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Bridged Polycyclic Compounds. XLVII. The Addition of Bromine and Chlorine to Benzonorbornadiene and Some Reactions of the Resulting Adducts[1]

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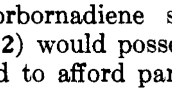
Halogen additions to benzonorbornadiene were carried out as possible initial steps in the synthesis of *syn*-7-substituted benzonorbornadienes (2). Polar addition of bromine gave the *exo*-5,*anti*-7 adduct. Addition of chlorine, depending on the conditions and the reagent, produced five of the seven possible isomeric adducts involving the 5, 6, and 7 positions. Polar chlorination is indicated to involve *exo* addition exclusively, giving rise only to the *exo,cis*-5,6 and the *exo*-5,*anti*-7 adducts. When nitryl chloride or sulfuryl chloride was the chlorinating agent, *trans*-5,6 and *exo*-5,*syn*-7 adducts were observed also. These seem to be the result of free-radical processes. With iodobenzene dichloride in carbon tetrachloride a fifth adduct, *endo*-5,*anti*-7, was formed in 5% yield along with the other four. Although it has not been our aim to study the addition mechanisms, these are discussed to the extent permitted by our data. The formation of the *exo*-5,*syn*-7 adduct appears to involve the rearrangement of an intermediate free-radical species. Some reactions of the halogenation products are discussed. Thus, 5-chloro-, *anti*-7-chloro-, and *anti*-7-bromobenzonorbornadiene were prepared by dehydrohalogenation of the corresponding dihalides, but the analogous preparation of *syn*-7-chlorobenzonorbornadiene did not succeed. Acetolysis results on the five dichlorobenzonorbornenes and the addition of deuterium chloride to *anti*-7-chlorobenzonorbornadiene are discussed in connection with the polar addition mechanisms. Various attempts at an S_N2 displacement on *anti*-7-bromobenzonorbornadiene were unsuccessful. Treatment of *anti*-7-bromobenzonorbornadiene with magnesium in tetrahydrofuran, followed by carbonation, yielded 4% of a 7-carboxy derivative, the major products being 7-7′ coupling products of benzonorbornadiene, only one of which (*syn,syn* or *anti,anti*) could be isolated pure.

In connection with our continuing interest in the carbonium ion reactions of bridged polycyclic compounds, we have been interested in the synthesis of the epimeric 7-substituted benzonorbornadienes **1** and **2**. There has been considerable attention given to the consequences of solvolyses of epimeric homoallylic compounds or of other reactions involving similar cationic intermediates.[2-8] Interest in these systems has focused upon the retention of configuration observed in certain of the epimers. Their retention has been rationalized as being caused by π-electron participation from either double bonds or aromatic rings with the electron-deficient cationic center when the π-electron system is *anti* to the leaving group. This participation is assumed to hold the configuration so that the entering group must coordinate from the *anti* side, leading to net retention of configuration. Our interest in **1** and **2** developed from the realization[7] that no examples apparently were described in which both epimers solvolyzed with retention of configuration. Thus, in all cases described in the literature, one homoallylic epimer solvolyzed with retention of configuration and the other with Wagner–Meerwein rearrangement, even in those cases[6,7] where the possibility for homoallylic participation existed in the second epimer.



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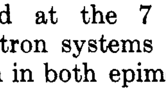

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a, X = OH
b, X = OTs
c, X = OAc
d, X = Cl
e, X = Br

When we began this work, it appeared to us that benzonorbornadiene substituted at the 7 position (**1** and **2**) would possess π-electron systems properly disposed to afford participation in both epimers. Indeed a variety of compounds related to **1** had been studied and had been shown to react with retention,[9-12]

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[1] Previous paper in series: S. J. Cristol and B. B. Jarvis, *J. Am. Chem. Soc.*, **89**, 5885 (1967).

[2] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

[3] S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

[4] S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

[5] E. E. van Tamelen and C. I. Judd, *ibid.*, **80**, 6305 (1958).

[6] C. H. DePuy, I. A. Ogawa, and J. C. McDaniels, *ibid.*, **82**, 2397 (1960).

[7] S. J. Cristol, J. R. Mohrig, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **85**, 2675 (1963).

[8] H. Tanida, T. Tsuji, and T. Irie, *J. Org. Chem.*, **31**, 3941 (1966).

[9] P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960).

[10] H. Tanida, *ibid.*, **85**, 1703 (1963).

[11] H. Tanida, T. Tsuji, and H. Ishiboti, *ibid.*, **86**, 4904 (1964).

[12] H. Tanida and H. Ishitobi, *ibid.*, **88**, 3663 (1966).

but no compound related to 2 has been described. It seemed to us then that the synthesis of substances 2 would be worthwhile for such studies. In the intervening years it has been shown that *anti*-7-dehydronorbornyl or 7-norbornadienyl systems solvolyze to give substantial amounts of tricyclic derivatives (*i.e.*, the reactions are accompanied by considerable homoallylic to cyclopropylcarbinyl rearrangement),[13-18] so that it is not at all certain that our results with 2 species would have the implications we had initially assumed. However, in view of interest in the chemistry of compounds we are reporting in this paper,[19,20] we wish to describe some of the results of the work which we have done thus far in the synthesis of 2 compounds.

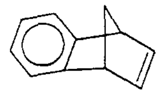
Results and Discussion

Our approaches to the synthesis of 2 compounds included the addition of various agents to the double bond of benzonorbornadiene (**3**). We hoped to obtain adducts which by elimination and displacement processes might ultimately be converted to 2. Although we have not yet succeeded in working out a practical route to 2,[21] we wish at this time to report our results on the addition of bromine and chlorine to **3** and on some conversions of the resulting adducts. Proton magnetic resonance and mass spectral aspects of the compounds encountered in this work are discussed in a concurrent paper.[22]

The first electrophilic addition to **3** was the Wittig and Knauss report of formation of a dibromide.[23] At about the same time, the related addition of bromine to a diacetoxy derivative (substituted in the benzene ring) of **3**, which proceeded with rearrangement, was described.[24] The polar additions of hydrogen chloride, deuterium chloride, and chlorine (as well as of acetic acid-O-d_1 and -d_4) were recently reported[19] and for the case of hydrogen chloride (and deuterium chloride) shown to be consistent with initial *exo* addition of the proton (or deuteron) followed by chloride attack on an intermediate symmetrical carbonium ion (or on a rapidly equilibrating set of ions simulating such intermediate) and leading to *exo*-5 chloride exclusively. Additional work in this area, partially paralleling ours, has been conducted by Wilt and co-workers[20] and will be referred to at appropriate places.

Addition of Halogen.—Addition of bromine to **3** in carbon tetrachloride solution at room temperature led in high yield to the formation of the *exo*-5,*anti*-7 dibromide **4**. No other products of this reaction were isolated. Addition of chlorine to **3** was effected with various reagents and under various conditions. Five of the seven possible dichloro isomers involving the 5, 6, and 7 positions of benzonorbornene (**5**–**9**, Chart I) were observed in varying proportions. In some instances, adduct formation was accompanied by formation of **1d**, presumably by the loss of a proton from a cationic intermediate.

CHART I



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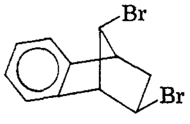

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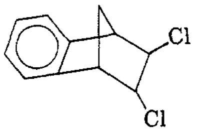

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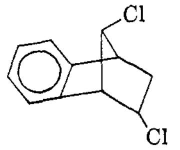

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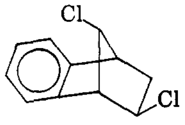

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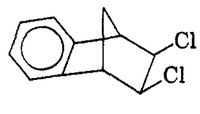

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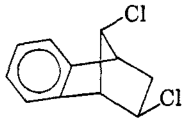

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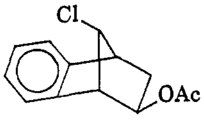
Structural assignments rest primarily on a correlation of the pmr and mass spectra, respectively, of these compounds.[22] The structures are further supported by certain chemical conversions, which will be described in the course of the following discussions.

Our investigation of the chlorination of **3** was guided by the desire to maximize the yields of **5** and **7** because these isomers either have or promised to be rearrangeable to benzonorbornenes having a 7 substituent *syn* to the benzene ring. To arrive at compounds of type 2 would then be a matter of reintroducing the double bond. The observed product distributions and yields are based on vpc analyses (for details see Experimental Section). They are summarized for some representative reactions in Table I. Optimum results (*i.e.*, convenience and high proportions of **5**) were obtained when iodobenzene dichloride was the source of chlorine. Distillation of the product mixture resulted in two major fractions containing primarily **5**–**7** and **8**–**9**. Compound **8** crystallized out during the distillation of the latter fraction and was followed by distillate rich in **9**.

The assigned structures are supported by the following chemical conversions. When a mixture of **5**, **6**, **8**, and **9** was treated with Zn–Cu couple in ethanol, benzonorbornadiene (**3**) arose at the expense of **5** and **8** only, indicating the presence of vicinal chlorines in these two isomers, but not in **6** and **9**. The latter two isomers remained unchanged. Silver ion assisted acetolysis of **5** and **7** led to *syn*-7-chlorobenzonorbornenyl *exo*-5-acetate (**10**), whereas **8** and **9** gave *anti*-7-chlorobenzonorobornenyl *exo*-5-acetate (**11**). Compounds **5**–**7** and **8**–**9** can thereby be related as Wagner–Meerwein isomeric pairs. Compound **6** was unreactive under these acetolysis conditions and could be isolated



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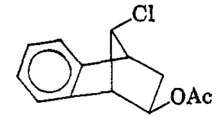

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(13) H. C. Brown and M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963).
(14) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).
(15) H. Tanida and Y. Hata, *J. Org. Chem.*, **30**, 977 (1965).
(16) H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.*, **88**, 864 (1966).
(17) A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966).
(18) M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966).
(19) S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 2741 (1966).
(20) J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *ibid.*, **32**, 893 (1967). We wish to thank Professor Wilt for making his results available to us before publication.
(21) Small yields of **2d** were obtained by dehydroarylsulfonoxylation of *exo*-5-(*syn*-7-chloro)benzonorbornenyl *p*-bromobenzenesulfonate. This preparative method has been developed further since the writing of this paper. A forthcoming paper will deal with the details of preparation and with the solvolytic behavior of **2d** presently under investigation.
(22) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3738 (1967).
(23) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).
(24) J. Meinwald and G. A. Wiley, *J. Am. Chem. Soc.*, **80**, 3667 (1958).

