Studies of Benzonorbornene and Derivatives. I. Chloro- and Bromobenzonorbornenes and Related Compounds[1,2]

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The radical chlorination of benzonorbornene (**1**) yielded the *exo*-2-chloride **3** along with a small amount of the *endo* epimer **4**. The addition of hydrogen chloride to benzonorbornadiene (**2**) also gave **3**, as did the reaction of thionyl chloride on *exo*-2-benzonorbornenol (**5**). The *endo* isomer **4** was prepared in a sequence started by reaction of iodobenzene dichloride with **2**. The addition afforded some *exo,cis*-2,3-dichlorobenzonorbornene (**10**), together with *exo*-2-*anti*-7-dichlorobenzonorbornene (**9**). This latter resulted also when chlorine was added to **2**. Dehydrochlorination of **10** yielded 2-chlorobenzonorbornadiene (**11**) which was reduced with diimide to **4**. This *endo*-chloride could not be prepared from *endo*-2-benzonorbornenol (**8**) or from isoindene and vinyl chloride. In solvolysis **3** was much faster than **4**. Addition of bromine to **2** gave the *exo*-2-*anti*-7-dibromide (**12**). Dehydrobromination of **12** led to *anti*-7-bromobenzonorbornadiene (**13**), which was hydrogenated to *anti*-7-bromobenzonorbornene (**14**). Attempts to make organometallic derivatives of **13** and **14** failed, as did attempted displacement reactions on **14**. Reaction of **14** with magnesium did afford the coupling product **15**. All the bromides were reactive to silver nitrate solution. The nmr spectra of these compounds are discussed in some detail and views on the mechanism of their formation are also presented.

Benzonorbornene (**1**,[3] Chart I) affords the possibilities of several mechanistically interesting investigations. We have for some time[4] been interested in its chemistry and report here on its radical chlorination as well as the reactions of benzonorbornadiene (**2**)[3] with several reagents effecting addition to its double bond. The reactions investigated are collected in the chart. Because the structures of the various products obtained were largely determined by nmr spectroscopy, a rather detailed analysis of the spectrum follows each compound and more data are given in the Tables I and II.

Chlorination of **1** was achieved with sulfuryl chloride in the presence of benzoyl peroxide,[5] with trichloromethanesulfonyl chloride plus benzoyl peroxide,[6] and with chlorine promoted by ultraviolet light. Only the first of these chlorinations was studied in detail although all three appeared to proceed in essentially the same way. The monochloro substitution product was isolated and characterized as a mixture of *exo*-2-chlorobenzonorbornene (**3**, 92.7 ± 0.7%) and *endo*-2-chlorobenzonorbornene (**4**, 7.2 ± 0.7%).[7a] The composition was established by nmr excellently, by gas–liquid partition chromatography (glpc), and also by solvolysis. The 2-methinyl protons of **3** and **4** were well separated at 60 Mc in their nmr spectra, the former exhibiting its resonance at 228 cps as a partly resolved multiplet while the latter was at 264 cps as a very clear doublet of triplets. The nmr aspects of these substances as well as some others are discussed in detail later.[8] Under the glpc conditions employed **3** eluted nearly five minutes before **4** and this, too, allowed an easy verification of structure and composition once the pure isomers were at hand. Solvolysis of the product mixture was performed in 80% ethanol at 104°. The *exo* isomer solvolyzed rapidly ($k_1 = 10^{-3}$ min^{-1}) while the *endo* isomer was inert. Based on the kinetics of pure **3**, the chlorination mixture contained about 90% **3**, in reasonable agreement with the nmr and glpc methods. The solvolysis products were identified as *exo*-2-benzonorbornenol (**5**)[9] and *exo*-2-ethoxybenzonorbornene (**6**) by comparison with authentic samples. Dehydrochlorination of the product mixture was slow but reaction with potassium *t*-butoxide in *t*-butyl alcohol under reflux afforded **2**. The rather forceful conditions needed to dehydrochlorinate the mixture were expected. Norbornyl-type halides employ an *exo,cis* elimination pathway that is more difficult than that of most other secondary halides. The matter has been thoroughly discussed.[10] The results with **1** in radical chlorination are very similar to those obtained by several workers with norbornane.[11a–c] *exo* substitution at the 2 position of norbornane always prevailed (over 90%), although in the case of photochemical chlorination with chlorine in the gas phase 30% *endo* product was obtained.[11c] Neither in the earlier work nor in that presented here was evidence obtained for methanobridge or bridgehead substitution products. While admittedly the 7-chloro isomers have yet to be made, the bromo and chloro analogs in this series are quite similar in their nmr spectra. Because bromide **14** (see later) possessed nmr characteristics quite different from **3**, **4** or their mixture from **1**, it is felt that such 7-chloro isomers were absent. 1-Chlorobenzonorbornene, the bridgehead isomer, has been prepared[12] and it is absent in the chlorination mixture. That such is the case implies that benzylic stabilization of the bridgehead radical derivable from **1** is minimal. Presumably **1** has the aromatic ring in an unfavorable and

