself the addition product of 10 and bromine. Reaction of 1,2-dibromotetrachloroethane with 10 added bromine to afford the *trans*-2,3 dibromide 15 predominantly. Its rearrangement in hydrobromic acid produced some *exo*-2,*syn*-7 dibromide 17, which was treated with zinc in ethanol to form the *syn*-7 bromide 4. Application of the Hunsdiecker reaction on the corresponding acid afforded the bridgehead bromide 5. The olefinic *anti*-7 bromide 6 resulted from 13 upon dehydrobromination. The highly reactive olefinic *syn*-7 bromide 7 was difficult to obtain, finally being synthesized *via* the tosylhydrazone of the *syn*-7-bromo ketone 24. The vinylic bromide 8 was made from 15 by dehydrobromination. Treatment of 8 with hydrobromic acid produced some 1,*exo*-2 dibromide 27, which could be dehydrobrominated to the bridgehead olefinic bromide 9. The spectra of these compounds are tabulated and discussed briefly. Certain miscellaneous transformations in this system are mentioned as well.

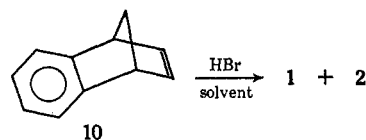
There are nine *ac*-bromobenzonorbornenes and -dienes as shown (1–9), numbered according to Bartlett



(1) (a) Paper I of this series: J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *J. Org. Chem.*, **32**, 893 (1967). (b) The present paper is taken from the dissertation of P. J. C., Loyola University of Chicago, 1969. (c) Certain portions have appeared in preliminary form: J. W. Wilt and P. J. Chenier, *J. Amer. Chem. Soc.*, **90**, 7366 (1968), and the Great Lakes Regional Meeting of the American Chemical Society, Milwaukee, Wis., June 1968, Abstracts of Papers, p 36. (d) For related work, cf. S. J. Cris-

and Giddings.³ Certain of them have been previously reported. Wiley and Barstow⁴ have reported the preparation of 1 and 2 as mixtures. An earlier paper of this series^{1a} has described the synthesis of 3 and 6. Bromides 6 and 7 have also been prepared by Cristol and coworkers.^{1d} The bridgehead bromide 5 was part of another study⁵ and it is included here for completeness. Likewise, a preliminary report^{1c} mentioning the sequence leading to 7 is here given in detail.

***exo*-2-Bromobenzonorbornene (1).**—Wiley and Barstow⁴ reported that the reaction of benzonorbornadiene (10) with hydrogen bromide in various solvents led to mixtures of 1 and the *endo* epimer 2. Independently,



tol and G. Nachtigall, *J. Org. Chem.*, **32**, 3727 (1967); S. J. Cristol and A. L. Noreen, *J. Amer. Chem. Soc.*, **91**, 3969 (1969).

(2) National Science Foundation Trainee, 1965–1968; University Fellow, 1968–1969.

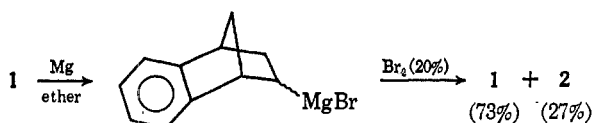
(3) P. D. Bartlett and W. P. Giddings, *ibid.*, **32**, 1240 (1960).

(4) G. A. Wiley and L. E. Barstow, Abstracts of the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, paper 5K; L. E. Barstow, *Tetrahedron Lett.*, 6309 (1968).

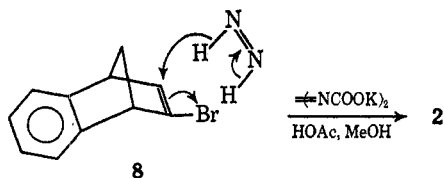
(5) H. F. Dabek, Jr., dissertation, Loyola University of Chicago, Chicago, Ill., 1969.

we found that the addition in ether led to both isomers also, 1 and 2 in an 86:14 ratio by nmr spectroscopy. When hydroquinone was added, only the *exo* epimer 1 resulted.

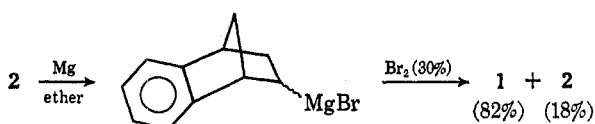
endo-2-Bromobenzonorbornene (2).—Treatment of the Grignard reagent from 1 with bromine produced both 2 and 1, but the preferred method was to reduce



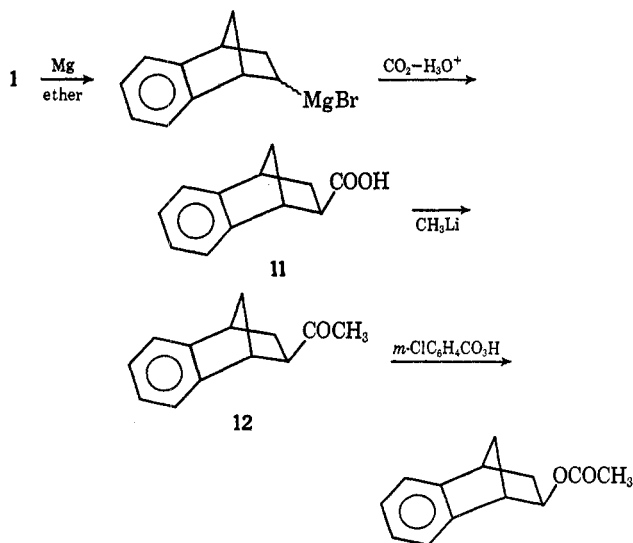
2-bromobenzonorbornadiene (8) with diimide (76% yield, no 1). *exo* addition of hydrogen from diimide was previously used^{1a} to prepare the *endo*-2 chloride.



Treatment of the Grignard reagent of 2 with bromine again give a mixture of 1 and 2. Although the low



yield of bromides from each of these reactions precludes discussion of the mechanistic implications, it would appear that electrophilic substitution at C-2 in this system shows an *exo* preference. In this connection, the reaction of carbon dioxide with the Grignard reagent from 1 is interesting. Only the *exo* acid 11 was isolated

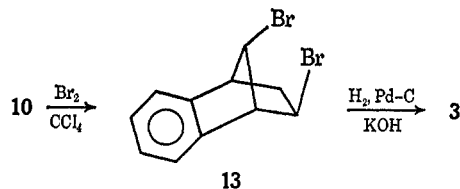


(17% yield). This acid could not be obtained from 1 with sodium cyanide in dimethyl sulfoxide or by hydrolysis of *exo*-2-trichloromethylbenzonorbornene.⁶

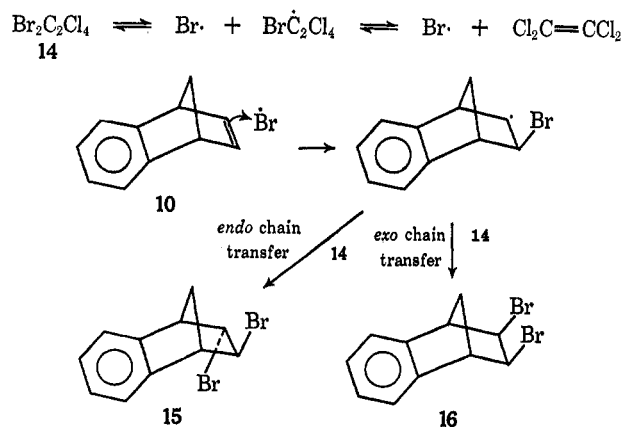
(6) L. H. Barstow and G. A. Wiley, *Tetrahedron Lett.*, 865 (1968). See also, E. Tobler and D. J. Foster, *J. Org. Chem.*, 29, 2839 (1964).