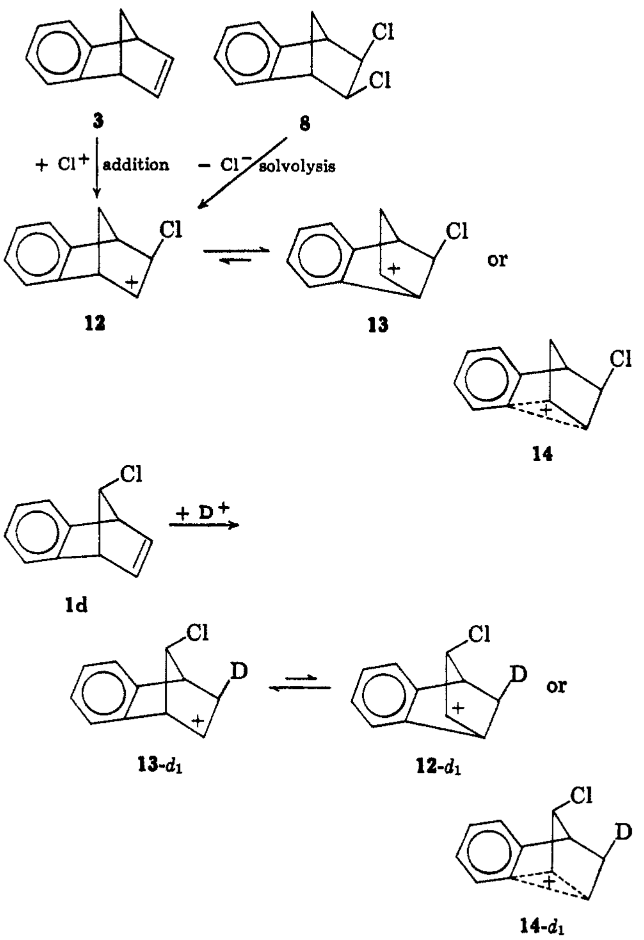
TABLE I

ADDITION OF CHLORINE TO BENZONORBORNADIENE

		Reaction,[a]	Product distribution,[b] mole %						Total
Reagent	Conditions: temp, °C/solvent/time, hr	%	1d	5	6	7	8	9	yield,[c] %
Cl_2–O_2	0–7/CCl_4/0.16–0.33, dark	30	11	...	..	..	4	85	100
Cl_2–N_2, excess olefin	*ca.* −50°/CCl_4/0.16–0.33, dark	100	11	...	..	..	5	84	100
Cl_2–N_2, excess olefin	As before, but with ultraviolet irradiation	100	13	...	..	..	4	83	100
Cl_2–N_2, excess olefin	0°/CCl_4/0.16–0.33, ultraviolet irradiation	100	22	Trace	..	..	9	69	100
Cl_2 (excess)–N_2	As before	100	*d*	3[d]	*d*	*d*	6[d]	77[d]	
SO_2Cl_2	2–5°/CCl_4/2 + 17 at room temp	50	9	3	..	1	4	83	90
SO_2Cl_2	0–5°/CCl_4/23, ultraviolet irradiation	90	..	41	..	13	21	25	50
SO_2Cl_2, Bz_2O_2	78°/CCl_4/4	100	4	25	..	5	16	50	62
NO_2Cl, excess	0°/CH_2Cl_2/0.16	100	..	19	..	1	44	35	32
Iodobenzene dichloride	Reflux/CCl_4/6	100	..	36	5	4	44	11	100

[a] Based on consumption of reactant applied in lesser amount. [b] Determined by vpc; for details, see Experimental Section. [c] Of chlorinated products, based on olefin consumed and estimated by vpc and weight of product mixture. [d] The distribution is here given in vpc area per cent. The balance of 14% was made up by peaks due to apparently higher chlorination products of unknown nature. Yields could therefore not be estimated, but are probably quantitative.

SCHEME I



somewhat impure as an oil after removal of the acetolysis products of **5** and **7** (**6** had initially been contained in the isomeric mixture of dichlorides). This relative nonreactivity of **6** compared to the *exo* isomers is understandable in view of the large difference in the solvolytic reactivity of the *p*-bromobenzenesulfonates of *exo*- and *endo*-5-benzonorbornenol demonstrated by Bartlett and Giddings.[9]

It is interesting to note that the solvolytic reactivity of an *exo* chlorine by far exceeds that of a 7 chlorine, whether *syn* or *anti*, in dichlorobenzonorbornenes. There have been no indications of products derived from solvolysis of the 7 chlorine even though experiments were carried out with sufficient excess of silver acetate to permit the conversion of at least part of the substrate to a diacetate. This behavior is in contrast to the solvolytic reactivity of *exo*-5,*anti*-7-dibromo- and *exo*-5,-*anti*-7-dichloronorbornenes, where it is found that the *anti*-7 substituent is the solvolytically more reactive one.[2,3] Our results are in line with the result that the *p*-bromobenzenesulfonate of *exo*-5-benzonorbornenol solvolyzes *ca.* 750 times as fast as the corresponding *anti*-7 ester.[9] It appears, then, that in the norbornene system the double bond endows the *anti*-7 substituent (which is the less reactive one in the saturated compound) with superior reactivity but that the benzene ring in benzonorbornenes, though providing about one-half as much assistance to ionization at C-7 as does the double bond in norbornene,[9] is not able to tip the balance in favor of higher reactivity of the *anti*-7 substituent.

An *exo* chlorine being indicated to be more reactive than a methylene bridge chlorine, our results conform entirely to expectations. Polar addition of chlorine to **3** as well as solvolysis of **8** and **9** may be pictured to occur *via* the intermediate nonclassical cation **14** or *via* the rapidly equilibrating pair of cations **12** and **13** (Scheme I). Two positions are open to attack by nucleophile in **14** and, in the case of chlorine (as well as bromine) addition and acetolysis, the incoming nucleophile shows a decided preference for the position nonvicinal to the already present substituent, leading in the case of chlorine addition almost exclusively to **9**.[25] Correspondingly, the acetolysis products are those derived from attack at the nonvicinal position. The argument[20] that this directive influence of the already present substituent may be steric in origin becomes less convincing when it is noted that the same directive influence appears to be operative in cationic intermediates with oppositely oriented chlorine, such as are derived from **5** and **7**.[26] It is indicated, then, that the apparent directive influence is largely a result of the expected greater stability of the Wagner–Meerwein rearranged

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[25] The report in ref 19 that the minor product of chlorine addition to **3** was the 5,6-*trans* adduct is in error. Aside from **9**, 4% of the 5,6-*exo,cis* adduct (**8**) were observed. The products obtained make it clear that a bridged chloronium ion is not a product-determining intermediate.

[26] Acetolysis of the mixture of **5** and **7** yielded a minor amount of an acetate (**20**) isomeric to **10** and **11**. Identification has been hampered by complexities in the pmr spectrum, but we believe this to be the *endo*-5-chloro-*exo*-6-acetoxy derivative arising from attack at the vicinal position in the intermediate cation. Since a corresponding product was not observed from the mixture of **8** and **9**, some steric contribution to the directive influence may be implied.

ion **13** compared with **12**, or of the relatively larger positive character at the nonvicinal position in **14**, assuming a nonclassical structure corresponding to resonance between **12** and **13**. These intermediates also readily accommodate the formation of the olefinic chloride **1d** by loss of a proton from **13** or **14**. As first pointed out by Taft,[27] olefin formation from an α-chlorocarbonium ion is not governed by the loss of the most acidic hydrogen (which would give rise to a vinyl chloride), but rather by loss of a proton from the apparently most electron-rich carbon adjacent to the cationic center. Hence **14** as well as **13** is expected to give rise to **1d**. Compound **12** would be less apt to eliminate a proton because it could only do so from the relatively electron-poor environment of the chlorine-bearing carbon if Bredt's rule is to be obeyed.

In the addition of deuterium chloride (and, by implication, of hydrogen chloride) to **3**, the attack by chloride on the (unsubstituted) cationic intermediate(s) has been shown to be indiscriminate with respect to the two open positions, but to occur exclusively *exo*.[19] When we added deuterium chloride to **1d**, the product distribution was the same as that from direct chlorine addition to **3**, an indication that the same intermediate(s) was involved. Irrespective of whether the first chlorine was situated initially at C-5 (from **3**) or at C-7 (from **1d**), the major product (95–96% **9**) was the one resulting from attachment of the second chlorine at a position β to the first one. The involvement of a four-centered transition state in the formation of **8** from **3** can therefore be ruled out. The location of the deuterium in the major product from **1d** was cleanly *exo*-6, as indicated by the differences in the pmr spectra of **9** and of the deuterium chloride adduct of **1d**.

The polar additions of halogen as well as of hydrogen halide to **3** follow a course of initial *exo* attack, in accord with previous findings on the norbornene system,[28,29] where cationic intermediates corresponding to **12–14** have been proposed. The recently advanced theory of torsional strain effects in the stereochemistry of attack and departure on norbornane derivatives supports *exo* attack whether or not classical or nonclassical intermediates are involved,[30] but it is not clear that these effects are large enough to rationalize the exclusive *exo* addition of the electrophile observed in polar addition. The polar formation of *exo*-5,*anti*-7 adducts, accompanied by some *exo*,*cis*-5,6 adduct, is not unexpected. Chlorine adducts other than **8** and **9**, however, are very likely the result of different mechanisms. As it has not been the aim of this work to study these mechanisms, our ability for comment is limited. More experimental data would be needed. Some comments seem in order, however.