(1) Taken from the M.S. theses of G. G. (1966), W. J. R., Jr. (1966), and A. R. Z. (1965).

(2) A portion of this work was presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 24P; Abstracts of Papers.

(3) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

(4) J. W. Wilt and C. A. Schneider, *Chem. Ind.* (London), 951 (1963); J. W. Wilt, C. A. Schneider, J. P. Berliner, and H. F. Dabek, Jr., *Tetrahedron Letters*, 4073 (1966).

(5) M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 2142; 3432 (1939); **62**, 925 (1940).

(6) E. S. Huyser, *ibid.*, **82**, 5246 (1960).

(7) (a) Such a result differs greatly from that reported earlier.[2] While the differences between the earlier and later work on this problem can never be completely resolved, the erroneous conclusions reached earlier were due largely to faulty conditions employed in the solvolysis studies. The present findings are based on several instrumental methods as well as kinetic analysis while the earlier data[2] were based essentially solely on the latter. We appreciate communications with Professor S. Cristol and Dr. R. Caple (University of Colorado) on several aspects of this problem and thank them for data then unpublished, but now available.[7b] (b) S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 2741 (1966).

(8) The spectra and further detail may be found in the theses.[1]

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

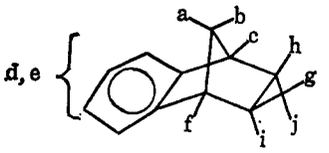
(10) N. A. LeBel, P. D. Beirne, and P. M. Subramanian, *ibid.*, **86**, 4144 (1964); J. K. Stille and F. M. Sonnenberg, *Tetrahedron Letters*, 4587 (1966).

(11) (a) J. D. Roberts, L. Urbanek, and R. Armstrong, *J. Am. Chem. Soc.*, **71**, 3049 (1949); (b) J. P. West and L. Schmerling, *ibid.*, **72**, 3525 (1950); (c) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

(12) J. W. Wilt and H. F. Dabek, Jr., unpublished work.

TABLE I

NMR SPECTRA OF VARIOUS BENZONORBORNENES[a-c]



Compd	Proton resonance, cps[d,e] a	b	c	f	g	h	i	j
3	100–125,[f] m	125, dt	198, m	205, m	os	100–125,[f] m	228, dm	100–125,[f] m
4	107, ddt	89, dt	190, m	200, m	264, dt	142, ddd	os	69, dt
9	238, m	os	206, dd	212, d	os	158, dt	225, ddd	126, dd
10	116, dp	148, dt	205, t	205, t	os	os	237, d	237, d
11[g]	*h*	*h*	228, m	218, m	—	—	—	—
12	246, m	os	209, dd	231, d	os	171, dt	222, ddd	129, dd
13[i]	261, m	os	243, dd	243, dd	—	—	—	—
14	237, p	os	202, dd	202, dd	140, dm	140, dm	74, dm	74, dm
15[j]	104	os	185	185	112	112	68	68