Its structure and stereochemistry were therefore established as shown. The final step⁷ led to only *exo*-2-benzonorbornenyl acetate, identical with that prepared from the known³ *exo*-2 alcohol. The isolation of only 11 reinforces the view that *exo* attack on the organometallic is favored.

anti-7-Bromobenzonorbornene (3).—A more convenient procedure than an earlier one^{1a} was to hydrogenolyze *exo*-2,anti-7-dibromobenzonorbornene (13).^{1a,d} The yield (36%) is poorer, but a difficult step is avoided.



syn-7-Bromobenzonorbornene (4).—It was clear from earlier experience that functionalization of the *syn*-7 position required a new approach to synthesis in this area. If a *trans* addition of the proper sort could be achieved with benzonorbornadiene (10), a subsequent Wagner–Meerwein shift could realize the goal. Because ionic additions invariably give some (and often mostly) rearranged adducts,^{1a,d} witness 13 above, a radical addition of bromine was required. We chose 1,2-dibromotetrachloroethane (14), an interesting bromine carrier first used by Huyser and DeMott,⁸ to brominate allylic positions. The pathways they suggested for the process led us to believe that in the absence of easily brominated allylic positions the reagent would add bromine to the double bond of an olefin. Indeed, quantitative addition of bromine to 10 via this reagent gave *trans*-2,3-dibromobenzonorbornene (15) and *exo,cis*-2,3-dibromobenzonorbornene (16) in a ratio of 89:11. No rearranged 13 was observed, the only other product being tetrachloroethylene.⁹

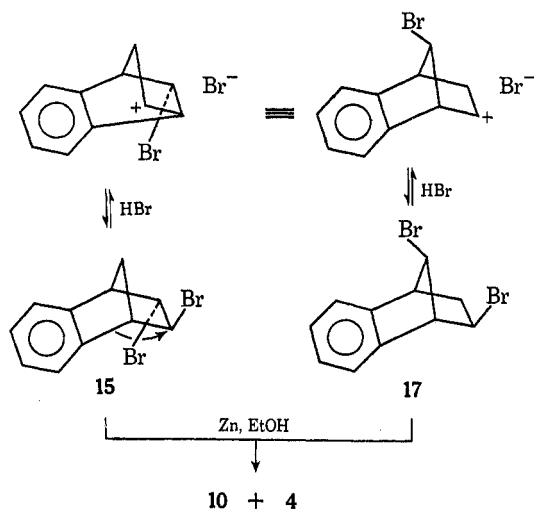


(7) This oxidation is stereospecific. Witness the formation of optically active *exo* acetate from active *exo*-norbornyl methyl ketone by J. A. Berson and S. Suzuki, *J. Amer. Chem. Soc.*, 81, 4088 (1959).

(8) E. S. Huyser and D. N. DeMott, *Chem. Ind. (London)*, 1954 (1963).

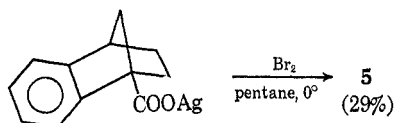
(9) This reaction should be valuable for skeletally retentive additions of bromine to those olefins where rearrangement under ionic conditions is serious, provided that allylic bromination is obviated structurally. For example, the reagent converts *anti*-7 bromide 6 into the *trans*-2,3,anti-7 tribromide (unpublished work) and norbornene into the *trans*-2,3 dibromide. The latter result was communicated to us by Professor A. J. Fry and co-workers (Wesleyan University) in a preprint of their forthcoming publication, for which we thank them.

Partial rearrangement of the unseparated **15** was then achieved with little loss (93% recovery) in refluxing hydrobromic acid.^{10,11}



The fate of the *exo,cis* isomer **16** in this reaction is unclear. Its Wagner–Meerwein rearrangement should lead to the *exo,anti* dibromide **13**. In any event, the simple expedient of zinc dust in ethanol converted the rearranged dibromide mixture into benzenorbornadiene (**10**) and the desired *syn*-7 bromide **4** (27%).

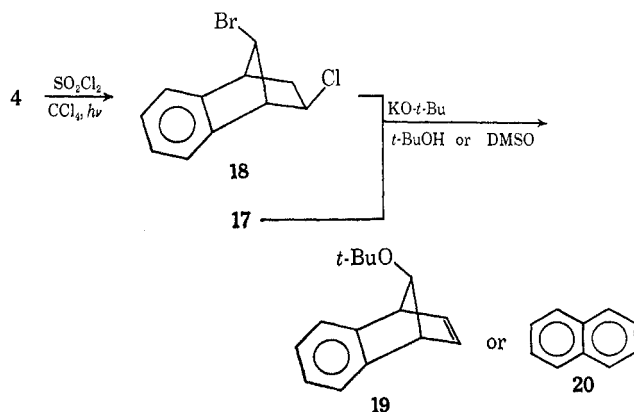
1-Bromobenzonorbornene (5).—This preparation involved Hunsdiecker degradation of the bridgehead acid as shown.¹² Use of carbon tetrachloride as solvent



gave considerable 1-chlorobenzonorbornene. The reaction will be discussed in detail elsewhere.

anti-7-Bromobenzonorbornadiene (6).—Its preparation and properties have been described.^{1a,d} The data for **6** in Tables I–III are included for completeness.

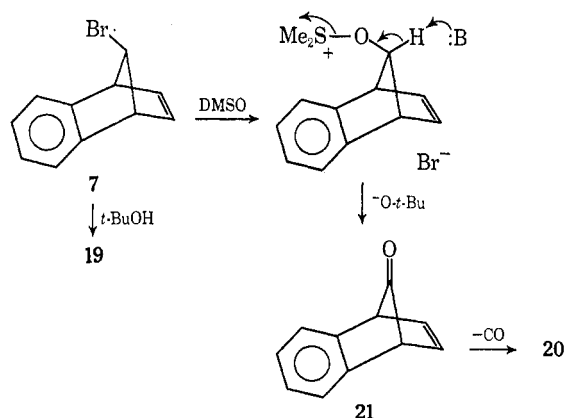
syn-7-Bromobenzonorbornadiene (7).—The synthesis of this elusive, highly reactive compound proved to be quite a challenge. Vigorous dehydrohalogenation of either *exo*-2-chloro-*syn*-7-bromobenzonorbornene (**18**) or the *exo,syn* dibromide **17** led to the ether **19** or to naphthalene (**20**) depending on the solvent used.



(10) Cf. H. Kwart and L. Kaplan, *J. Amer. Chem. Soc.*, **76**, 4072 (1954).

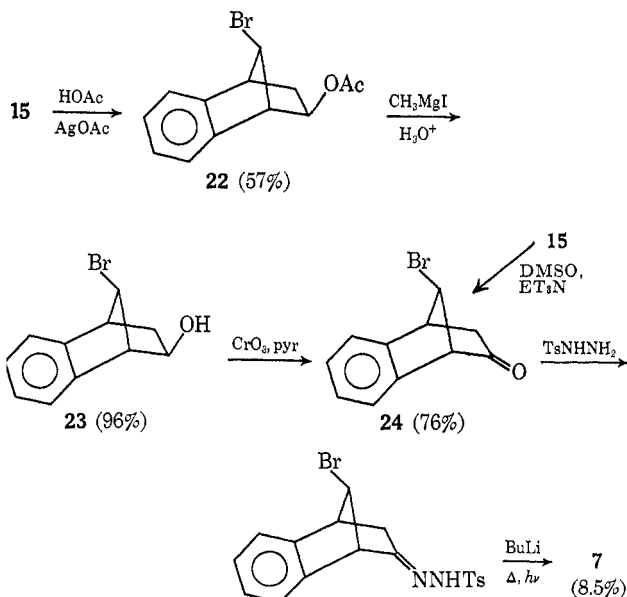
(11) In the depiction of the rearrangement below the intermediate ions have been shown as classical species (they are undoubtedly delocalized) and the attendant inversion of the bicyclic ring system with rearrangement has been omitted, both for reasons of simplicity in formulation.

Other, more mild, elimination attempts gave no reaction (see Experimental Section). Clearly the desired **7** was produced in some of the attempts, but its very high solvolytic reactivity allowed ether formation in *t*-butyl alcohol or oxidation¹³ in dimethyl sulfoxide. In this



latter solvent, the anticipated dienone **21** produced led to naphthalene.¹⁴

The successful synthesis of **7** proceeded from the *trans* dibromide **15**. Solvolytic rearrangement of **15** (with *ca.* 11% **16** also present) in acetic acid containing silver acetate readily afforded *exo*-2-acetoxy-*syn*-7-bromobenzonorbornene (**22**). Since alkaline hydrolysis of **22** was disappointing, the alcohol **23** was prepared by treatment of **22** with methyl Grignard reagent. *syn*-7-Bromobenzonorbornen-2-one (**24**) resulted upon oxidation of **23** with chromium trioxide in pyridine.



(12) The acid has been described: J. W. Wilt, C. A. Schneider, J. P. Berliner, and H. F. Dabek, Jr., *Tetrahedron Lett.*, 4073 (1966).

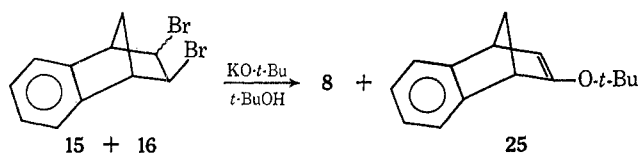
(13) N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. O. Larson, O. Levand, and W. M. Weaver, *J. Amer. Chem. Soc.*, **79**, 6562 (1957); H. R. Nace and J. J. Monagle, *J. Org. Chem.*, **24**, 1792 (1959).