The original purpose of treating **3** with nitryl chloride was the preparation of nitrochloro adducts. We did not succeed in isolating any single such adduct from the complex crude reaction mixture, the only isolable products being the dichlorides indicated in Table I. These were obtained as a mixture from alumina chromatography of the crude product. Vapor pressure osmometry gave a molecular weight of 213 (required, 213) for the dichloro adducts and the components were eventually isolated in enriched form by preparative vpc. When the *trans* and *exo,syn* adducts were recognized among the products, we became immediately interested in devising conditions that would maximize the yields of these compounds because, as indicated earlier, they promised to be convertible to *syn*-7 derivatives suitable for our purposes. According to Shechter,[31] most additions of dinitrogen tetroxide and of nitryl chloride to olefins probably proceed by free-radical processes, initiated by spontaneous fission of the addend. The formation of dichlorides could then be understood as being the result of initial attack by a chlorine atom, completed in about one-third of all cases by either abstraction of or combination with another chlorine atom. Since adduct formation was quantitative (by weight increase) in each experiment, there must have been formed a corresponding amount of adducts involving combination with two nitrogen dioxide radicals. Dinitrogen tetroxide is reported to give rise to adducts containing nitro, nitrite, nitrate, and nitroso groups in various combinations[31] and the complexity of the crude nitryl chloride adduct of **3** is therefore understandable since chlorine may now occur in combination with any or all of these substituents.

endo attack by bromine radicals on norbornene has been reported to occur to the extent of about 20%, although the major path of addition leads to *exo,cis* adduct.[28] On this basis, the predominance of *exo,cis* dichloride **8** and *trans* dichloride **5** among the dichlorides from reaction with nitryl chloride can be understood. The presence of rearranged *exo,anti* dichloride **9** may be due to polar reaction with free chlorine (from radical combination), but the formation of the rearranged *exo,syn* dichloride **7** (which became more important in reactions with sulfuryl chloride) is less straightforward. It was never detected in purely ionic addition of chlorine. If this can be taken to indicate a free-radical origin for **7**, we may assume that a rearrangement occurred in the radical derived from initial *endo* attack on **3**. Examples of rearranging free radicals are well substantiated in the norbornenyl–nortricyclyl system,[32] but an analogous rearrangement would not precisely apply to the present case, where the double bond has been replaced by a benzene ring. To account for the observed products, the rearrangement would correspond with the Wagner–Meerwein rearrangement in polar additions to **3**. Such rearrangements have been searched for in free-radical additions to norbornene, but they have not been observed.[33] While rearrangements in free-radical additions to norbornadiene are quite common, they are generally not of the Wagner–Meerwein type but rather lead to tricyclic derivatives. A notable exception has been observed in free-radical additions of thiols to hexachloronorbornadiene.[34] In these additions, attack is reported to occur from the *endo* side (attributed to steric interference by the 7-

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[27] R. W. Taft, Jr., *J. Am. Chem. Soc.*, **70**, 3364 (1948).

[28] H. Kwart and J. L. Nyce, *ibid.*, **86**, 2601 (1964).

[29] M. L. Poutsma, *ibid.*, **87**, 4293 (1965).

[30] P. von R. Schleyer, *ibid.*, **89**, 701 (1967).

[31] H. Shechter, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **25**, 55 (1964).

[32] (a) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958); (b) E. S. Huyser and G. Echegaray, *J. Org. Chem.*, **27**, 429 (1962); (c) J. W. Wilt and A. A. Levin, *ibid.*, **27**, 2319 (1962); (d) S. J. Cristol and D. I. Davies, *ibid.*, **29**, 1282 (1964); (e) C. R. Warner, R. J. Strunk, and H. G. Kuivila, *ibid.*, **31**, 3381 (1966).

[33] S. J. Cristol and G. D. Brindell, *J. Am. Chem. Soc.*, **76**, 5699 (1954).

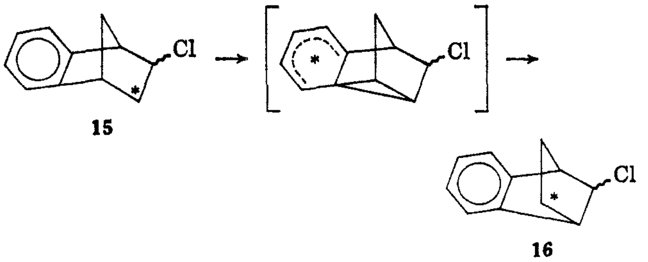
[34] (a) J. A. Claisse, D. I. Davies, and C. K. Alden, *J. Chem. Soc.*, 1498 (1966); (b) C. K. Alden, J. Claisse, and D. I. Davies, *ibid.*, 1540 (1966).

chloro substituents) at the unchlorinated double bond and leads not only to unrearranged 2,3 adduct (54% from thiophenol, 20–22% from methanethiol or ethanethiol), but also to substantial quantities of rearranged *syn*-7 thioethers (28% from thiophenol, 45–50% from methanethiol or ethanethiol). A homolytic 1,2 shift has been suggested for this (Wagner–Meerwein type of) rearrangement, the driving force being provided by the greater stability of the radical intermediate having the unpaired electron on a chlorine-substituted carbon rather than on a hydrogen-bearing carbon. However, such a driving force would not be applicable in the apparent rearrangements implied by our chlorination results.

In the commonly observed dehydronorbornyl to nortricyclyl rearrangement, the formation of unrearranged relative to rearranged products has been found to be concentration dependent[32a,d] as well as to depend on the nature of the addend (benzenesulfonyl halides), the proportion of unrearranged to rearranged product increasing as one goes from chloride to bromide to iodide. This showed conclusively that two distinct product-determining intermediates were involved and not a single nonclassical homoallylic radical.

Our observations in the benzonorbornyl system would require a rearrangement of **15** to **16** and this may simply be viewed as the result of a 1,2-aryl migration. 1,2-Aryl migrations in β-aryl radicals are, of course, well known and generally proceed to form a more stable (secondary, tertiary, benzylic) radical species.[35] Such an obvious driving force cannot be operative in the presently examined case, which further differs from the more commonly observed phenyl shifts by involving the migration of a bond from a fused benzene ring. Fused benzene ring migration has been observed previously in the decarbonylation of (1-methylindanyl)-acetaldehyde,[36] which yielded 2-methyltetralin to the extent of 35%, but again involved transformation from a primary to a more stable tertiary radical. However, it has been shown by tracer experiments in the decarbonylation of 3-phenylpropionaldehyde that phenyl shifts may occur in the absence of such a driving force,[37] and Walling[35] points out that, provided the postulate about the identical reactivity of radical species irrespective of their origin is correct, we may expect rearrangements in β-aryl radicals whenever their lifetime is sufficiently long for rearrangement to be able to compete with other (abstraction) processes.

In the absence of any information to the contrary, we may then accept the rearrangement demanded by our observations as being the result of a 1,2-aryl migration as shown. The vicinal dichlorides, **5** and **8**, would then be derived from **15**, and the rearranged ones, **7** and **9**, from **16**. Compounds **5** and **7** may be viewed as arising from initial *endo* attack and **8** and **9** from initial *exo* attack. Chain transfer from the *exo* side in all cases would then result in the observed products. The actually observed distribution of dichloro adducts from reaction with nitryl chloride is such as to indicate initial *endo* attack in at most 20% of the cases. Products corresponding to two *endo* addition steps have not been observed. The *trans* dichloride **5** could, of course, have arisen from initial *exo* attack followed by *endo* chain transfer as well; yet in the case of **7** it is clear that the initial step was *endo* attack since the 7 substituent is the one that must have entered first and its *syn* orientation can only be the result of *endo* attack.



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As will be borne out further in the following, there is indirect evidence that the chlorination products bearing either *syn* or *endo* chlorines are the result of free-radical processes. None of our observations support a polar origin for these compounds.

If we examine our results with sulfuryl chloride as the chlorinating agent, the product distributions observed under the various conditions appear to be indicative of both ionic and free-radical pathways. Products requiring *endo* addition at some stage of the reaction become more prominent under free-radical inducing conditions, whereas in the absence of peroxide or ultraviolet irradiation the distribution resembles that of polar addition. The presence of **1d** in two of the cases may be indicative of the relative importance of polar addition. The total yield of chlorination products seems to be related to the relative importance of polar and radical addition, being diminished as the presumably polar reaction products become less important. The product not accounted for by adduct formation was found to be present as a polymer. It was obtained as the residue from distillation of the crude product. This material was largely insoluble in various organic solvents; yet some apparently low molecular weight fractions could be extracted and were obtained as a white precipitate. The remainder formed a glassy, transparent, thermoplastic mass. Infrared spectra of the white powder and of the glassy mass were practically identical and indicated these substances to be sulfones. We rationalize their occurrence as being the result of a sulfur dioxide–olefin copolymerization, proceeding concurrently with the free-radical addition of chlorine. In a purely free-radical reaction the yields of chlorination products would thereby be limited severely, whereas higher yields would be expected if polar reactions became more important. Such a trend is clearly seen in the product distribution and yield data for sulfuryl chloride reactions in Table I. Our prospects of obtaining high yields of the desired isomers **5** and **7** by this route were thus not good. The data suggested that the maximum yields would be about 25%.

Our attempts to change the product distribution obtained in direct chlorination with molecular chlorine were unsuccessful. The product distributions make it apparent that free chlorine in liquid phase will always very predominantly, if not exclusively, add by the polar pathway discussed earlier and produce **8**, **9**, and some **1d**. Chloro olefin **1d** was not seen when excess chlorine was employed, but there appeared then peaks in the chromatograms probably indicative of higher chlorina-

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(35) C. Walling in P. de Mayo "Molecular Rearrangements," part I, Interscience Publishers, Inc., New York, N. Y., 1963, pp 409–415.

(36) J. W. Wilt and C. A. Schneider, *J. Org. Chem.*, **26**, 4191 (1961).

(37) L. H. Slaugh, *J. Am. Chem. Soc.*, **81**, 2262 (1959).

tion products derived from **1d**. The competition between free-radical and ionic pathways in the liquid phase chlorination of norbornene has been described by Poutsma.[29] Our results indicate that benzonorbornadiene is much less apt to follow the free-radical route under these conditions than is norbornene.