[a] See ref 8. [b] Spectra of **3**–**11** were determined in carbon tetrachloride relative to tetramethylsilane on a Varian A-60A spectrometer. The spectra of **12**–**15** were taken similarly, though in deuteriochloroform and on a Varian A-60 spectrometer. The chemical shifts are ±1 cps. [c] The spectra of **1** and **2** have been reported (see ref 49). [d] Abbreviations: d, doublet; dd, doubled doublet; ddd, doublet of doubled doublets; ddt, doublet of doubled triplets; dm, doubled multiplet; dp, doublet of pentuplets; dt, doublet of triplets; m, multiplet; os, other substituent; p, pentuplet; —, proton absent in compound; t, triplet. [e] The aromatic protons (d, e) were narrow multiplets centered between 421 and 437 cps, except in the substitution products of **2** where a multiplet from 410 to 440 cps was observed. Likewise, in **15** a broader resonance from 418 to 432 cps was evident. [f] A more exact chemical shift is unknown because of the complexity of the multiplet. [g] Vinyl proton, 383 cps, dt. [h] Assignment unclear; dt at 151 cps, dd at 135 cps. [i] Vinyl protons, 402 cps, dt. [j] All multiplets.

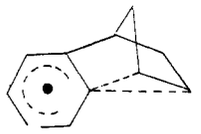
TABLE II

COUPLING CONSTANTS[a]

Protons coupled	*J*, cps
ab[b]	9–9.5
ac, af, ai, aj[c]	1.5
bc, bf	1.5
ch, fg	4
fk[d]	3–3.5
gh	9
gi, hj	10–13
gj, hi	3–4
ij	5–8

[a] For compounds listed in Table I. The values at times varied within the range given depending on the compound. [b] In **11** the *J* value is 7 cps. [c] In **4** the *J* value is 4 cps. [d] The k proton is the vinyl proton.

rigid stereoelectronic position for any significant delocalization (Bredt's rule). The same situation prevails in triptycene.[13] The apparent absence of 7-substituted products from **1** is noteworthy. One might have anticipated some π-electron stabilization of the intervening radical on the basis of the known stability of the corresponding cation[9] and the possible stability of the analogous 7-norbornenyl radical.[14] The observation that *anti*-7-bromobenzonorbornene (**14**) readily coupled upon attempted Grignard formation (see later) seemingly implies some stability of the 7-benzonorbornenyl radical; so the failure to observe substitution here might be due to another factor. Chlorination normally involves little bond breaking at the transition state,[15] so the stability of the product radical plays less a role than, for example, in bromination; yet bond strength is definitely a factor. Perhaps the HCH angle at the 7 position, which is greater than 109° because of the small $C_1C_7C_4$ angle,[16] strengthens the 7-CH bonds and decreases the likelihood of radical abstraction there. An analogy may be found in the reduced reactivity of cyclopropane CH bonds toward radicals.[17] Here, too, the wide HCH angle (116°) tightens the bond. Product composition was not significantly changed when the chlorination of **1** was carried to 14 or 67% completion, indicating product stability under reaction conditions. The preponderance of the *exo*-2 isomer then indicates that chain transfer occurred preferentially from the *exo* side of the molecule. This is also the case for norbornane substitution.[11] But in this case, the preference for *exo* substitution has been ascribed to steric retardation of *endo* substitution by the transannular 5,6-*endo* hydrogens. Obviously, as **1** has no such hydrogens, this cannot be the reason for its *exo* substitution. An attractive possibility for such specificity would be to have chain transfer occur with a nonclassical radical, as shown. Such a radical would



necessarily transfer from the *exo* side, but much evidence exists against such bridged, nonclassical radicals;[18] so an alternative explanation is more likely. The most obvious alternative is that the aromatic ring sterically shields the *endo* side of the molecule, making **1** exactly comparable with norbornane itself. Other possibilities do exist, however. For instance, hydrogen abstraction from **1** may be selectively *exo*

(13) P. D. Bartlett, M. J. Ryan, and S. G. Cohen, *J. Am. Chem. Soc.*, **64**, 2649 (1942).