(14) Ketone **21** has never been isolated. Its ready decarbonylation to naphthalene has been documented.⁵ The general instability of 7-norbornadienone and its analogs has been ascribed to an unfavorable interaction of the filled π orbitals of the olefinic and carbonyl systems by S. Yankelevich and B. Fuchs, *Tetrahedron Lett.*, 4945 (1967). The decarbonylation of such compounds to aromatic molecules and carbon monoxide is an orbitally allowed sigmasymmetric transformation; cf. D. M. Lemal and S. D. McGregor, *J. Amer. Chem. Soc.*, **88**, 1335 (1966). Stabilization of 7-norbornadienone as its iron tricarbonyl has recently been reported by J. M. Landesberg and J. Sieczkowski *ibid.*, **90**, 1655 (1968).

The ketone could also be prepared directly from dibromide **15** with silver fluoroborate and triethylamine in dimethyl sulfoxide.¹⁵ However, this direct route was not extensively explored. After several other unsuccessful procedures, pure *syn*-**7** bromide was obtained by irradiation of the lithium tosylhydrazone salt of **24**, rotating as a thin film.¹⁶

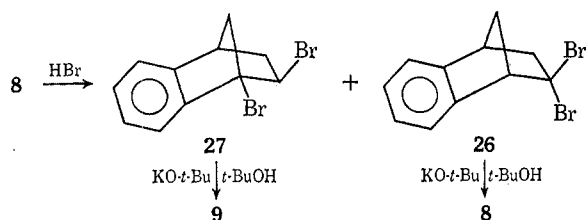
When **7** was heated in dimethyl sulfoxide with potassium *t*-butoxide, it yielded naphthalene (**20**), implicating the presence of **7** in the earlier attempts at its synthesis described above.

2-Bromobenzonorbornadiene (8).—Dehydrobromination of the mixture of *trans* dibromide **15** and the *exo,cis* dibromide **16** readily produced **8** (52%), along with a small amount (2%) of the vinyl ether **25**. The vinyl



ether was removed by hydrolysis to 2-benzonorbornenone with 15% sulfuric acid. Bromide **8** could also be converted into this ketone in concentrated sulfuric acid.

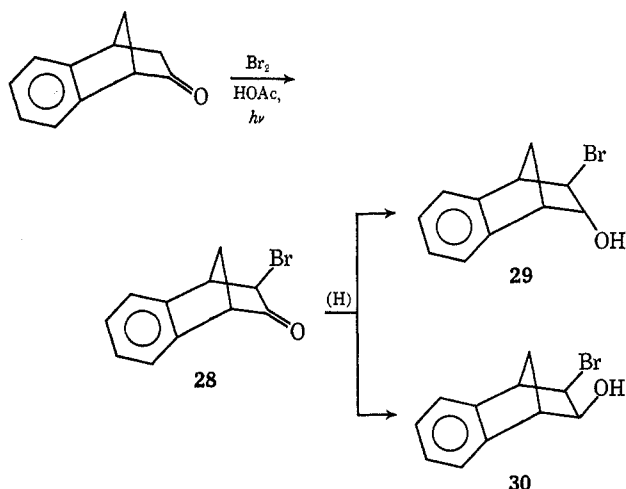
1-Bromobenzonorbornadiene (9).—Addition of hydrobromic acid to the vinyl bromide **8** was attended by partial Wagner–Meerwein rearrangement to the desired 1,*exo*-2-dibromobenzonorbornene (**27**)¹⁷ (72% yield, **27** and **26** in a 60:40 ratio by nmr spectroscopy).



Dehydrobromination of the mixture then produced **8** (38%) and the bridgehead isomer **9** (54%). Separation was simple by chromatography.

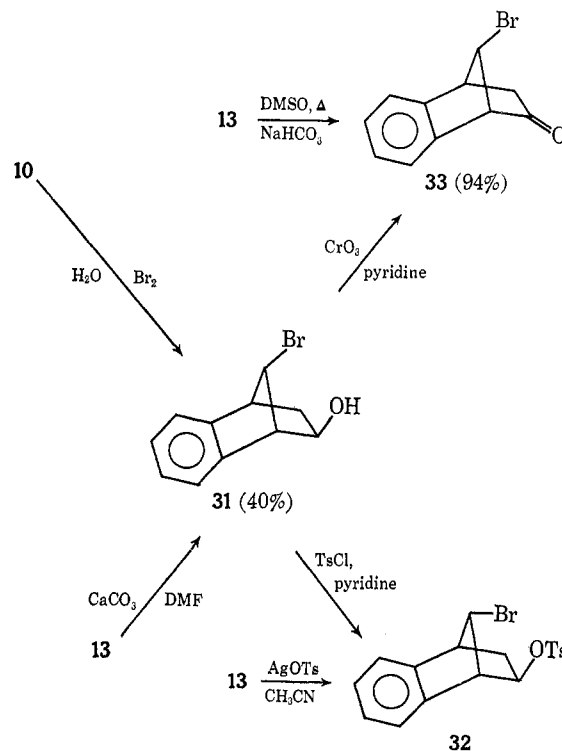
Miscellaneous.—The synthesis of bromo ketones **28** and **33** and a few of their transformations are mentioned briefly here.

2-Benzonorbornenone was brominated readily to the *exo*-3-bromo ketone **28**. No evidence for any *endo* epimer was found.¹⁸ Reduction to the bromohydrins **29** and **30** was achieved with three different reagents. Diborane in tetrahydrofuran gave a mixture of **29** and **30** in the ratio of 80:20, respectively, while



sodium borohydride in methanol–water and lithium aluminum hydride in ether gave ratios of 45:55 and 37:63. It appears that an *exo*-3 bromine provides less steric hindrance than an *anti*-7 bromine because ketone **33** is reported to yield only *exo* alcohol (*endo* attack) with lithium aluminum hydride.¹⁹ All attempts to rearrange **29** to a *syn*-**7** alcohol derivative (see the conversion of **15** into **17**) were fruitless.

Conversion of olefin **10** into the bromohydrin **31** was accomplished with bromine water. Dibromide **13** also gave **31** upon solvolysis, and its tosylate upon treatment with silver tosylate in acetonitrile. The identity of this tosylate **32** with that from **31** confirmed the reaction pathway. The *anti*-7-bromo ketone **33** was produced from **31** by oxidation or from **13** by treatment with base in dimethyl sulfoxide.¹³ Reac-



(15) Cf. D. M. Lemal and A. J. Fry, *J. Org. Chem.*, **29**, 1673 (1964).

(16) (a) This "dry" method for carbenoid decomposition is similar to that described by G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *J. Amer. Chem. Soc.*, **87**, 935 (1965). See also, R. R. Sauers and R. J. Kiesel, *ibid.*, **89**, 4695 (1967). (b) S. J. Cristol and A. L. Noreen (University of Colorado) have independently synthesized bromide **7** from the corresponding acetate. We thank Professor Cristol for a preprint of their work.¹⁴

(17) For similar reactions, see J. W. Wilt, C. F. Parsons, C. A. Schneider, D. G. Schultenover, and W. J. Wagner, *J. Org. Chem.*, **33**, 694 (1968), and A. J. Fry and W. B. Farnham, *Tetrahedron Lett.*, 3345 (1968).

(18) Only *exo* bromination is observed with 2-norbornanone also. Cf. H. Krieger, *Suomen Kemistilehti*, **31B**, 320 (1958). As the enols are the intermediates, these brominations again show the *exo* preference for addition reactions in these systems.

tion of the tosylhydrazone of **33** with butyllithium²⁰ failed to produce the *anti*-7 bromide **6**, as did attempts

(19) R. Caple, F. M. Hsu, and C. S. Ilenda, *J. Org. Chem.*, **33**, 4111 (1968).

(20) R. H. Shapiro and M. J. Heath, *J. Amer. Chem. Soc.*, **89**, 5734 (1967); G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967).

to invert **33** to *syn*-7 derivatives using lithium chloride in *N,N*-dimethylformamide or silver acetate in acetic acid. These last reactions do invert other substituted norbornanones.²¹

Tables.—Table I is self-explanatory. As for Table II, the nmr spectra of substituted benzonorbornenes

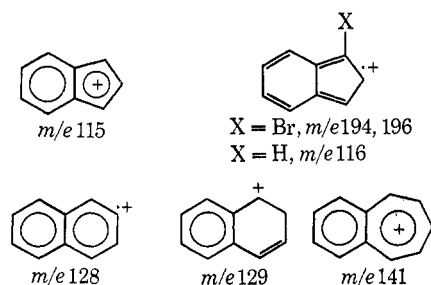
TABLE I
PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR BROMIDES 1-9

	Mp or bp (mm), °C	Found, %—	
		C	H
Bromobenzonorbornene			
<i>exo</i> -2- (1) ^a	76.5-77 (0.1)	59.25 ^b	5.27
<i>endo</i> -2- (2) ^c	92-94 (1)	59.70 ^d	5.07
<i>anti</i> -7- (3) ^e	33-34	59.22	4.97
<i>syn</i> -7- (4)	122.5-123	59.26	4.97
1- (5) ^f	68-70 (0.1)	59.42	5.13
Bromobenzonorbornadiene			
<i>anti</i> -7- (6) ^e	53-54	59.64 ^g	4.32
<i>syn</i> -7- (7)	61.1-61.7	59.87	4.29
2- (8) ^h	80.5-81 (0.9)	59.75	4.10
1- (9)	<i>i</i>	59.95	4.27