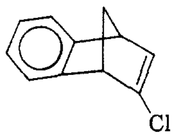
The most favorable results, regarding our purpose, were obtained with iodobenzene dichloride as the chlorinating agent. Combined yields of **5** and **7** were about 40%; yet the complexity of the crude product mixture was increased by the presence of still another dichloride, **6**. Iodobenzene dichloride has been variously reported to give exclusively *cis* chlorination (cholesterol),[38] *trans* chlorination (dioxene),[39] and *trans* as well as some *cis* chlorination (acenaphthylene),[40] the latter in the absence of free-radical inhibitor. The formation of *trans* adduct has been ascribed to epimerization of an intermediate ion pair.[41] Andrews and Keefer[42] have shown that iodobenzene dichloride can dissociate to give free chlorine. It seems possible that chlorine formed by dissociation leads to the small amount of **9** observed *via* a polar process, although experiments with an oxygen-free system as used with norbornene[29,43] still gave approximately the same amount of **9**. An alternative path for the formation of both **6** and **9** involves the *exo* transfer of a chlorine atom to **3** followed by rearrangement (**15** → **16**), followed in turn by chain transfer with iodobenzene dichloride to give either **9** or **6**.

The differing ratios of products with radical chlorinations involving nitryl chloride, sulfuryl chloride, and iodobenzene dichloride make it clear that the net addition of a chlorine atom to the olefin may occur with chlorine atoms, with $SO_2Cl\cdot$,[44] and with $PhICl\cdot$[45] and that the resulting carbon radicals may react with molecular chlorine, with sulfuryl chloride, and with iodobenzene dichloride.

Reactions of Halogenated Products.—In the following we wish to describe some reactions of some of the products obtained from the additions of halogen to benzonorbornadiene. Certain of these will lend further support to the structures assigned to the halogenation products; others were aimed at the synthesis of *syn*-7-substituted benzonorbornadienes, *i.e.*, compounds of type 2. Pmr and mass spectral evidence for the product structures are to be found in the concurrent paper.[22]

The dehalogenation of 5,6-dichlorobenzonorbornenes (**5** and **8**), the acetolysis of various dichlorobenzonorbornenes, and the addition of deuterium chloride to *anti*-7-chlorobenzonorbornadiene (**1d**) have already been discussed in the preceding section in connection with the polar mechanism of halogen addition to benzonorbornadiene (**3**).

Dehydrohalogenations with potassium *t*-butoxide in dimethyl sulfoxide were carried out successfully on **4**, **5**, **8**, and **9**. Good yields of **1d** and **1e** were obtained from **9** and **4**, respectively. Compounds **5** and **8** gave rise to the vinylic chloride **17**, but the dehydrohalogenation of the *exo,syn* dichloride **7** failed. While all of the **7** was consumed, none of the expected elimination product (**2d**) was detected.[21] Compound **1e** could be converted to the known *anti*-7-benzonorbornadienol[9] (**1a**) by acetolysis in acetic acid–silver acetate followed by treatment with ethylmagnesium bromide and hydrolysis,[46] a reaction sequence lending support for the structure of **1e** and indirectly for that of **4**. Since the corresponding *p*-bromobenzenesulfonate solvolyzed without rearrangement,[9] it is reasonable to expect the same behavior for **1e**, and conversion to the known acetate and further to the known alcohol (**1a**) indicates the bromine at position 7 in **1e** as well as in **4** to be oriented *anti* to the benzene ring. Alcohol **1a** could be reconverted to **1e** by reaction[47] with triphenylphosphine dibromide in dimethylformamide. The net inversion observed for this reaction on open-chain alcohols[48] (SN2 displacement on a phosphorus-containing intermediate) does not appear to be applicable in the present case. It appears that a carbonium ion mechanism is involved instead and this result is in line with the work of Schaefer and Weinberg.[49] They observed essentially complete inversion and absence of racemization in the treatment of optically active *endo*-norborneol with triphenylphosphine and bromine, but in the case of the corresponding *exo* isomer obtained, for instance, 79.1% of racemic *exo*-norbornyl bromide, 11.9% of optically active *endo*-norbornyl bromide, and 8.7% of nortricyclene. This departure from the normally observed clean SN2 process has been interpreted as the result of intervention by the norbornyl cation(s); *i.e.*, the intermediate *exo*-norbornoxytriphenylphosphonium species quite readily yields the norbornyl cation, whereas in the *endo* intermediate substitution occurs by direct displacement. A similar ionization of the *anti*-7-benzonorbornadienoxytriphenylphosphonium intermediate, probably assisted by the fused benzene ring and the double bond,[9] might therefore have been anticipated.



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Various attempts to convert **1e** to a derivative of type 2 by other SN2 displacements were unsuccessful. The bromide resisted attack by nucleophiles such as nitrite ion in dimethyl sulfoxide, phthalimide anion in dimethylformamide, methoxide ion in dimethyl sulfoxide–absolute methanol, and hydroxide ion in dimethyl sulfoxide–ethanol–water under various conditions (for details see Experimental Section). In all these cases, **1e** was recovered nearly quantitatively. Similar observations were made by Wilt and co-workers,[20] who explain the resistance of **1e** to SN2 displacement as possibly being the result of the small C-1–C-7–C-4 angle, which, owing to the rigidity of the benzonorbornadiene skeleton, is prevented from widening to

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(38) D. H. R. Barton and E. Miller, *J. Am. Chem. Soc.*, **72**, 370 (1950).

(39) R. K. Summerbell and H. E. Lunk, *ibid.*, **79**, 4802 (1957).

(40) S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *ibid.*, **78**, 4939 (1956).

(41) M. J. S. Dewar and R. C. Fahey, *ibid.*, **85**, 2248 (1963).

(42) L. J. Andrews and R. M. Keefer, *ibid.*, **80**, 1723 (1958).

(43) D. D. Tanner and G. C. Gidley, private communication.

(44) G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4031 (1955).

(45) (a) G. Bloomfield, *J. Chem. Soc.*, 114 (1944); (b) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958); (c) D. F. Banks, E. S. Huyser, and J. Kleinberg, *J. Org. Chem.*, **29**, 3692 (1964); D. D. Tanner and P. B. Van Bostelen, *ibid.*, **32**, 1517 (1967).

(46) M. S. Singer, Ph.D. Dissertation, University of Colorado, 1966.

(47) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964).

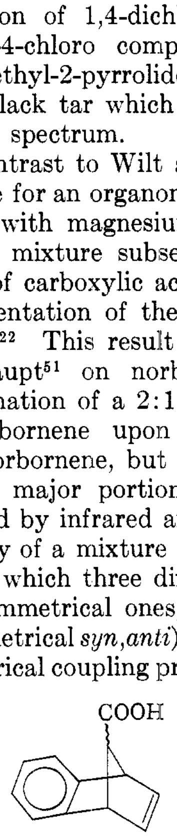
(48) G. A. Wiley, B. M. Rein, and R. L. Hershkowitz, *Tetrahedron Letters*, 2509 (1964).

(49) (a) J. P. Schaefer and D. S. Weinberg, *J. Org. Chem.*, **30**, 2635 (1965); (b) *ibid.*, **30**, 2639 (1965).

the degree required for the SN2 transition state. If this is so, then it is surprising that the carbonium ion derived from **1e**, which would have the same strain as the SN2 transition state, is formed quite readily,[46] unless participation with the π cloud of the benzene ring in the presumed cation intermediate modifies the geometry of the system.

Treatment of **1e** with excess sodium amide in liquid ammonia yielded only a brown, viscous oil, the infrared spectrum of which did not contain any evidence for the presence of an amine function. Similarly, when **1e** was refluxed, in analogy to a reported procedure for the conversion of 1,4-dichlorobicyclo[2.2.2]octane to the 1-cyano-4-chloro compound,[50] with cuprous cyanide in N-methyl-2-pyrrolidone, the only isolable material was a black tar which lacked nitrile absorption in its infrared spectrum.

In contrast to Wilt and co-workers,[20] we did obtain evidence for an organometallic derivative when **1e** was treated with magnesium in tetrahydrofuran and the reaction mixture subsequently carbonated. A single isomer of carboxylic acid **18** was isolated in 4% yield (the orientation of the carboxyl group has not been settled).[22] This result parallels that of Klumpp and Bickelhaupt[51] on norbornadiene. Sauers[52] reported the formation of a 2:1 mixture of *anti*- and *syn*-7-carboxynorbornene upon similar treatment of *syn*-7-bromonorbornene, but did not report yields. The remaining major portion of our product mixture was indicated by infrared and pmr spectroscopy to consist primarily of a mixture of isomeric 7-7′ coupling products, of which three different ones may be anticipated (two symmetrical ones, *syn,syn* and *anti,anti*, and the unsymmetrical *syn,anti*). A small amount of one of the symmetrical coupling products (**19**) could be isolated in crystalline form. Its symmetry was indicated by the appearance of its pmr spectrum, which showed a sharp singlet at τ 7.13, attributed to the 7 and 7′ protons, a triplet at 6.35 for the bridgehead protons, a distorted triplet at 3.44, corresponding to four olefinic protons, and an A_2B_2 (A_4B_4) system centered at 2.97 for eight aromatic protons. Further aspects of this spectrum are discussed in the concurrent paper.[22] In addition, benzonorbornadiene was isolated in 27% yield by distillation from the crude product mixture. 7-7′ coupling products have been reported by Wilt and co-workers[20] for *anti*-7-bromobenzonorbornene and by Tanida and co-workers[53] for 7-chloronorbornadiene.



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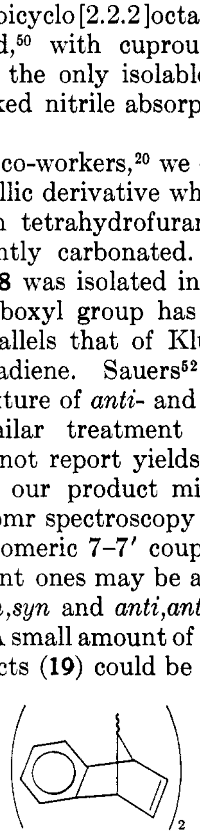

19, *syn,syn* or *anti,anti*

Experimental Section

Vapor Phase Chromatography.—Analyses of product mixtures were performed on a 6 m × 0.25 in. copper tubing column packed with 20% Fluorosilicon QF-1-0065 (Analabs) on Anakrom ABS, 70/80 mesh (Analabs), in an Aerograph Model A-90-P-3 gas chromatograph (Varian-Aerograph) under the following conditions: column temperature, 185 ± 2°; injector temperature, 220°; detector temperature, 235–240°; helium flow rate, 120 ml/min. Preparative separations were effected on a 5 m × 0.375 in. copper tubing column packed with a stationary phase of the same composition and installed in an Aerograph Autoprep Model A-700 gas chromatograph (Varian-Aerograph) under comparable conditions (somewhat adjusted so as to suit the individual separation problem).