(14) J. W. Wilt and A. A. Levin, *J. Org. Chem.*, **27**, 2319 (1962).

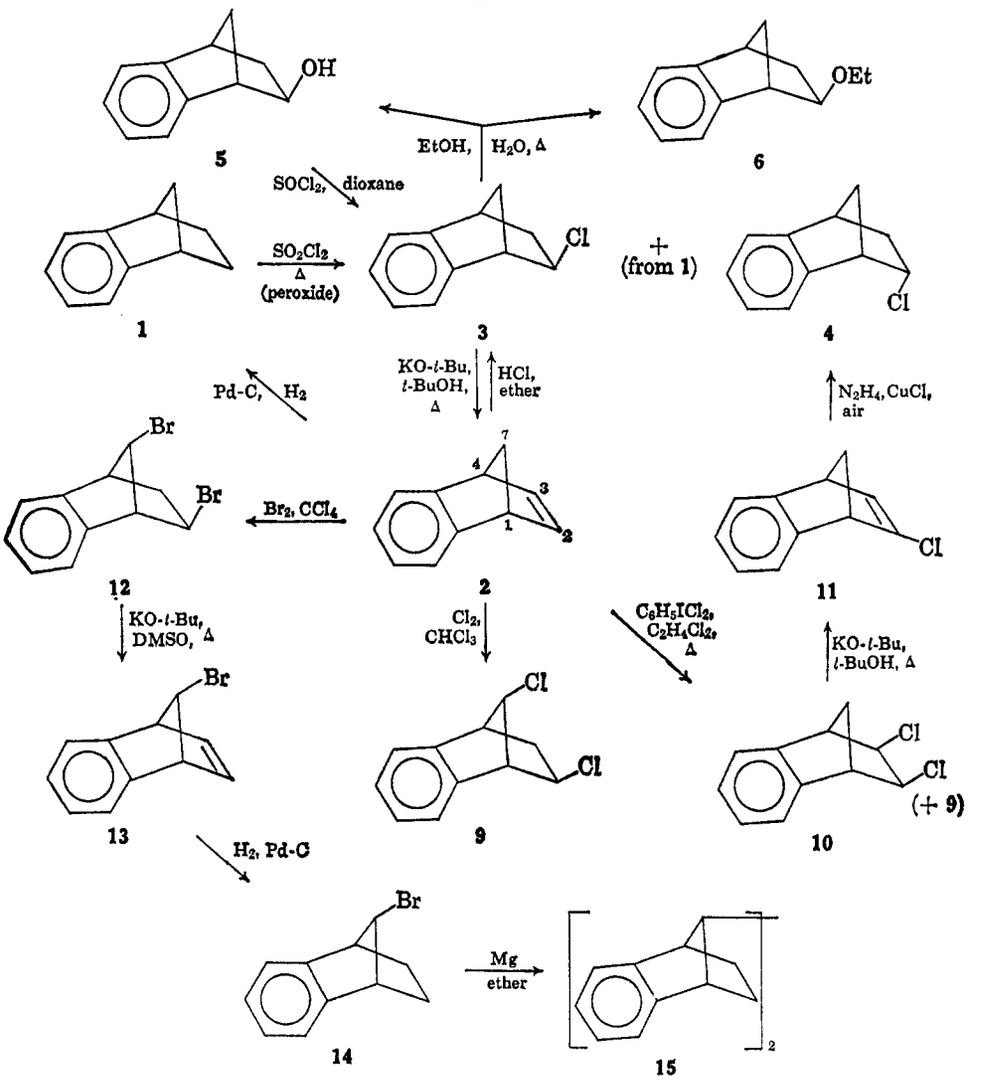
(15) *Cf.* W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 170–176.

(16) While the necessary data for **1** and **2** are lacking, this bridge angle is less than tetrahedral in both norbornane [H. Krieger, *Suomen Kemistilehti*, **B31**, 348 (1958)] and norbornadiene [W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5653 (1956)].