^a n_D^{15} 1.5950, d_4^{25} 1.405. ^b Calcd for C₁₁H₁₁Br (1-5): C, 59.22; H, 4.97. ^c n_D^{15} 1.5927, d_4^{25} 1.437. ^d The bromide contained by glpc 1.45% *endo*-2-*t*-butoxybenzonorbornene. Calcd for this mixture: C, 59.55; H, 5.04. ^e Data taken from ref 1a. ^f Data taken from ref 5. ^g Calcd for C₁₁H₉Br (6-9): C, 59.75; H, 4.10. ^h n_D^{15} 1.5958, d_4^{25} 1.444. ⁱ Collected as an oil by glpc.

have been discussed at length in the literature.^{1a,d} No further elaboration is given here with the exception that certain features of the 7-proton resonances might be mentioned. Cristol and Nachtigall reported^{1d} that the 7-chlorobenzonorbornadienes showed the *syn*-7 proton (δ 4.15) in the *anti*-7 chloride upfield from the *anti*-7 proton (δ 4.42) in the *syn*-7 chloride. Likewise, we find the *syn*-7 proton in **6** (δ 4.35) is upfield from the *anti*-7 proton in **7** (δ 4.64). Also, the *syn*-7 proton in **3** (δ 3.95) is upfield from the *anti*-7 proton in **4** (δ 4.12). These chemical shifts conform to the long-held view that protons *syn* to an aromatic ring resonate upfield relative to their epimeric *anti* protons.²²

The general pattern of the mass spectra for some selected bromides (Table III) agrees with that of similar compounds reported by Cristol and Nachtigall.^{1d} Some major fragments are shown below. The *m/e*



value 143 is a P — Br fragment while the *m/e* values of 220, 222, and 224 are the parent molecular ions for the bromides **6**, **7**, and **2**, **4**, and **5**, respectively.

(21) J. T. Lumb and G. H. Whitham, *Chem. Commun.*, 400 (1966); P. G. Gassman, J. M. Hornback, and J. L. Marshall, Abstracts of the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, paper 93 (*Organic*). See also H. Krieger,¹⁹ and E. Tobler, D. E. Battin, and D. J. Foster, *J. Org. Chem.*, **29**, 2834 (1964).

(22) The prediction of chemical shifts for bridge protons in norbornene and its derivatives is a complicated matter. Cf. B. Franzus, W. C. Baird, Jr., N. F. Chamberlain, T. Hines, and E. I. Snyder, *J. Amer. Chem. Soc.*, **90**, 3721 (1968), and A. P. Marchand and J. E. Rose, *ibid.*, **99**, 3724 (1968).

The base peak *m/e* 115 or 116 for **2**, **4**, and **5** reflects a retro Diels-Alder fragmentation, which eliminates CH₂CHBr in **2** but CH₂CH₂ and Br in **4** and **5**. Only the bridgehead bromide **5** shows a bromine-containing fragment, *m/e* 194 and 196, probably as a consequence of the difficult formation of a bridgehead cation by bromine loss (*m/e* 143). Note the difference in this respect of bromide **4**. Presumably a hydrogen shift in the fragment *m/e* 194 and 196 and bromine loss then occur to afford the base peak *m/e* 115 from **5**.

The base peak *m/e* 141 for bromides **6** and **7** is benztropylium ion. It is interesting to note the great difference between **6** and **7** in the percentages of the naphthalene radical-cation fragment (*m/e* 128). The analogous chlorides to **6** and **7** show only slight fragmentation of this sort, though again the *syn*-7 chloride shows more.^{1d}

Experimental Section

Melting points and boiling points are uncorrected for stem exposure. The former were taken on a Fisher-Johns block. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill. For nmr spectra, see Table II. Infrared (ir) spectra were obtained on a Beckman IR-5A spectrophotometer. Only strong or structurally significant absorptions are given (in μ). Italicized absorptions were useful in contrasting isomers with one another. Ultraviolet spectra, given as λ_{max} , were taken on a Unicam SP 800 instrument. For mass spectra, see Table III. Gas-liquid partition chromatography (glpc) was performed on a Wilkens (Varian) Aerograph Model A-90P with helium gas carrier.

exo-2-Bromobenzonorbornene (1).—Benzonorbornadiene (10, 13 g, 0.091 mol) was mixed with hydrobromic acid (48%, 70 ml) in a pressure bottle, sealed, and heated at 60-70° in a water bath with shaking for 3 hr. After 3 hr of further shaking, water was added and the mixture was extracted with ether. The ether extracts were made neutral, dried, and distilled. Bromide **1** was collected as an oil [17.5 g, 86%, bp 95-100° (1.0-1.3 mm)]. The redistilled material had the properties given in the tables and ir λ_{max} 6.87, 6.96, 8.11, 8.33, 10.31, 10.75, and 13.30 μ . The bromide decomposed on both Reoplex 400 (polypropylene glycol adipate) and SE-30 columns at 187-190°, but no *endo* isomer was ever observed. It gave an immediate reaction with alcoholic silver nitrate.

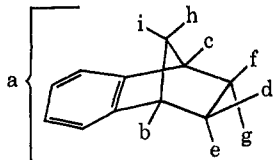
The stirred addition of dry hydrogen bromide to **10** (8.6 g, 0.06 mol) was carried out in anhydrous ether at 0°. The saturated solution was allowed to stand at 25° overnight. Isolation of the product as above yielded bromides **1** and **2** [7.0 g, 52%, bp 96-99° (1.2 mm), 86% **1** and 14% **2** by nmr]. Addition of hydroquinone (0.2 g) to the ether used in the above reaction on a one-quarter scale gave only *exo* bromide **1** (81% crude yield).

endo-2-Bromobenzonorbornene (2).—2-Bromobenzonorbornadiene (**8**, see later text, 5.0 g, 0.023 mol) was dissolved in methanol (20 ml) and to it was added potassium azodicarboxylate²³ (5.24 g, 0.027 mol). The solution was stirred while glacial acetic (3.68 g, 0.061 mol) in additional methanol (20 ml) was added dropwise over a period of 1.5 hr, followed by further stirring for 1.5 hr. Water was added and the mixture extracted with hexane. The extracts were washed, dried, and freed of solvent. The remaining oil was distilled to give, after a small forecut of benzonorbornene and **8**, the *endo* bromide **2** [3.85 g, 76%, bp 92-98° (1.2 mm)]. Redistilled material possessed the properties in the tables and ir λ_{max} 6.87, 6.95, 7.80, 8.28, 8.50, 11.58, and 13.2-13.4 μ . The bromide showed trace contamination on Reoplex 400 at 197° but no decomposition and no *exo* bromide. The contaminant gave a faint cloudiness with alcoholic silver nitrate after 15-30 sec at 25° and a definite reaction on warming.

Reaction of the Grignard Reagents of 1 and 2 with Bromine.—Bromide **1** (3.02 g, 14 mmol) was slowly converted into its Gri-

(23) J. Thiele, *Justus Liebigs Ann. Chem.*, **271**, 127 (1892). The crude salt was used as purification was unprofitable.

(24) Bromide **8**, as prepared in this work, contains a slight amount of 2-butoxybenzonorbornadiene. Diimide converts this latter substance into the *endo*-2 ether.