Analytical calculations were based on peak areas estimated by triangulation. The area proportions were set equal to the weight proportions of the individual components and, where components of different molecular weights were involved, the molar proportions were calculated so that in combination with the known actual weight of the product mixtures yields could be estimated. The validity of this procedure was confirmed by vpc analyses of mixtures of known composition of pure compounds, including chlorobenzonorbornadienes, dichlorobenzonorbornenes, and chloroacetoxybenzonorbornenes. Agreement between dichloro- and chloroacetoxy compounds showed a scatter of no more than ±5% of the actual weight per cent, averaging to zero and attributable to uncertainties in area estimation. The olefinic chlorides, while showing similar scatter, gave vpc responses averaging to 7.5–8% (of the actual weight per cent) above that required for the known weight per cent. However, an adjustment for this higher response was not made because the olefinic chlorides formed only minor constituents of the mixtures analyzed and the adjustment would have remained within the experimental error limits. These are estimated at ±10% relative, but not exceeding ±3% absolute, for all percentage values derived from vpc analyses.

All compounds were found stable under the vpc conditions listed above, though, when column temperatures around or above 200° were applied, the *exo,cis* dichloride **8** began to show a tendency to rearrange to **9**.

Retention times (to the nearest minute) for the compounds analyzed under the stated conditions were as follows: **3**, 6; **17**, 11; **1d**, 14; **5**, 23; **6**, 24; **7**, 27; **8**, 34; **9**, 38; **11**, 54; **20**, 60; **10**, 65.

Analysis of product mixtures as referred to in the following were not solely based on coincidence of vpc retention time. This was done only after products from the various sources had been shown to be identical by other means, *e.g.*, pmr, infrared, and/or mass spectra of samples obtained by preparative vpc.

Spectra.—Pmr and mass spectra are treated in a concurrent paper.[22] Infrared spectra were recorded on a Perkin-Elmer Model 21 infrared spectrophotometer.

Melting and Boiling Points.—All melting points were determined in capillaries (stirred oil bath) and are uncorrected. Boiling temperatures observed during distillations are uncorrected; they may be considerably different from the true constants because distillations were frequently conducted deliberately slowly to increase the separation efficiency; *i.e.*, owing to heat loss the thermometer readings are likely to be too low in these cases.

Benzonorbornadiene (3) was prepared according to Wittig and Knauss[23] and obtained in yields of 55–65%.

Bromination of Benzonorborndaiene (3).—In 150 ml of reagent-grade carbon tetrachloride contained in a 500-ml three-necked reaction flask was dissolved 21.3 g (0.15 mole) of **3**. A solution of 24.0 g (0.15 mole) of bromine (Baker, purified grade) in 100 ml of carbon tetrachloride was added from a dropping funnel over a period of 45 min. The temperature was maintained between 20 and 25° throughout the addition and the reaction mixture was protected from light by wrapping the flask in aluminum foil. Bromine color had just begun to persist when the addition was complete. The solvent and excess bromine were removed under reduced pressure and with warming to 50°, yielding 48.4 g of an amber clear oil as the crude product. This was stored in a refrigerator for 2 days, during which time it assumed a nearly black appearance. When the flask containing the cooled crude product was handled again, crystallization was induced. The dark, somewhat oily crystalline aggregrates were dissolved in 200 ml of 95% ethanol for recrystallization, which yielded 38.3 g (85%) of white crystalline *exo*-5,*anti*-7-dibromobenzonorbornene (**4**), mp 78–79°. The final mother liquor yielded 3.6 g of a dark oily residue. By infrared comparison, this oil consisted primarily of more **4**. A pure sample of **4** was obtained after treatment with activated charcoal in 95% ethanol and recrystallization, mp 78–79.5° (lit.[23] mp 77–77.5° reported for the dibromide obtained by Wittig and Knauss).

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(50) H. D. Holtz and L. M. Stock, *J. Am. Chem. Soc.*, **86**, 5183 (1964).

(51) G. W. Klumpp and F. Bickelhaupt, *Tetrahedron Letters*, 865 (1966).

(52) R. R. Sauers, *Chem. Ind.* (London), 176 (1960).

(53) H. Tanida, Y. Hata, Y. Matsui, and I. Tanaka, *J. Org. Chem.*, **30**, 2259 (1965).

Anal. Calcd for $C_{11}H_{10}Br_2$: C, 43.74; H, 3.34. Found: C, 43.92; H, 3.30.

Chlorination of Benzonorbornadiene (3).—The preparation of *exo*-5,*anti*-7-dichlorobenzonorbornene (9), mp 50–51°, has been described.[19,25] Similarly prepared and carefully purified material was now found to melt at 52–53°. Our experiments now were aimed at a study of the effects on the product distributions of varying the conditions of the reaction as well as the reagent.

Chlorination with Elemental Chlorine.—Elemental chlorine was introduced into solutions of **3** (2.1 g, 0.015 mole, in 2.9 ml of carbon tetrachloride; total volume 5.0 ml) in admixture with either nitrogen or oxygen. The gas mixtures were prepared from chlorine, passed through a sulfuric acid drying tower, and either dry nitrogen or oxygen from supply tanks. The gas streams were adjusted to deliver known volumes of gas per unit time and were adjusted to result in a mixture of about 50% chlorine and 50% diluent gas (by volume). The gas mixture was bubbled into the olefin solution for periods of time corresponding to the delivery of the desired amount of chlorine (two-thirds of an equivalent for runs with excess olefin), which ranged from 10 to 20 min. During the gas addition, the cylindrical Pyrex reaction flask (test-tube shaped, with side neck; 20-ml capacity) was immersed in a suitable cooling bath and, if desired, was located next to an ultraviolet light source (General Electric H100A4T mercury lamp; about 1 in. distance). The resulting crude product solutions were immediately analyzed by vpc, as described, and the peaks correlated with chromatograms of mixtures of known composition. Conditions for individual runs were as listed in Table I. Absorption of chlorine, except when an excess was used, appeared to be complete in all cases except when oxygen was admixed with the chlorine. The products observed in the latter case corresponded to only 30% of the applied chlorine (30% reaction). The yields (based on olefin consumed) were in all cases found to be quantitative by the weight increase noted after removal of solvent.

Chlorination with Sulfuryl Chloride.—Chlorine additions with sulfuryl chloride were initially based on those with cyclohexene reported by Kharasch and Brown[54] and then modified to accommodate the various conditions listed in Table I.

In a typical experiment, sulfuryl chloride (Matheson Coleman and Bell) was freshly distilled and collected in a tared dropping funnel (5.6 g of SO_2Cl_2, 0.042 mole). Reagent grade carbon tetrachloride (10 ml) was added to it. Benzonorbornadiene (1 equiv, 5.9 g, 0.042 mole) was weighed into a 50-ml three-necked reaction flask and 10 ml of carbon tetrachloride and about 1 mg of benzoyl peroxide were added. A reflux condenser, a thermometer, and the dropping funnel were inserted in the flask and the assembled apparatus was then purged with dry nitrogen. About 10% of the sulfuryl chloride solution was added to the magnetically stirred flask contents and, because no signs of a reaction were apparent, the mixture was heated to a gentle reflux. Addition of another small quantity of benzoyl peroxide now appeared to initiate the reaction and the remainder of the reagent was added over the next 15 min during which time the source of heat (oil bath) was removed because the reaction liberated sufficient heat to maintain the mixture at reflux. Sulfur dioxide was evolved. The solution was refluxed for an additional 3.5 hr (mild evolution of SO_2 continued); the solvent was removed under reduced pressure, leaving behind 11.0 g of a viscous, oily residue. This residue (10.7 g) was subjected to distillation under reduced pressure. Colorless, oily distillate (5.7 g), bp 101–109° (0.30–0.35 mm), was collected. Vpc analysis revealed the composition of the distillate as (mole %) 4:25:5:16:50 **1d**–**5**–**7**–**8**–**9**, respectively, for a total yield of 0.026 mole (62%) of chlorinated products. The balance of material was a dark, glassy, resinous substance, which remained as the distillation residue. This material showed strong infrared absorption at 7.56 and 8.79 μ, characteristic of a sulfone. We assumed it to be the product of a benzonorbornadiene–sulfur dioxide copolymerization. No unreacted benzonorbornadiene was detected.

Low-temperature chlorinations with sulfuryl chloride were conducted correspondingly. For irradiated experiments, the Pyrex reaction flask was set up 3–4 in. distant from a General Electric H100A4T mercury lamp.

Combined crude products from several experiments were fractionally distilled (30 × 1 cm column packed with glass helices) and thereby separated into portions rich in either **5** and **7** (95% combined; bp 72–80° at 0.20–0.25 mm) or **8** and **9** (80% combined; bp 86–90° at 0.25–0.30 mm). A small sample further enriched in **7** to 64% was examined by pmr[22] and could be assigned the structure of *exo*-5,*syn*-7-dichlorobenzonorbornene. The minor (36%) component had the pmr spectrum of *trans*-5,6-dichlorobenzonorbornene (**5**). Compounds **5** and **7** have never been isolated pure, but the two fractions resulting from the distillation were found useful as such for the preparative conversion to the epimeric 7-chloro *exo*-5-acetates, respectively.