(17) G. S. Hammond and R. W. Todd, *ibid.*, **76**, 4081 (1954).

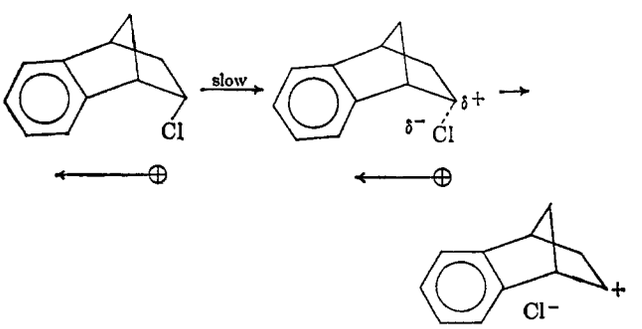
(18) *Inter alia*, M. M. Martin and D. C. De Jongh, *ibid.*, **84**, 3526 (1962).

CHART I



1 3 4 5 6 9 10 11 12 13 14 15

because of steric effects or because the aromatic ring complexed the chlorine atom during its approach from the *endo* side and decreased its reactivity toward abstraction.[19] If this selective abstraction were coupled with a fast transfer prior to configurational inversion of the radical, the *exo* epimer would predominate in the products. More data on radical substitutions in this system are needed, however, to establish this point. The solvolysis of the mixture of **3** and **4** illustrated the well-known solvolytic reactivity of an *exo* isomer compared to the *endo* in 2-norbornyl systems. Bartlett and Giddings[9] have aptly demonstrated this difference in their study of the brosylates of the epimeric 2-benzonorbornenols. The results indicate probable assistance by the aromatic ring in **3**, accelerating its rate relative to that of **4**. The *endo* isomer in fact appeared abnormally unreactive. When finally prepared pure, **4** gave no silver chloride precipitate even on extended reflux with alcoholic silver nitrate. On the other hand, **3** reacted very quickly. This disparity in reactivity made a quantitative comparison of the solvolytic behavior of **3** and **4** quite difficult.[20] The reactivity of **3** is a bit less than that of *exo*-5-norbornenyl chloride. The latter has $k_1 = 1.3 \times 10^{-3}$ min^{-1} at 85° in 80% ethanol,[21] while **3** required a temperature over 100° to produce this rate. It would appear that the norbornene-type double bond exceeds the *ortho*-fused aromatic ring in anchimeric ability in these compounds. Perhaps the electron-rich aromatic ring acts against the necessary charge development in the solvolysis of **4**, as shown, and thereby occasions its noteworthy inertness. There would also be some steric hindrance in **4** to the departure of the *endo* chloride. No estimate can be offered now as to which of these modes of retardation is more important.

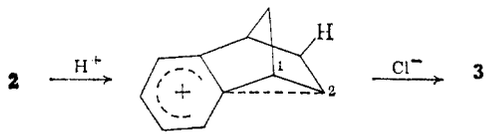


(19) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958). We thank Dr. M. M. Martin (University of Michigan) for several informative discussions of this point.

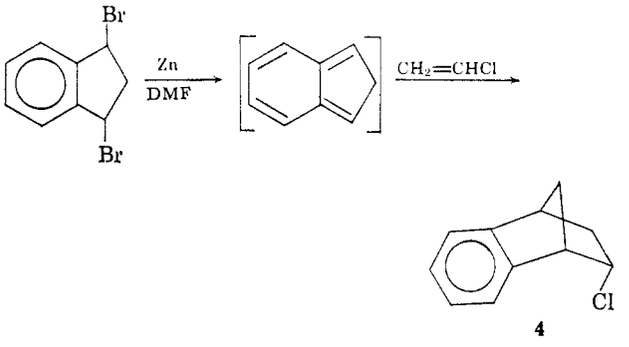
(20) The solvolytic reactivity of these halobenzonorbornenes is under investigation and more quantitative data will be reported later.

(21) J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950); J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954).