TABLE II
 NMR SPECTRA OF VARIOUS BENZONORBORNENES^a


	Proton resonance, δ								
	b	c	d	e	f	g	h	i	
Bromide									
1 ^b	3.5 (m)	3.2 (m)	Br	3.75 (m)	1.6-2.5 (m)				
2	3.4 (m)	3.25 (m)	4.45 (dt)	Br	2.5 (ddd)	1.3 (dt)	1.55 (dt)	1.87 (ddt)	
3 ^c	3.37 (dd)	3.37 (dd)	2.83 (m)	1.23 (m)	2.33 (m)	1.23 (m)	Br	3.95 (p)	
4	3.43 (dd)	3.43 (dd)	2.0 (m)	1.2 (m)	2.0 (m)	1.2 (m)	4.12 (t)	Br	
5 ^d	Br								
6 ^e	4.05 (dd)	4.05 (dd)	Vinyl, 6.7 (dt)			Br		4.35 (m)	
7 ^e	3.99 (q)	3.99 (q)	Vinyl, 6.85 (t)			4.64 (t)	Br		
8	3.75 (m)	3.75 (m)	Vinyl, 6.63 (dt?)			2.49 (dt)	2.18 (m)		
9	Br	3.8 (m)	Vinyl, 6.73 (d)			2.83 (dd)	2.62 (m)		
Dihalide									
13 ^c	3.85 (d)	3.49 (dd)	Br	3.7 (ddd)	2.85 (dt)	2.15 (dd)	Br	4.1 (m)	
15	3.45 (m)	3.45 (m)	Br	3.76 (t)	4.61 (t)	Br	2.33 (dt)	2.03 (m)	
16	3.45 (m)	3.45 (m)	Br	4.01 (d)	Br	4.01 (d)	2.33 (dt)	2.03 (m)	
17	3.65 (m)	3.65 (m)	Br	2.3 (cm)	2.2 (cm)	1.2 (m)	4.12 (t)	Br	
18	3.55 (m)	3.55 (m)	Cl	3.89 (dd)	2.2 (m)	2.2 (m)	4.77 (t)	Br	
Bromo ketone									
24 ^e	3.85 (m)	3.85 (m)	CO		2.55 (dd)	2.2 (d)	4.74 (t)	Br	
28	3.7 (m)	3.7 (m)	CO		Br	3.94 (d)	2.80 (dt)	2.45 (m)	
33	3.7 (m)	3.7 (m)	CO		2.75 (dd)	1.82 (dd)	Br	4.4 (m)	
Bromohydrin									
23 ^e	3.4 (m)	3.4 (m)	OH ^f	3.97 (dd)	1.85 (m)	1.85 (m)	4.76 (t)	Br	
29	3.3 (m)	3.3 (m)	4.61 (dd)	OH ^f	Br	3.3 (m)	2.35 (dt)	1.95 (m)	
30	3.3 (m)	3.3 (m)	OH ^f	3.6 (dd)	Br	4.08 (dd)	2.35 (dt)	1.95 (m)	
31	3.5 (m)	3.5 (m)	OH ^f	3.8 (m)	2.05 (m)	2.05 (m)	Br	4.15 (m)	
Miscellaneous									
11 ^e	3.65 (m)	3.65 (m)	COOH ^g	1.9 (cm)					
12	3.45 (m)	3.45 (m)	COCH ₃ ^h	2.45 (m)	1.75 (cm)				
22	3.5 (m)	3.5 (m)	OCOCH ₃ ⁱ	4.68 (ddd)	1.95 (m)		4.51 (t)	Br	
32 ^e	3.65 (m)	3.65 (m)	OTs ^j	4.58 (ddd)	2.50 (dt)	1.90 (ddd)	Br	4.05 (m)	

^a The spectra were determined on a Varian A-60A spectrometer. The solutions were ca. 15% solutions in carbon tetrachloride with 1% TMS (δ 0.0) added unless otherwise indicated. The δ values for multiplets are the centers. The usual abbreviations for splittings are used; cm is a broad, complex multiplet. The aromatic protons a were found in the range of δ 6.8-7.5 and are not given. The integrations for all resonances were within 10% of the proper values. ^b Neat sample. ^c From ref 1a. ^d From ref 5. ^e CDCl₃ solvent (1% TMS). ^f OH resonance variable. ^g COOH, δ 11.7 (s). ^h COCH₃, δ 2.17 (s). ⁱ OCOCH₃, δ 2.03 (s). ^j OTs (CH₃), δ 2.45 (s).

TABLE III

PARTIAL MASS SPECTRA OF SELECTED BROMIDES^a

Bromide	Fragment ions, <i>m/e</i> , % base peak										
	115	116	128	129	141	143	194	196	220 ^b	222 ^b	224 ^b
2	37	100 ^c	18	9	10	22				7	7
4	100 ^c	12	31	28		94				13	13
5	100 ^c	11	20		10	41	16	15		10	9
6	36		4		100 ^c				4	4	
7 ^d			96		100 ^c				25	22	

^a All spectra except that of 7 were determined on a Perkin-Elmer Model 270 mass spectrometer at 70 eV with the samples introduced directly upon elution from an SE-30 glpc column at ca. 160°. ^b Parent molecular ions. ^c Base peak. ^d This spectrum was obtained on a Bendix time-of-flight mass spectrometer, Model 12-107, at 70 eV with the bromide introduced at ambient temperature from a Kel-F vacuum line. The spectrum was scanned from 125 to 250 amu only.

gnard reagent in ether in the usual way, though heating was required. Dry bromine (2.16 g, 14 mmol) was then added dropwise at 0°. After 30 min, the excess bromine was destroyed. Work-up afforded bromides 1 and 2 (20%, nmr analysis indicated a 73:27 ratio of 1 and 2). The same reaction applied in scale to bromide 2 (1.51 g, 7 mmol) gave ca. 30% 1 and 2 in the ratio (by nmr) of 82:18. Again Grignard formation was slow and difficult, even with heating.

Reaction of the Grignard Reagent of 1 with Carbon Dioxide. Benzonorbornene-*exo*-2-carboxylic Acid (11).—Under nitrogen, bromide 1 (10.05 g, 0.045 mol) and ethylene bromide (8.46 g, 0.045 mol) were added in dry ether to magnesium (0.09 g-atom) in further ether. Grignard formation was complete in 1 hr. The solution was then forced into a saturated solution of carbon dioxide in ether at -5°. After 30 min, Dry Ice chunks were added. Sulfuric acid (10%) was next slowly added, followed by water. The ether layer was separated and treated with sodium hydroxide solution (10%). The alkaline material was then acidified with 1:1 hydrochloric acid to precipitate acid 11 (1.46 g, 17%, mp 108-11°). Recrystallization from petroleum ether (bp 30-60°) gave the analytical sample: mp 112-113.5°; nmr in Table II; λ_{KBr} 3.0-4.0, 5.93, 8.10, 8.24, and 13.31 μ .
 Anal. Calcd for C₁₂H₂₂O₂: C, 76.57; H, 6.43. Found: C, 76.76; H, 6.46.

Another preparation that omitted the ethylene bromide and the nitrogen gave only 5% 11. Some benzonorbornene and *exo*-benzonorbornenol (air oxidation) were also detected, along with a solid, probably a dimeric coupling product,²⁵ which was not studied further. The *exo* nature of 11 was demonstrated by transformations described later.

***anti*-7-Bromobenzonorbornene (3).**—This more convenient synthesis was used. *exo*-2,*anti*-7-Dibromobenzonorbornene^{1a} (13, 13.6 g, 0.045 mol) was dissolved in warm 95% alcohol (250 ml). To this was added potassium hydroxide (2.52 g) in a little alcohol

(25) Bromide 3 coupled to a dimer under similar conditions.^{1a}

and palladium on charcoal (5%, 0.35 g). The mixture was hydrogenolyzed in a Parr apparatus for 4 hr at 30 psig (ambient temperature). The catalyst was filtered away and the solvent was evaporated. Pentane and water were added and the pentane layer was separated, dried, and distilled free of solvent. After a small forecut of benzonorbornene, bromide **3** was obtained [3.65 g, 36%, bp 93–135° (overheated) (1 mm), lit.^{1a} bp 107–108° (2.5 mm)]. The material solidified on standing, mp 30–35°, lit.^{1a} mp 33–34°. Its spectra agreed with those reported. It was homogeneous on an SE-30 column at 172°.

syn-7-Bromobenzonorbornene (4).—Olefin **10** (19.5 g, 0.137 mol) and 1,2-dibromotetrachloroethane²⁶ (22.1 g, 0.069 mol) were dissolved in carbon tetrachloride (50 ml) and irradiated with a General Electric 275-W sun lamp under a reflux condenser. The solution became yellow, then red. After 1.75 hr the solvent and tetrachloroethylene (ir λ 11.0 μ) were removed on a rotary evaporator and the residue was distilled to 100° (1 mm) to remove excess **10** (75% recovery of excess). The remaining material was taken up in ether and decolorized and the solvent was removed. The oily, pale red residue (20.6 g, 100%) consisted of 89% *trans*-**2,3-dibromobenzonorbornene (15)** and 11% *exo,cis*-**2,3-dibromobenzonorbornene (16)** by nmr: ir λ^{neat} 6.84, 7.84, 8.55, 13.1–13.3, and 14.09 μ . No *exo-2,anti-7* dibromide **13** was observed. All attempts to purify the material were unsuccessful, although it could be made colorless by repeated treatments with decolorizing carbon.

No dibromides were observed upon attempted bromination of mixtures of **1** and **2** using either a 22-W light bulb or a low pressure uv apparatus. Similarly, an attempt to rearrange dibromide **13** to either **15** and/or **16** with aluminum bromide in carbon disulfide (25°, 2 weeks) failed to change the material.