Chlorination with Nitryl Chloride.—Nitryl chloride was prepared according to Shechter[55] by the dropwise addition of 7.0 g (0.06 mole) of freshly distilled chlorosulfonic acid (Eastman, practical grade) to a four- to fivefold excess of vigorously stirred (mechanical stirrer) and cooled (ice bath) solution of anhydrous nitric acid in sulfuric acid in a 100-ml reaction flask. The solution was prepared by mixing appropriate proportions of 90% nitric acid (Baker) and fuming (30% SO_3) sulfuric acid (Baker). The use of this large an excess of nitric acid was found to permit better control of the reaction (better dissipation of heat), which tended to produce nitrosyl chloride rather than the desired nitryl chloride when the temperature control was less efficient. The nitryl chloride gas generated was conducted by means of glass tubing to a U-shaped receiver and condensed to a pale yellow liquid by cooling in a Dry Ice–acetone mixture. The exit of the U-tube could be opened by means of a two-way stopcock to either the atmosphere (*via* drying tube containing Drierite) or to a cylindrical reaction flask (test-tube shaped, with side neck; 20-ml capacity), the gas inlet tube extending to the bottom of same and ending in a fritted-glass closure. The reaction flask contained 4.2 g (0.030 mole) of benzonorbornadiene dissolved in 10 ml of reagent grade methylene chloride. Nitryl chloride was introduced slowly over a period of 1 hr by permitting it to vaporize from the U-tube into the reaction flask, which was kept at 0° by immersion in an ice bath. The reaction mixture assumed an emerald green color. Removal of solvent and excess reagent under reduced pressure discharged the green color and left behind 6.7 g of an orange viscous oil. The weight increase corresponded to quantitative adduct formation. The infrared spectrum of this crude product indicated the presence of nitro and nitrite groups and was identical with the spectra of other, similarly prepared products. The crude product was chromatographed in carbon tetrachloride solution on a 35 × 2 cm column of neutral Woelm alumina, activity I. Elution with carbon tetrachloride yielded an initial fraction of 2.0 g of a colorless oil, the infrared spectrum of which did not contain any indication of nitrogen functions but could otherwise be matched to peaks present in the spectrum of the crude product. Continuing elution with more and more polar solvent mixtures resulted in the collection of 3.5 g of additional material in many small, overlapping fractions. Representative fractions were examined by infrared spectra, which showed bands varying in sequence from those characteristic of ketones to nitroso to amides to carboxylic acids, none of which could be accounted for by the spectrum of the crude product. The material had evidently undergone profound changes during chromatography and no other primary reaction product was isolated. The (average) molecular weight of the first eluted fraction was determined as 213 by osmometry (Mechrolab vapor pressure osmometer, Model 301 A), supporting the assumption that a dichloro adduct was at hand (required mol wt, 213). Vpc analysis of this fraction indicated the presence of four components in ratios of 19:1:44:35. The three major components were isolated in enriched form by preparative vpc and could then be identified as *trans*-5,6-dichlorobenzonorbornene (**5**), *exo*,*cis*-5,6-dichlorobenzonorbornene (**8**), and *exo*-5,*anti*-7-dichlorobenzonorbornene (**9**), respectively, with the aid of their pmr spectra.[22] The mixture of dichloro adducts represented a total yield of 32%.

Adducts from other nitryl chloride experiments were worked up with even less success by attempts to reduce the nitro functions first with lithium aluminum hydride or by distillation. The latter yielded a distillate of dichloro adducts contaminated with some nitro compounds while the major part of the crude product (the residue) underwent severe decomposition.

Chlorination with Iodobenzene Dichloride.—Iodobenzene dichloride was prepared according to a published procedure.[56] Benzonorbornadiene (33.1 g, 0.23 mole) was dissolved in 120

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[54] M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 3432 (1939).

[55] H. Shechter, F. Conrad, A. L. Daulton, and R. B. Kaplan, *ibid.*, **74**, 3052 (1952).

[56] H. J. Lucas and E. R. Kennedy in "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 482.

TABLE II

Starting material, mole %	Crude product, mole %
5, 77	1.1
6, 7.3	7.7
7, 15.6	1.1
20,[a] 0	7.9
10, 0	82

[a] Reference 26.

ml of reagent grade carbon tetrachloride in a 500-ml three-necked reaction flask (thermometer, reflux condenser, magnetic stirrer) and heated to reflux. An equivalent of solid iodobenzene dichloride (63.2 g, 0.23 mole) was added in small portions through a side neck over a period of 30 min. Immediate reaction was indicated by rapid dissolution of the reagent (which is only sparingly soluble in carbon tetrachloride) and increased local boiling action. The resulting clear, yellow solution was maintained at gentle reflux for additional 6 hr.[57] The solvent was then removed under reduced pressure. The oily residue was distilled and the distillate collected from 82–86° at 23 mm (42.5 g) constituted a 91% recovery of iodobenzene. Vpc analysis of the remaining brown, oily residue (51.9 g) indicated the presence of the dichlorobenzonorbornenes **5** through **9** in a ratio of 36:5:4:44:11, respectively, in addition to small amounts (less than 5%) of low retention time impurities (iodobenzene, benzonorbornadiene, and three others). An essentially quantitative yield of dichloro adducts was indicated. Fractional distillation of this and similar crude products yielded principally two fractions, the first of which (bp 70–75° at 0.2–0.3 mm) contained low-boiling impurities and dichlorides **5** through **9** in a ratio of 3:61:7:4:21:4, respectively. The second fraction (bp 75–80° at 0.2 mm) formed a partially crystalline slurry in an oil and consisted essentially of **8** and **9**. The first fraction was refractionated for further enrichment in the lower boiling isomers to the following composition: **5**, 79%; **6**, 9%; **7**, 4%; **8**, 8%. Mixtures of this nature were used successfully in the preparation of the *syn*-7-chloro *exo*-5-acetate **10** and from the reaction residues the unreactive compound **6** could be isolated in highly enriched form by preparative vpc, which permitted its examination by pmr and mass spectrometry[22] and the assignment of the structure of *endo*-5,*anti*-7-dichlorobenzonorbornene. Similarly, mixtures of **8** and **9** were used in the preparation of the *anti*-7-chloro *exo*-5-acetate **11**. The solid contained in the second fraction from distillation was collected by filtration, then recrystallized from 95% ethanol to yield 16.1 g (33%) of pure *exo,cis*-dichlorobenzonorbornene (**8**), mp 75.5–76.5°.

Anal. Calcd for $C_{11}H_{10}Cl_2$ (**8**): C, 61.99; H, 4.73. Found: C, 61.82; H, 4.55.

None of the remaining isomers was isolated pure from this reaction.

Acetolyses of Dichlorobenzonorbornenes. Acetolysis of a Mixture of 5, 6, and 7.—A mixture (747 mg, 3.51 mmoles) of the dichlorobenzonorbornenes **5**, **6**, and **7** (composition see below) was stirred and heated at reflux with 1 equiv (586 mg, 3.51 mmoles) of silver acetate (reagent grade) in 8 ml of reagent grade glacial acetic acid for 13.5 hr. The reaction mixture was then filtered to remove the purplish brown precipitate of silver chloride as well as some undissolved unreacted silver acetate. The filtrate was shaken with 8 ml of carbon tetrachloride and 40 ml of water. The carbon tetrachloride extract was collected and the aqueous layer extracted once more with 5 ml of carbon tetrachloride. The combined extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated, yielding 790 mg of a crystalline residue with some oily contamination. The crude product was redissolved in 8 ml of 95% ethanol for recrystallization. A sample of the ethanolic solution was analyzed by vpc and yielded the composition data listed in Table II. The crude product corresponded to 96% recovery of material (0.34 mmole of dichloride and 3.03 mmoles of acetoxy chloride). Comparison between the compositions before and after the reaction permitted the conclusion that both **5** and **7** had given rise to **10** (and to some **20** derived from either one or both) and that **6** had been unreactive. The recrystallization yielded 540 mg (70%, based on **5** and **7**) of white crystalline *exo*-5-acetoxy-*syn*-7-chlorobenzonorbornene (**10**), mp 85–88°.

TABLE III

COMPOSITION[a] OF REACTION MIXTURE

Component	Before	After
3	0	34
5	26	13
6	12	11
8	22	1
9	15	11

[a] In relative peak areas; the relative response of benzonorbornadiene compared with that of the dichlorides has not been determined.

One additional recrystallization from 95% ethanol yielded an analytically pure sample, mp 88–89°.

Anal. Calcd for $C_{13}H_{13}O_2Cl$: C, 65.96; H, 5.53. Found: C, 65.59; H, 5.40.

Compound **20**, an isomer of **10** and believed to be the *endo*-5-chloro-*exo*-6-acetoxy derivative,[26] was isolated from the mother liquor residues of this and similar experiments by preparative vpc. After recrystallization from 95% ethanol it formed a white crystalline solid which melted at 94–96°.

Anal. Calcd for $C_{13}H_{13}O_2Cl$: C, 65.96; H, 5.53. Found: C, 65.74; H, 5.78.

Acetolysis of *exo*-5,*anti*-7-Dichlorobenzonorbornene (9).—To 1.35 g (6.34 mmoles) of **9**, dissolved in 14.5 ml of reagent grade glacial acetic acid, was added 1.06 g (6.34 mmoles) of silver acetate. The mixture was stirred and heated at reflux for 5.5 hr The reaction mixture was worked up as before. The crude product, 1.52 g of a light yellow oil (an essentially quantitative yield), was analyzed by vpc and found to consist of 3 mole % of unreacted **9** and 97 mole % of acetate **11**, in addition to traces of low retention time contaminants. The oil did not show any tendency to crystallize.

A similar oily crude product from another experiment was distilled under reduced pressure and a fraction corresponding to the acetate collected at a bath temperature of 160–170° at 0.3 mm (3.92 g, 70% yield in this case). The distillate solidified upon standing for 2 days to a faintly yellowish crystalline mass, mp 51–57°. Recrystallization from Skelly B solvent (petroleum ether, bp 60–70°) afforded 3.59 g (62%) of white crystals of *exo*-5-acetoxy-*anti*-7-chlorobenzonorbornene (**11**), mp 58.5–59.5°.

Anal. Calcd for $C_{13}H_{13}O_2Cl$: C, 65.96; H, 5.53. Found: C, 65.71; H, 5.57.