The addition of dry hydrogen chloride gas to **2** in ether led to *exo*-2-chlorobenzonorbornene (**3**).[7,22] Nmr, glpc, and infrared analyses indicated that no *endo* isomer **4** was formed. The nmr spectrum of **3** was consonant with its structure, although its analysis proved somewhat more complex than most of the other halo derivatives. Most clearly evident because of its position further downfield of the aliphatic protons was the *endo*-2 proton centered at 228 cps as a partly resolved multiplet.[23] Coupling occurred with the *endo*- and *exo*-3 protons, J = 5–6 and 3–4 cps, respectively, and less so with the *syn*-7 proton, J = 1.5 cps, *via* a long-range mechanism. Such long-range coupling in norbornanes is now well documented.[24] Overlapping of the center lines gave a seven-line multiplet, however, rather than the expected eight-line pattern. Other details may be found in the tables. The infrared spectrum of **3** was very rich and had many differences from that of **4**. Particularly useful in this regard were absorptions at 10.28 and 13.8 μ. The exclusive formation of **3** is perhaps best rationalized *via* the nonclassical cationic intermediate shown. As this intermediate



is symmetrical, attack by chloride occurs equally either at C-1 or C-2 of the molecule. However, either attack produces **3**. The initial proton addition is very likely *exo*[25] and could proceed *via* a protonated double bond π complex. If so, the addition of hydrogen chloride is an *exo,cis* addition. After this work had been completed, an informative article by Cristol and Caple appeared.[7b] They showed by deuterium tracer studies that the symmetrical intermediate mentioned above (or a pair of rapidly equilibrating classical ions that simulate it) was indeed involved in the formation of **3** by this method. In addition, their work showed that an *endo* protonated double-bond π complex was incompatible with the stereochemistry of the deuterated adduct. Formation of *exo*-2-benzonorbornenol (**5**) from **2**[9] by the acid-catalyzed addition of acetic acid followed by saponification is another example of such an addition. This preparation of **5** was duplicated and the alcohol so obtained was converted by means of thionyl chloride in ether followed by heating in dioxane[26] to **3**. The various samples of **3** from **1**, **2**, and **5** were identical in every respect. This ready availability of **3** made its identification and study fairly easy but to identify and characterize the *endo* isomer **4** with certainty also required a *bona fide* sample. To this end, alcohol **5** was epimerized *via* oxidation to the ketone **7** and this was reduced with lithium aluminum hydride to *endo*-2-benzonorbornenol **8**, as described.[9] Reaction of **8** with thionyl chloride as before employed with **5** led to a complex mixture of products, none of which was the desired **4**. As far as was determined, the reaction product contained some unchanged **8**, a material with infrared characteristics of a sulfite ester and, curiously, some 2-benzonorbornenone (**7**). It has been reported recently that *endo*-2-norbornenol afforded a variety of products when treated with thionyl chloride in solvents other than pyridine.[27] Presumably **8** reacted analogously, although this route to **4** was abandoned quickly and no further investigation of the reaction was carried out. The clear difference between **5** and **8** in their reactions with thionyl chloride supports the belief that this reaction proceeds by dissociation of the intermediate chlorosulfite ester to ions which then recombine with loss of sulfur dioxide.[28] The *exo*-chlorosulfite from **5**, on the basis of the easy solvolysis of **3**, would readily undergo such a dissociation. The *endo*-chlorosulfite from **8**, on the other hand, on the basis of the solvolytic inertness of **4**, would not do so. As a consequence, other (as yet unclear) side reactions then predominated in this latter case. The attractive possibility of utilizing "isoindene" as a diene in addition to vinyl chloride was next tried as a method to obtain **4**. Alder and co-workers[29]



have successfully carried out reactions of this type, although the dienophiles employed were better than vinyl chloride, *viz.*, acrylate esters, maleic anhydride, and acrolein. In the present case only indene was isolated from several attempts at the adduction. Further study of the process is warranted, however, because it certainly represents the most direct and simple approach to *endo*-2 substituted benzonorbornenes. In the sequence that eventuated in **4**, the addition of chlorine to **2** was first investigated. Reaction of **2** with chlorine in chloroform led cleanly to *exo*-2-*anti*-7-dichlorobenzonorbornene (**9**), as determined by nmr. This result is the same as that obtained with bromine (see later) and parallels that found by Meinwald and Wiley[30] for bromination of an aromatically substituted benzonorbornene. Cristol and Caple[7b] likewise reported the preponderant formation of **9** in the reaction of **2** with chlorine in carbon tetrachloride. They also observed, however, 4% of the *trans*-2,3-dichloro isomer *via* glpc

(22) G. A. Wiley and L. E. Barstow, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March, 1966, paper 5K.