The mixed dibromides **15** and **16** (51.5 g) were then refluxed with stirring in hydrobromic acid (48%, 200 ml) for 8 hr. The solution was diluted with water and extracted with hexane. The hexane extracts were washed, dried, and evaporated to yield an oil (48 g, 93%). Via nmr analysis this oil contained 57% *exo-2,syn-7-dibromobenzonorbornene (17)* and 43% starting **15**. What happened to **16** was not determined. At reflux times of 4 and 65 hr, this same ratio was found, whereas only a 1-hr reflux gave a product, containing less **17** (44%). For the nmr, see Table II; the ir spectrum consists of λ^{neat} 8.33, 10.56, and 12.89 μ (for **17**). The mixture of **15** and **16** was also treated with aluminum bromide in carbon disulfide, but ca. 67% of the material was unchanged after 12 hr at 25° and dark insoluble material was formed as well.

To a warm slurry of fresh zinc dust (23 g, 0.352 g-atom) in ethanol (absolute, 200 ml) was added the above mixture of dibromides **17** and **15** (30.8 g, 0.102 mol). After the material was heated under reflux for 4 hr, water was added to the cooled mixture, followed by ether. The ether extracts were washed well, dried, and distilled to afford olefin **10** [5.3 g, 36%, bp up to 80° (1.2 mm)]. The residual *syn-7* bromide (6.2 g, 27%) solidified on cooling and scratching. Recrystallization from a petroleum ether (bp 30–60°) and ether mixture gave white platelets with the properties given in the tables and ir λ^{KBr} 8.20, 9.00, 10.2, 11.67, 12.3, and 13.0–13.2 μ ; bp 96° (0.9 mm); homogeneous on a Reoplex 400 column at 190°. The bromide gave only a faint cloud with alcoholic silver nitrate upon boiling 2 min.

1-Bromobenzonorbornene (5).—The bromide was prepared in another study⁵ by reaction of silver benzonorbornene-1-carboxylate in pure, dry petroleum ether (bp 30–60°) with bromine under nitrogen. Bromide **5** was obtained in 29% yield along with a substantial amount of ester (?) material. The analytical sample was obtained by glpc from Reoplex 400 at 188° (see the tables): ir λ^{neat} 6.90, 7.80, 10.10, and 13.3 μ . Use of carbon tetrachloride as solvent gave a mixture of **5** and the 1-chloro analog.

anti-7-Bromobenzonorbornadiene (6).—The compound was available from an earlier study.^{1a}

syn-7-Bromobenzonorbornadiene (7).—Silver oxide (22.8 g, 0.098 mol) and acetic anhydride (10 g, 0.098 mol) were added to glacial acetic acid (200 ml) and the mixture (warm) was shaken until the solid was white (ca. 15 min). The mixture of dibromides **15** and **16** (58.9 g, 0.195 mol) was added and the material then was refluxed with stirring for 13 hr. The silver bromide was filtered off and washed well with ether. Water was added to the filtrate, followed by ether. The ether extracts were combined

with the silver bromide washings, made neutral, dried, and evaporated. The residual solid was taken up in hot hexane, decolorized, and chilled for 36 hr to produce *exo-2-acetoxy-syn-7-bromobenzonorbornene (22)*, 31.6 g, 57%, mp 86–95°. Recrystallization was effected from petroleum ether (bp 30–60°) to give **22** as a white, microcrystalline solid: mp 101–102°; for the nmr, see Table II; ir λ^{KBr} 5.79, 7.30, 8.0–8.2, 9.68, and 9.86 μ .

Anal. Calcd for C₁₃H₁₄O₂Br: C, 55.53; H, 4.66. Found: C, 55.70; H, 4.63.

The bromoacetate **22** (29.1 g, 0.103 mol, once recrystallized) in dry ether (200 ml) was added in portions to methylmagnesium iodide (0.309 mol) in dry ether (430 ml) over a 30-min period at –5°. The material was refluxed for 2 hr, cooled, and treated with sulfuric acid (10%) cautiously over a 15-min period, followed by water. The layers were separated and the ether phase was combined with some washes of the aqueous phase. The ether was then removed from the dried extracts to yield *syn-7-bromo-exo-2-benzonorbornenol (23)*, 23.7 g, 96% which was recrystallized from petroleum ether (bp 30–60°) and other mixtures as a white solid: mp 126–128° subl; for the nmr, see Table II; ir λ^{KBr} 2.97, 7.25, 8.20, 8.46, 9.59, 9.9–10.2, 10.79, 11.09, 13.00 and 13.37 μ .

Anal. Calcd for C₁₁H₁₁OBr: C, 55.25; H, 4.64. Found: C, 55.28; H, 4.87.

Attempted saponification of **22** with potassium hydroxide in aqueous methanol produced dark red, nondescript material which could not be profitably purified.

Chromium trioxide (29.1 g) was carefully added with stirring to pyridine (290 ml) at 15°. To this suspension was added crude alcohol **23** (9.7 g, 0.041 mol) in further pyridine (10 ml). The material was stirred at 25° for 55 hr, diluted with water, and extracted with ether. The extracts were made neutral, rinsed, and dried. Removal of the ether left *syn-7-bromobenzonorbornene-2-one (24)*, 7.3 g, 76%. Upon recrystallization from hexane-ether, the material formed white flakes: mp 133.5–135°; for the nmr, see Table II; ir λ^{KBr} 5.77, 7.83, 9.22, 9.36, 11.06, 12.44, 12.95, and 13.36 μ .

Anal. Calcd for C₁₁H₉OBr: C, 55.72; H, 3.83. Found: C, 55.76; H, 4.11.

The **2,4-dinitrophenylhydrazone** was recrystallized from ethyl acetate-ethanol as a light orange solid, mp 177.5–180.5°, uv λ^{max} (EtOAc) 359 m μ (ϵ 26,000).²⁷

Anal. Calcd for C₁₇H₁₃O₄BrN₄: N, 13.43. Found: N, 13.54.

Bromo ketone **24** was inert to boiling silver nitrate. Attempted formation of **24** by Oppenauer oxidation of **23** (quinone, aluminum *t*-butoxide in benzene) gave only traces of neutral products. Use of chromium trioxide in pyridine for 25 hr above gave a 6:1 ratio of **24** to **23**. Reaction of dibromide **15** (20 mmol) with silver fluoroborate in dimethyl sulfoxide followed by triethylamine²¹ gave 0.6 g (13%) of **24**.

The tosylhydrazone of **24** was made in the usual fashion from equimolar proportions of **24** and tosylhydrazine in methanol containing a few drops of glacial acetic acid. After a reflux period of 1.5 hr, the material stood overnight. The precipitated solid (10.61 g, 76%) was recrystallized from ethyl acetate to yield a white, crystalline solid, mp 221.5–222.5° dec; ir λ^{KBr} 7.52 and 8.61 μ .

Anal. Calcd for C₁₈H₁₇O₂BrN₂S: C, 53.34; H, 4.23. Found: C, 53.48; H, 4.24.

Finely crushed tosylhydrazone (crude, 4.05 g, 10 mmol) was converted into the lithium salt by treatment in suspension with *n*-butyllithium in hexane (1.6 M, 12.5 ml, 20 mmol), under nitrogen with rapid stirring for 45 min. Water was added cautiously. The aqueous layer was separated and the water was removed by rotary evaporation at ca. 60° under vacuum in such a way as to deposit the salt as a thin film on the walls of the flask. Proper filming is important. The flask was then placed 4 cm from a GE 275-W sun lamp and rotated under vacuum (5–10 mm) with the condensing flask of the rotary evaporator cooled in Dry Ice and acetone and aligned in a horizontal fashion. As the reaction proceeded, the lamp was moved right up to the flask. The *syn-7* bromide **7** collected as a colorless mass of crystals at the condenser joint (0.143–0.187 g, 6.5–8.5%, mp 50–58°). It was

(26) We thank the Dow Chemical Co., Midland, Mich., for samples of this material early in the work. We later made it by reaction of tetrachloroethylene with bromine (275-W sun lamp, white solid, dec pt ca. 100°).

(27) The 2,4-dinitrophenylhydrazone of benzonorbornene-2-one has λ^{max} (EtOH) 361 m μ (ϵ 43,600).⁸ While all the bromo ketones studied here had essentially this same λ^{max} for their 2,4-dinitrophenylhydrazone derivatives, none possessed the molar absorptivity reported for the parent ketone.

readily recrystallized from petroleum ether (bp 30–60°) as white clusters, mp 61.1–61.7°, with the properties given in the tables and $\text{ir } \lambda^{\text{KBr}}$ 3.33, 7.78, 8.20, 11.78, 12.81, 13.28, and 14.50 μ .

The bromide gave an immediate test with alcoholic silver nitrate. It decomposed on an SE-30 column at 180°. Use of tetrahydrofuran instead of only hexane in the formation of the tosylhydrazone salt gave material that produced only some naphthalene in the decomposition described.