Acetolysis of *exo,cis*-5,6-Dichlorobenzonorbornene (8).—When 903 mg (4.24 mmoles) of **8** was refluxed with 716 mg (4.28 mmole) of silver acetate in 10 ml of glacial acetic acid for 15 hr, followed by work-up as described before, 941 mg of an almost colorless oil were obtained as the crude product. By vpc analysis, this oil consisted exclusively of unreacted **8** (48 mole %) and acetate **11** (52 mole %, corresponding to 2.18 mmoles; 97% yield, based on **8** not present in crude). The considerably lower conversion at longer reaction time (compared to acetolysis of **9**) appears to be a reflection of the inductive effect of the chlorine substitutent α to the reaction center.

Dehalogenation of Dichlorobenzonorbornenes.—Zinc–copper couple was prepared from 1.63 g (25 mg-atoms) of reagent grade zinc dust and 13 ml of 2% aqueous cupric sulfate solution (1.6 mmoles) by combining the materials in an erlenmeyer flask and swirling. The resulting black solid was collected by filtration (filtrate colorless), then washed twice with water and once with 95% ethanol. The solid was added to a solution of 486 mg (2.28 mmoles) of a dichlorobenzonorbornene mixture in 15 ml of 95% ethanol contained in a 50-ml reaction flask. The mixture was stirred and refluxed for 6 hr. It was filtered and the clear filtrate was added to 25 ml of ethyl ether. The resulting solution was washed twice with 25 ml of water. The remaining ethereal solution was dried over anhydrous magnesium sulfate and evaporated, yielding 375 mg of a nearly colorless, clear oil, which exhibited the characteristic odor of benzonorbornadiene. Vpc analysis before and after reaction gave the results listed in Table III. It is indicated that **3** was derived primarily from the *exo,cis* dichloride (**8**) and secondly from the *trans* dichloride (**5**). The 5,7 dichlorides, **6** and **9**, remained essentially unaffected. Also present were two minor unknown peaks (2–3 area parts) of retention time intermediate between **3** and **5**.

Dehydrohalogenation of *exo*-5,*anti*-7-Dibromobenzonorbornene (4).—To 28.0 g (0.093 mole) of **4** dissolved in 300 ml of dried dimethyl sulfoxide (Crown-Zellerbach; stored over Linde

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[57] Considerable unreacted benzonorbornadiene had previously been found present when the reaction was worked up immediately or soon after completion of adding the reagent.

Molecular Sieves; prior to use stirred for 2 hr with calcium hydride and vacuum distilled; bp 57–60° at 2–3 mm) in a 500-ml three-necked reaction flask (mechanical stirrer, thermometer, reflux condenser with drying tube) was added 13.4 g (0.11 mole) of commercial potassium *t*-butoxide (MSA Corp.) over a period of 5 min. The stirred mixture was heated (steam bath) to 75–80° and kept at this temperature for 70 min, then cooled to below room temperature. During the heating period, a dark purple coloration soon appeared but did not change any further. The mixture was cooled and 350 ml of water was added. The resulting dark brown emulsion was extracted four times with 250-ml portions of ether. Separation of layers was never quite complete and these larger amounts of ether were used to make the extraction as effective as possible. The black-brown ether extracts were filtered through Celite to remove some suspended black solids, then washed with three 500-ml portions of water to remove dimethyl sulfoxide. The extract was dried over magnesium sulfate, filtered, and evaporated, yielding 18.5 g (90%) of dark brown crystalline product. This was heated with 1 tsp of activated charcoal in 150 ml of 95% ethanol for 40 min on a steam bath. Filtration through Celite yielded a clear, bright yellow filtrate. Chilling induced crystallization and 16.8 g (82%) of faintly yellowish crystals of *anti*-7-bromobenzonorbornadiene (**1e**), mp 57–59°, were collected in two crops. One additional recrystallization and carbon treatment yielded a pure sample, mp 58–59°.

Anal. Calcd for $C_{11}H_9Br$: C, 59.75; H, 4.10. Found: C, 59.92; H, 4.19.

Dehydrohalogenation of *exo*-5,*anti*-7-Dichlorobenzonorbornene (9).—Corresponding to the experiment described immediately above, 1.09 g (5.1 mmoles) of **9** and 1.02 g (9.1 mmoles) of potassium *t*-butoxide were combined in 10 ml of dried dimethyl sulfoxide in a 35-ml reaction flask and kept at 80° for 75 min. Work-up as before yielded 875 mg (97%) of a brown, crystalline mass as the crude product. Recrystallization after treatment with activated charcoal in 95% ethanol gave 650 mg (72%) of faintly yellowish crystals of *anti*-7-chlorobenzonorbornadiene (**1d**), mp 46–48°, in two crops. A sample was sublimed and melted at 47–48°.

Anal. Calcd for $C_{11}H_9Cl$: C, 74.79; H, 5.14. Found: C, 75.03; H, 5.33.

Dehydrohalogenation of *exo,cis*-5,6-Dichlorobenzonorbornene (8).—A solution of 1.64 g (14.6 mmoles) of potassium *t*-butoxide in 15 ml of dried dimethyl sulfoxide was added dropwise over a period of 25 min to 2.66 g (12.5 mmoles) of **8** dissolved in 10 ml of dimethyl sulfoxide and contained in a 50-ml reaction flask under nitrogen. A mildly exothermic reaction (temperature rise from 20 to 30°) was initially noticed, but when the temperature dropped again some heat was applied to maintain a temperature of 50° during the last 10 min of addition. The solution had assumed a yellow color and there were no further visible indications of any reaction. To ensure complete reaction, the solution was kept at 72–74° for an additional 1.5 hr. There was no further change in appearance. The reaction mixture was added to 50 ml of water and extracted with three 25-ml portions of ether. The extract was washed several times with water, dried over magnesium sulfate, and evaporated to yield 2.17 g of a light yellow, slightly turbid oil as the crude product. Vpc analysis indicated the presence of 3.5% of unreacted dichloride, the balance consisting of 5-chlorobenzonorbornadiene (**17**) which was formed in 92% yield. The crude product was distilled under reduced pressure. A fraction of 1.47 g, bp 75–80° (2–2.5 mm), formed a colorless liquid and was free of impurities by vpc; however, yellow coloration soon developed upon standing at room temperature. The liquid was subjected to reduced pressure in a sublimer and a sample of colorless liquid, $n^{27}D$ 1.5728, was collected from the cold finger.

Anal. Calcd for $C_{11}H_9Cl$: C, 74.79; H, 5.14. Found: C, 74.86; H, 5.24.

Dehydrohalogenation of *exo*-5,*syn*-7-Dichlorobenzonorbornene (7).—Because pure **7** was not available, a mixture of the dichlorobenzonorbornenes **5** (35%), **6** (21%), and **7** (44%) was subjected to dehydrochlorination conditions similar to the above. To 701 mg (3.29 mmoles) of the mixture dissolved in 10 ml of dried dimethyl sulfoxide in a 25 ml reaction flask were added 500 mg (4.5 mmoles) of potassium *t*-butoxide. The mixture was stirred at room temperature for 15 min, interrupted once by brief application of heat on a steam bath. Work-up as described before yielded 287 mg of products and unreacted dichlorides as a yellow oil. The aqueous portion of the work-up liquor contained a substantial amount of suspended brown solids of unknown nature. Careful vpc analysis of starting material and extracted products gave the results listed in Table IV. The analyses may be interpreted to indicate the high-yield (97%) formation of **17** from **5** and some conversion of **6** to **1d** (elimination) and to **9** (isomerization). The disappearance of 98% of **7** was not accounted for. In particular, none of the expected **2d**[58] was detected. We have suspended further attempts to dehydrochlorinate **7** until a more suitable, pure starting material becomes available.

TABLE IV

Component	Starting material, mmoles	Crude product, mmoles
1d	0.00	0.16
2d	0.00	0.00
5	1.16	0.00
6	0.70	0.19
7	1.43	0.03
9	0.00	0.07
17	0.00	1.12

Addition of Deuterium Chloride to *anti*-7-Chlorobenzonorbornadiene (1d).—Deuterium chloride was generated by dropwise addition of 2.0 ml of deuterium oxide (99.5% D_2O; General Dynamics Co.) to 20 ml of reagent grade acetyl chloride in a 50-ml reaction flask. The flask was immersed in an ice bath and its contents were stirred magnetically. The gases evolved were conducted through a reflux condenser and two Dry Ice–acetone traps into a trap cooled by liquid nitrogen. The whole apparatus initially contained a helium atmosphere and a slow stream of helium was maintained through the apparatus throughout the deuterium chloride generation. Solid deuterium chloride deposited in the liquid nitrogen cooled trap. To the solid deuterium chloride was added 6 ml of *p*-dioxane (Eastman reagent; treated with and freshly distilled from lithium aluminum hydride) by means of a syringe inserted through the clamped-off tubing connected to the trap. The mixture was permitted to come to room temperature and the formed 7.2 ml of a clear, colorless solution. An aliquot was titrated with standard sodium hydroxide solution to a phenolphthalein end point and the solution was calculated to be 4.6 *N* in DCl. This solution (5 ml, 23 mmoles of DCl) and 0.90 g (5.1 mmoles) of **1d** were sealed in a glass tube and kept at 93–94° (steam bath) for 260 hr. The initially colorless solution gradually assumed a pale yellow color. The tube contents after heating, still strongly acidic, were analyzed by vpc and found to contain **1d**, **8**-d_1, and **9**-d_1 in a ratio of 32:2.6:65, in addition to two low retention time compounds apparently derived from DCl attack on dioxane. Compound **1d** was indicated to have reacted to the extent of about 70%. Low-boiling materials were removed by distillation and the fraction containing the two low retention time compounds was shown not to be derived from **1d** by the absence of aromatic proton resonances in its pmr spectrum. The distillation residue (0.66 g) consisted (by vpc) of 80% of the 5,7 dichloride, in addition to unreacted **1d** (15%), the *exo,cis* dichloride (3%), and two unknown trace components. The pmr spectrum of this residue confirmed the presence of 15–16% unreacted **1d** and clearly indicated the *exo*-5,*anti*-7 dichloride to bear an *exo*-6 deuterium. The *endo*-6-hydrogen resonance formed a doublet at τ 7.96, the resonance for the *exo*-6 hydrogen (7.33 in **9**[22]) was absent, from the resonance of the *endo*-5 hydrogen (6.28) the *trans* coupling of 4.5 cps had been removed, and the resonance of the bridgehead proton H-1 (6.62) had been sharpened owing to the removal of coupling to the adjacetnt *exo* proton, now substituted with deuterium. In addition to the distillation residue, 0.33 g of material was collected by rinsing the distillation apparatus with solvent. This portion contained 67% of the 5,7 dichloride, so that a total of 0.75 g of *exo*-deuterio **9** had been collected in these two portions. Also collected were 0.21 g of unreacted **1d** and, based on **1d** not recovered, the *exo*-6-deuterio-*exo*-5,*anti*-7-dichlorobenzonorbornene (**9**-d_1) can be estimated to have been obtained in 86% yield, the deuterated *exo,cis*-5,6-dichlorobenzonorbornene (**8**-d_1) in 3–4% yield. The deuterated compounds have not been isolated pure.