(23) For some of the many studies in *endo* and *exo* epimer identification by nmr, *cf.* (a) W. D. Kumler, J. N. Shoolery, and F. V. Brutcher, *J. Am. Chem. Soc.*, **80**, 2533 (1958); (b) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); (c) T. J. Flautt and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 3212 (1963); (d) J. C. Davis, Jr. and T. V. Van Auken, *ibid.*, **87**, 3900 (1965).

(24) (a) J. Meinwald and Y. Meinwald, *ibid.*, **85**, 2514 (1963); (b) P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964). See also ref 23d.

(25) Initial *exo* attack in polar addition is the rule in norbornene and derivatives of norbornene. For a discussion, see H. Kwart and J. L. Nyce, *ibid.*, **86**, 2601 (1964). Such is also generally the case in norbornadiene, although exceptions are becoming more common. *Cf.* F. Lautenschlaeger, *J. Org. Chem.*, **31**, 1679 (1966). Examples of additions to **2** are rare at this point, though a fine very recent study has appeared (ref 7b).

(26) E. S. Lewis and C. E. Boozer, *J. Am. Chem. Soc.*, **74**, 308 (1952).

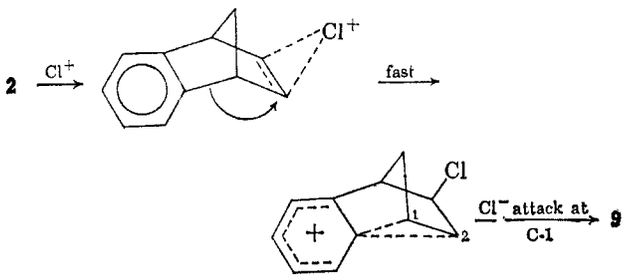
(27) J. K. Stille and F. M. Sonnenberg, *ibid.*, **88**, 4915 (1966).

(28) D. J. Cram, *ibid.*, **75**, 332 (1953).

(29) (a) K. Alder and F. Pascher, *Chem. Ber.*, **75**, 1501 (1942); (b) K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961).

(30) J. Meinwald and G. A. Wiley, *J. Am. Chem. Soc.*, **80**, 3667 (1958). *anti* is used to denote the 7 substituent away from the aromatic ring in **9**.

analysis. The nmr spectrum of **9** was completely in accord with its structure. The *endo*-2 proton exhibited an eight-line pattern centered at 225 cps which could be rationalized in terms of three distinct couplings, those to the *endo*- and *exo*-3 protons (J = 8 and 4 cps, respectively) and the *syn*-7 proton (J = 1.5 cps). This *syn*-7 proton showed a five-line pattern at 238 cps indicating nearly equal coupling (J = 1–1.5 cps) with the two bridgehead protons and the two *endo* protons at C-2 and C-3. An *anti*-proton placement at C-7 was, therefore, ruled out because *anti*-7 coupling to *endo* protons at C-2 or C-3 is not found (see the later discussion of the nmr spectrum of **4**).[31] Furthermore, the nmr spectrum of dibromide **12** was quite similar to that of **9**. Because degradative work on **12** showed the bromines were indeed at C-2 and C-7, this correspondence in nmr spectra between **9** and **12** is believed to establish the structure of **9** even though no further work was done on it in this study. The addition of chlorine probably follows the path shown. This is essentially