2-Bromobenzonorbornadiene (8).—The dibromides 15 and 16 (38 g, 0.13 mol) were added to potassium *t*-butoxide (0.15 mol, freshly made) in *t*-butyl alcohol (250 ml). The solution was stirred under reflux for 22 hr. Most of the solvent was evaporated and water was added, followed by ether. The ether extracts were washed, dried, and freed of ether. Distillation then gave vinyl bromide 8 [14.5 g, 52%, bp 80–100°, redistilled at 80.5–81° (0.9 mm)] as a yellow oil. Although the oil was homogeneous on Reoplex 400 at 190°, nmr analysis showed that 2.3% 2-*t*-butoxybenzenorbornadiene was present (δ^{CCl_4} 1.13, s, *t*-Bu). Therefore the crude oil (5 g) in hexane (15 ml) was shaken with sulfuric acid (15%, 50 ml) in a pressure bottle at ambient temperature for 2 hr. Processed material now showed 1.4% ether present. Repetition of the above finally produced analytically pure bromide: see the tables; $\text{ir } \lambda^{\text{neat}}$ 3.31, 6.39, 6.90, 7.87, 10.05, 11.9, and 13.2–13.4 μ .

The oil darkens on standing. It readily developed a precipitate of silver bromide with alcoholic silver nitrate. We ascribe this uncommon reactivity for a vinyl halide to its highly strained double bond. Presumably addition of solvent along with electrophilic assistance in bromide ion loss by silver ion occurs.²⁸ When bromide 8 was hydrolyzed in concentrated sulfuric acid (0°, 15 min), the processed material yielded an oil with an ir spectrum very similar to that of benzenorbornene-2-one. Since the melting point of the 2,4-dinitrophenylhydrazone derivative (mp 164–168°) could not be improved by further recrystallization (lit.³ mp 175.4–177°), some contaminant is probably also present.

1-Bromobenzonorbornadiene (9).—In a pressure bottle, vinyl bromide 8 (1.02 g, 4.6 mmol) was treated with hydrobromic acid (48%, 50 ml) at 60–70° for 3 hr in a shaker. Further shaking at 25° was continued for 3 hr, water was added, followed by petroleum ether (bp 30–60°). The organic extracts were made neutral, washed, dried, and then freed of solvent to leave an oil (1.00 g, 72%) consisting of 1, *exo*-2-dibromobenzonorbornene (27, 60%) and 2,2-dibromobenzonorbornene (26, 40%): δ^{CCl_4} 1.9–2.9, 3.1–3.6, 3.7–4.1, and 7.0–7.6 (all cm); λ^{neat} 5.78 (weak, trace of benzenorbornene-2-one), 6.88, 10.32, 10.70, and 13.25 μ . The composition was decided on the basis of dibromide 27 via the integration of the aromatic proton downfield (δ 7.25–7.6) from the others (sharp AA'BB', centered at δ 7.1). Such a deshielded proton indicates a bridgehead-substituted benzenorbornene and is frequently a useful diagnosis for them.⁵ Treatment of bromide 8 with hydrobromic acid under reflux gave a complex product mixture with an increased amount of ketonic material.

The mixture of 26 and 27 (1 g, 3.3 mmol) was then added to potassium *t*-butoxide (16.6 mmol, freshly made) in *t*-butyl alcohol (25 ml) and refluxed with stirring for 70 hr. Isolation of product as described for 8 gave a red oil (0.66 g) which was distilled in a micro Hickman still at 0.08 mm, bath to 140°, to give 0.4 g (63%) of a mixture of starting 8 (38%) and the bridgehead bromide 9 (54%), along with olefin 10 (8%). Separation was effected on a Reoplex 400 column at 154° affording 9 as a colorless oil: see the tables; $\text{ir } \lambda^{\text{neat}}$ 3.31, 7.72, 8.56, 10.29, 11.11, 13.20, 13.76, and 14.40 μ .

***syn*-7-Bromo-*exo*-2-chlorobenzonorbornene (18).**—In a flask irradiated by a GE 275-W sun lamp, *syn*-7 bromide 4 (4.4 g, 0.02 mol) in carbon tetrachloride (20 ml) was treated dropwise under reflux with sulfuric chloride (3.24 g, 0.024 mol) in additional carbon tetrachloride (20 ml). After 3 hr of irradiation, the cooled solution was diluted with more solvent and water added. The organic phase was washed to neutrality, rinsed, and dried. Upon removal of the solvent, a mixture of starting 4 and 18 (4.6 g) was obtained in the ratio of 15:85, respectively. This mixture could be resolved by glpc on Reoplex 400 at 194° to give 18 as a white crystalline solid: mp 100–102.5° subl; nmr in Table II; $\text{ir } \lambda^{\text{KBr}}$ 8.23, 12.78–12.90, 13.27, 14.20, and 15.2–15.5 μ .

(28) For a discussion of uncatalyzed polar addition to 10, cf. S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 2741 (1966).

Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{BrCl}$: C, 51.29; H, 3.92. Found: C, 51.28; H, 4.09.

Dehydrohalogenation Studies on 18 and 17.—Reaction of crude chlorobromide 18 with potassium *t*-butoxide in *t*-butyl alcohol under reflux for 6 days gave a lower boiling fraction of bromide 4 (contaminant in 18) and *syn*-7-*t*-butoxybenzenorbornadiene, bp 97–105° (0.8 mm), δ^{CCl_4} 6.60 (t, CH=CH), 4.08 (t, *anti*-7 H), and 1.05 (s, *t*-Bu), and a higher boiling fraction, mostly 18. No bromide 7 was detected.²⁹ Similarly, reaction of the dibromide mixture of 17 plus 15 under these conditions (reflux, 67 hr gave the *t*-butyl ether along with vinyl bromide 8. Again no 7 was found.

Treatment of 17 plus 15 with freshly sublimed potassium *t*-butoxide in dimethyl sulfoxide at 125° for 3 hr produced a mixture of naphthalene and bromide 8. This dehydrohalogenation did not affect 18 in 1 hr but in 28 hr at 130° naphthalene formed. Processes employing sodium amide in benzene (reflux, 4 hr) and collidine-lutidine (reflux, 5 hr) were without effect on 17 plus 15. Similarly, potassium triethylcarbinoxide in its alcohol (reflux, 1 hr) or lithium diisopropylamide in ether (reflux, 12 hr) did not react with 18.

***exo*-3-Bromobenzonorbornene-2-one (28).**—Benzenorbornene-2-one^{3,30} (7.92 g, 0.05 mol) in glacial acetic acid (30 ml) was heated short of reflux with a GE 275-W sun lamp while bromine (16 g, 0.1 mol) in additional glacial acetic acid (20 ml) was added dropwise over a 1.5-hr period. After 45 min of further irradiation, water was added and the material was extracted with ether. The extracts were made neutral and dried and the solvent was removed. Distillation then gave bromo ketone 28 [9.6 g, 81%, bp 134–150°, redistilled at 131–132° (2 mm)] as a pale yellow oil: for nmr, see Table II; $\text{ir } \lambda^{\text{neat}}$ 5.71, 6.85, 8.91, 13.16, and 15.50 μ . No evidence was found for the *endo* bromo ketone. The bromo ketone reacted slowly with alcoholic silver nitrate at 25° but much faster on heating.

Anal. Calcd for $\text{C}_{11}\text{H}_9\text{OBr}$: C, 55.72; H, 3.83. Found: C, 55.55; H, 4.08.

The 2,4-dinitrophenylhydrazone was yellow-orange from ethyl acetate-ethanol, mp 203–206.5° dec, λ^{max} (EtOAc) 359 m μ 29,000.²⁷

Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{O}_4\text{BrN}_4$: N, 13.43. Found: N, 13.34.

Reduction of Bromo Ketone 28.—Reduction was carried out in the usual manner employed with each of the reagents. (1) Excess diborane swept into 28 (7.63 g, 0.032 mol) in tetrahydrofuran afforded upon processing³¹ a mixture of *exo*-3-bromo-*endo*-2-benzonorbornenol (29) and *exo*-3-bromo-*exo*-2-benzonorbornenol (30) as a viscous oil [7.46 g, 97%, bp 105–117° (0.2 mm) in a Hickman still]: see Table II for nmr; $\text{ir } \lambda^{\text{neat}}$ 2.97, 9.3–9.6, 13.1–13.2, and 13.84 μ . The ratio of 29 to 30 was 80:20 from nmr analysis and was unchanged upon column chromatography. (2) Addition of 4 equiv of sodium borohydride in water to 28 in methanol at 25° for 3 hr gave a ratio of 45:55. (3) Addition of excess lithium aluminum hydride in ether to 28 at 25° for 4 hr gave a ratio of 37:63. Numerous attempts to rearrange the mixture of 29 and 30 into other products containing some *syn*-7 derivative were unsuccessful: 48% hydrobromic acid, lithium bromide in dimethylformamide, silver tosylate in acetonitrile, and potassium hydroxide in various solvents.