Attempted Displacement Reactions on *anti*-7-Bromobenzonorbornadiene (1e).—Compound **1e** was recovered and no prod-

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[58] Compound **2d** has since been obtained[21] and its absence in the chromatogram of this crude product has been verified.

ucts were detected after the following treatments: (a) 5 mmoles of **1e** was dissolved in 25 ml of a 2 *N* solution of sodium nitrite in dimethyl sulfoxide and kept at 48.5° for 14.5 hr (recovery 98%); (b) to 5 mmoles of **1e** dissolved in 8 ml of dimethylformamide was added 1.02 g (5.5 mmoles) of potassium phthalimide and the resulting suspension stirred for 23 hr at 107° (recovery 93%); (c) 10 mmoles (2.21 g) of **1e** was dissolved in a mixture of 45 ml of dimethyl sulfoxide, 5 ml of water, and 10 ml of 95% ethanol, which also contained 2.24 g (40 mmoles) of potassium hydroxide and the mixture was stirred for 66 hr at 80–81° (recovery 93%); (d) to a solution of 1.08 g (20 mmoles) of sodium methoxide in 20 ml of dry dimethyl sulfoxide and 5 ml of absolute methanol was added 1.11 g (5 mmoles) of **1e** and the resulting solution kept at 82–83° for 97 hr (recovery 82%).

In an attempt to prepare an amino derivative, 1.11 g (5.0 mmoles) of **1e** was treated for 30 min with an excess (about 0.1 mole) of sodium amide in 90 ml of anhydrous ammonia. Excess sodium amide was destroyed by careful addition of 5 g of aqueous ammonia (30% NH_3), whereafter the ammonia was permitted to evaporate. Addition of water (50 ml) and extraction with ether yielded 707 mg of a brown, viscous oil the infrared spectrum of which was essentially that of **1e**. The presence of amine functions was not indicated in the infrared spectrum. Treatment with 95% ethanol removed the unreacted **1e** (about 500 mg, 45%) and 132 mg of a brown, powdery material was eventually obtained. This apparently polymeric material (softens at 75°, flows at 200–220°) was not characterized beyond establishing the absence of amine functions by infrared.

An attempt to prepare a cyano derivative by refluxing 2.21 g (10.0 mmoles) of **1e** with 2.7 g (30 mmoles) of cuprous cyanide in 25 ml of N-methyl-2-pyrrolidone for 47 hr[59] produced only 1.24 g of a black tar which showed no nitrile absorption in its infrared spectrum.

Grignard Compound from *anti*-7-Bromobenzonorbornadiene (1e) and Carbonation Thereof.—Magnesium turnings (733 mg, 30 mmoles) and 5.82 g (25.8 mmoles) of **1e** were heated at a gentle reflux in 40 ml of tetrahydrofuran (distilled from lithium aluminum hydride) in an atmosphere of dry nitrogen for a period of 3.5 hr. The solution was decanted from unreacted magnesium (only 68% of the theoretical amount had been consumed) and, under a nitrogen blanket, poured into a Dry Ice–tetrahydrofuran slurry. Water (50 ml) was added to the mixture after it had come to room temperature. Two liquid phases formed. The mixture was allowed to stand for 12 hr at room temperature, during which time the tetrahydrofuran largely evaporated. The remaining mixture was equilibrated with 30 ml of saturated sodium bicarbonate solution and extracted twice with 50 ml of ether. The extracts were combined, dried (magnesium sulfate), and evaporated, yielding 3.50 g of a yellow-brown oil in which a precipitate began to form. The precipitate was collected by filtration (254 mg, pasty consistency) and washed with some 95% ethanol to remove oily contamination. A white powder (155 mg) remained and, after one recrystallization from chloroform, yielded 81 mg (2.2%) of symmetrically coupled bis-7,7′-benzonorbornadienyl (**19**) as large, colorless crystals, mp 209–221°. One further recrystallization from chloroform yielded (first crop) 37 mg of colorless crystals, mp 222–224.5°. The pmr spectrum[22] led to the assignment of the symmetrical structure **19**, but the configuration at the 7 positions could not be established.

Anal. Calcd for $C_{22}H_{18}$: C, 93.58; H, 6.42. Found: C, 93.39; H, 6.48.

The oil from which this compound had been isolated was distilled under reduced pressure and yielded 1.00 g (27%) of benzonorbornadiene as the only distillable material. A glassy residue remained. The infrared spectra of compound **19**, of benzonorbornadiene, and of the residue exhibited great similarities and it was assumed that the residue consisted of a mixture of 7,7′-coupled products of benzonorbornadiene (three epimers possible).

The basic aqueous layer remaining after the extraction of hydrocarbons contained some suspended white solids after it had been acidified with hydrochloric acid. It was extracted continuously for 26 hr (liquid–liquid extractor) with ether. The dried extract yielded, after evaporation, 375 mg of white crystalline flakes with some yellowish contamination. The material was treated with activated charcoal in chloroform and recrystallized, yielding 200 mg (4.2%) of colorless crystals of 7-carboxybenzonorbornadiene (**18**), mp 195–199°. The pmr spectrum[22] was compatible with the assigned structure(s). The infrared spectrum indicated the presence of the carboxyl group and also exhibited a very strong band which has been observed at or near 14.35 μ in all 7 derivatives of benzonorbornadiene examined. This band is also found with benzonorbornadiene itself and probably involves olefinic hydrogen bending vibrations. One further recrystallization from aqueous acetone yielded a sample melting at 198–200°.

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.52; H, 5.41.

Treatment of *anti*-7-Benzonorbornadienol (1a) with Triphenylphosphine Dibromide.—In a published procedure[47] for the use of triphenylphosphine dibromide in the conversion of alcohols to alkyl bromides the reagent is generated *in situ* from triphenyl phosphine and bromine in the presence of the alcohol. For the case of the olefinic alcohol **1a** we preferred to prepare the reagent separately to avoid any bromine addition to the double bond. The reagent was prepared by the dropwise addition of a solution of 8.0 g (0.05 mole) of bromine (Baker, purified) in 30 ml of carbon tetrachloride to a stirred solution of 13.1 g (0.05 mole) of triphenylphosphine (Eastman, reagent grade) in 50 ml of carbon tetrachloride at room temperature over a period of 25 min. A bright yellow precipitate began to form as soon as the addition was begun and the moderately exothermic reaction caused the temperature to rise slowly to 40°. The resulting creamy yellow suspension was stirred for an additional 20 min. The yellow solid was then collected by filtration. The filter cake was kept covered with carbon tetrachloride (contact with air was found to cause deterioration to a dark colored greaselike material) and transferred to a small vacuum desiccator. Solvent was removed under reduced pressure and the product formed a free-flowing yellow powder. Dry nitrogen was admitted to the desiccator. From the colorless filtrate 2.2 g (17%) of pure triphenylphosphine (mp 78–79°) was recovered upon evaporation, indicating the insolubility of the product in carbon tetrachloride. The incomplete conversion may have been due to a higher uptake of bromine by the triphenylphosphine (ring bromination?). The weight of the product was not obtained, but the yield, based on the unrecovered phosphine, appeared to be quantitative. The product was used successfully as obtained.

In an atmosphere of dry nitrogen, 2.7 g (6.4 mmoles) of triphenylphosphine dibromide was transferred to a 50-ml tared reaction flask. To it was added 0.79 g (5.0 mmoles) of *anti*-7-benzonorbornadienol (**1a**) (which had originally been prepared from **1e**[46]), and 25 ml of dimethylformamide (redistilled from KOH–CaO). The mixture was stirred and refluxed (bath temperature, 170°) for 2 hr while an atmosphere of dry nitrogen was maintained over the reaction. The mixture was permitted to cool, then added to 50 ml of water and extracted three times with 20 ml of ether. Partial evaporation of the dried (magnesium sulfate) extract caused the precipitation of 0.55 g of triphenylphosphine oxide, which was removed by filtration. Complete evaporation yielded 1.51 g of a brown, liquid residue which still contained triphenylphosphine oxide as well as some dimethylformamide. The contaminants were removed by passing the crude product in carbon tetrachloride solution through a 12 × 1.5 cm column of Woelm alumina. Most (707 mg) of the product was eluted in the first 50 ml of eluate, the total obtained with 150-ml elution (with carbon tetrachloride) amounting to 762 mg (69%) of slightly impure *anti*-7-bromobenzonorbornadiene (**1e**), mp 54–56°. A mixture with pure **1e** (mp 58–59°) melted at 55–57°. The pmr spectrum confirmed the identity between **1e** as prepared here and that obtained by dehydrobromination of **4**.

Registry No.—**1d**, 10239-89-1; **1e**, 7605-10-9; **3**, 4453-90-1; **4**, 7605-09-6; **5**, 14296-33-4; **6**, 14296-34-5; **7**, 14296-35-6; **8**, 14362-81-3; **9**, 7605-06-3; **10**, 14296-37-8; **11**, 14362-78-8; **17**, 7605-08-5; **18**, 14296-57-2; **19**, 14518-80-0; **20**, 14362-75-5.

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[59] Procedure and work-up were based on ref 40.