***anti*-7-Bromobenzonorbornene-2-one (33).**—In the manner used to prepare *endo* bromohydrin, 32 olefin 10 (20.5 g, 0.144 mol) was converted into a mixture of dibromide 13 and *anti*-7-bromo-*exo*-2-benzonorbornenol (31). The bromohydrin was separated by recrystallization from petroleum ether (bp 30–60°) and ether as a white solid (13.8 g, 40%): mp 97–99.5°; nmr in Table II; $\text{ir } \lambda^{\text{CCl}_4}$ 2.85, λ^{KBr} 6.87, 7.39, 8.09, 8.61, 9.42, 10.46, 12.12, 13.22, and 13.90 μ (lit.¹⁹ mp 95–96°). The bromohydrin also resulted

(29) Dehydrochlorination of *anti*-7-bromo-*exo*-2-chloronorbornene proceeds similarly: H. Kwart and R. K. Miller, *J. Amer. Chem. Soc.*, **78**, 5678 (1956).

(30) This ketone was additionally characterized as its *oxime*, mp 115.5–117° from methanol-water (unpublished work with R. Gajewski). *Anal.* Calcd for $\text{C}_{11}\text{H}_{11}\text{ON}$: C, 76.27; H, 6.40. Found: C, 76.60; H, 6.42. In the course of other transformations attempted on this ketone not herein described, its *azine* was also prepared, mp 174–186° (mixture of stereoisomers) from ether-benzene. *Anal.* Calcd for $\text{C}_{22}\text{H}_{20}\text{N}_2$: N, 8.97. Found: N, 8.92.

(31) H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, **82**, 681 (1960).

(32) D. Porter and C. M. Suter, *ibid.*, **57**, 2022 (1935). See also, W. J. Pope and J. Reed, *J. Chem. Soc.*, **99**, 2071 (1911); **101**, 760 (1912).

from reaction of dibromide **13** with excess calcium carbonate in wet dimethylformamide (reflux 3 days).

Anal. Calcd for $C_{11}H_{11}OBr$: C, 55.25; H, 4.64. Found: C, 55.01; H, 4.93.

The tosylate **32** was made in the usual fashion (white needles from ether-benzene, mp 117–119.5°) and also from dibromide **13** upon treatment with silver tosylate in acetonitrile containing a few drops of pyridine; nmr appears in Table II.

Anal. Calcd for $C_{18}H_{17}O_2BrS$: C, 54.97; H, 4.36. Found: C, 55.18; H, 4.52.

Oxidation of bromohydrin **31** (7.13 g, 0.03 mol) at 25° for 40 hr with chromium trioxide in pyridine as described earlier for bromo ketone **24** gave bromo ketone **33** as a pale yellow solid (6.65 g, 94%, mp 52–55°). Recrystallization from petroleum ether (bp 30–60°) and other mixtures gave the analytical sample: mp 54.7–55.4°; nmr in Table II; ir λ^{max} 5.74, 8.07, 9.26, 12.19, and 13.80 μ (lit.¹⁹ mp 54.5–55.5°).

Anal. Calcd for $C_{11}H_9OBr$: C, 55.72; H, 3.83. Found: C, 55.89; H, 4.15.

Its 2,4-dinitrophenylhydrazone was a yellow solid, mp 251.5–252° from ethyl acetate, λ^{max} (EtOAc) 357 m μ (ϵ 25,000).²⁷

Anal. Calcd for $C_{17}H_{15}O_4BrN_4$: M, 13.43. Found: N, 13.55.

The bromo ketone was inert to boiling alcoholic silver nitrate for 2 min. It also resulted from dibromide **13** when it was heated in dimethyl sulfoxide containing an equimolar amount of sodium bicarbonate¹³ at 130–170° for 1 hr.

Its tosylhydrazone (white solid, mp 217–224° dec, crude yield 72%) was prepared in standard fashion. In two reactions with methylolithium at 25°,²⁰ one gave no bromide **5** with 53% recovery of the tosylhydrazone, while the other gave traces of **6** with 80% recovery. No better results were found with *n*-butyllithium.

Bromo ketone **33** was recovered (88%) unchanged after a 2-hr reflux in dimethylformamide containing 1.1 equiv of lithium chloride. Likewise, a 20-min reflux of **33** in glacial acetic acid containing excess silver acetate afforded unchanged **33** (95%) contaminated slightly by an acetate that appeared by nmr to be still an *anti*-7 derivative.

Homogeneity and *exo* Stereochemistry of Benzonorbornene-2-carboxylic Acid (11).—A sample of acid **11** (*unpurified*, 0.5 g, 2.7 mmol) was methylated with diazomethane. Upon work-up the oily residue (0.52 g, 97%) solidified. Other than light material, only one peak was seen upon glpc on Reoplex 400 at 185°. The material so collected appeared to be but *one* ester [white crystalline solid; mp 52.5–53.5°; δ^{CCl_4} 7.05 (m, Ar-H), 3.67 (s, -COOCH₃), 3.5 (m, 1 H), 3.3 (m, 4 H), and 1.2–2.5 (cm, ring H's); λ^{max} 5.82, 8.1–8.7, and 13.32], presumably methyl benzonorbornene-*exo*-2-carboxylate.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.18; H, 7.09.

Methylolithium (0.15 mol) in ether was added to the crude acid **11** (1.03 g, 5.5 mmol) in ether and the solution was stirred for 30 min. The material was cautiously hydrolyzed and processed in the usual manner. No recovered **11** was obtained but rather glpc on Reoplex 400 at 186° afforded colorless methyl *exo*-benzonorbornenyl ketone (**12**, 0.276 g, 27%, oil): nmr in Table II; ir λ^{max} 5.92, 6.91, 7.43, 8.5–8.7, and 13.0–13.5 μ .

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.89; H, 7.52.

The 2,4-dinitrophenylhydrazone formed light orange platelets from ethyl acetate-alcohol, mp 193.5–195°.

Anal. Calcd for $C_{19}H_{18}O_4N_4$: N, 15.29. Found: N, 15.52.

No other peak near **12** (retention time, 20 min) was observed in glpc. However, *exo*-2-isopropenylbenzonorbornene (55%, retention time, 7.2 min) was observed: δ^{CCl_4} 4.8 (m, =CH₂), and 1.8 (s, CH₃); λ^{max} 6.09 and 11.31. As no such resonances were in the nmr spectrum of the reaction material itself, clearly this olefin was formed during glpc by dehydration of the corresponding alcohol. This latter arose from reaction of excess methylolithium on **12**.

Ketone **12** (0.1 g, 0.5 mmol) and *m*-chloroperbenzoic acid (Aldrich, 0.13 g of 85% material, 0.64 mmol of reagent) were dissolved in ethylene chloride (7 ml) and refluxed for 1.25 hr. Further solvent was added and the solution was then washed to neutrality, rinsed, and dried. After removal of the solvent, the crude oil remaining was shown by nmr analysis to be unchanged **12** (64%) and *exo*-2-benzonorbornenyl acetate (34%), the latter being identical with authentic material prepared⁸ from olefin **10**. No evidence was found for any *endo*-2 product during the entire sequence from acid **11**, establishing the stereochemistry of this acid therefore to be *exo*, and totally *exo*.

Abortive attempts to synthesize acid **11** included reaction of *exo*-2 bromide **1** with sodium cyanide in dimethyl sulfoxide at 70° for 6 hr (no conversion, **1** recovered) and hydrolysis of *exo*-2-trichloromethylbenzonorbornene⁶ with concentrated sulfuric acid on a steam bath for 5.5 hr (apparent sulfonation of the aromatic ring).

Registry No.—**1**, 23526-72-9; **2**, 23526-73-0; **3**, 7605-11-0; **4**, 23526-75-2; **5**, 23537-58-8; **6**, 7605-10-9; **7**, 22436-26-6; **8**, 23537-79-3; **9**, 23537-80-6; **11**, 23537-81-7; **12**, 23537-82-8; 2,4-dinitrophenylhydrazone of **12**, 23537-83-9; **13**, 14362-55-1; **15**, 23537-85-1; **16**, 23537-86-2; **17**, 23612-80-8; **18**, 23537-87-3; **22**, 23526-80-9; **23**, 23526-81-0; **24**, 23526-82-1; 2,4-dinitrophenylhydrazone of **24**, 23526-83-2; tosylhydrazone of **24**, 23526-84-3; **28**, 23526-85-4; 2,4-dinitrophenylhydrazone of **28**, 23526-86-5; **29**, 23526-87-6; **30**, 23526-88-7; **31**, 17497-61-9; **32**, 23526-90-1; **33**, 23526-91-2; 2,4-dinitrophenylhydrazone of **33**, 23526-92-3; benzonorbornen-2-one oxime, 23537-88-4; benzonorbornen-2-one azine, 23537-89-5.

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