the path given for the formation of *exo*-2-*syn*-7-dichloronorbornane from chlorine and norbornene.[32] Both paths involve a delocalized cationic intermediate that undergoes nucleophilic capture largely at one position. Inspection of FMO[33] molecular models of the cation rationalizes this preferential site of capture in that capture at C-1 involves less steric hindrance from the adjacent *exo*-chlorine than does capture at C-2. The powerful anchimeric ability of the aromatic ring probably drives the chloronium ion to the bridged ion quite rapidly, accounting for the absence of products derivable from the chloronium ion. Products from both types of ions are found in the chlorination of norbornene itself.[32] It was, therefore, obvious that a chlorinating agent employing a different mode of addition was needed if **4** was to be obtained. Recourse was had to iodobenzene dichloride, which has been reported to add chlorine to olefins *via* a *cis*-addition mechanism,[34a] although the *trans* adducts obtained on occasion belie this.[34b] Reaction of iodobenzene dichloride with **2** in ethylene chloride led to mostly **9** again, but also to *exo*,*cis*-2,3-dichlorobenzonorbornene (**10**), as well as to a minor, unidentified third product.[35] The nmr spectrum of **10** was fairly simple, exemplifying the symmetry of the molecule. The *endo*-2,3 protons appeared as sharp doublets (J = 1.5 cps) at 237 cps indicating the long-range coupling with the *syn*-7 proton. The splitting and chemical shift confirm the *endo*,*cis* nature of these protons.[36] This coupling was repeated in the B portion of the 7-methylene AB pattern. The B portion (the *syn*-7 proton) was coupled with all bridgehead and *endo* protons and was a doublet of quintets at 116 cps. The A portion (*anti*-7 proton) was a doublet of triplets at 148 cps and, therefore, coupled to the bridgehead and geminal protons only. The bridgehead protons were triplets at 205 cps, indicating that no coupling existed between the bridgehead and *endo*-2,3 protons.[24] The difference in the two chlorination reactions probably does reflect a difference in mechanism. The production of **9** in the second method may be ascribed to the presence of free chlorine formed by dissociation of the iodobenzene dichloride under the conditions used,[37] or to a rearrangement of **10** which, by virtue of its *exo*,*cis* nature, could be thermally labile. While the product mixture was separable by distillation, such separation proved unnecessary because dehydrochlorination conditions were found which left **9** unchanged but which converted **10** to 2-chlorobenzonorbornadiene (**11**); this was fractionally distilled away from the unchanged **9**. The unidentified third component of the mixture was now also absent and it is probable that it too gave **11**. This material was, therefore, possibly *trans*-2,3-dichlorobenzonorbornene.[35] The nmr spectrum of **11** showed clearly one vinyl proton at 383 cps. Two bridgehead protons were present at 218 and 228 cps. The narrower absorption at 218 cps is probably C-1's proton since there is less possibility for line-broadening vicinal coupling here. It is interesting that the 2-chloro substituent apparently caused an upfield shift in both the C-1 proton (+10 cps) and the vinyl proton (some 20 cps upfield from that of **2** itself). Similar behavior has been found in this laboratory for 2-chloronorbornene also. Possibly the recently uncovered[38] diamagnetic anisotropy of the chlorine nucleus is responsible. Two bridge methylene protons (J = 7 cps) were also present at 135 and 151 cps, though which is which has not been determined. The small geminal J value is characteristic of benzonorbornadienes and reflects the widened HCH angle at the bridge.[39] In view of the severe conditions required for the dehydrobromination of **12** (see later), the reluctance of **9** to eliminate hydrogen chloride relative to **10** is understandable. The vicinal chlorines in **10** increase the acidity of the methinyl hydrogens and promote attack by base. At the same time, in the activated complex, the incipient double bond is stabilized by conjugation with the remaining chlorine. Compound **9** has neither advantage. The conversion of **11** to **4** was achieved by use of diimide, generated from hydrazine in air

(31) Davis and Van Auken[23d] suggest that this difference in long-range coupling ability is more valuable for differentiation of the bridge protons than are chemical shift differences. We agree.

(32) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Am. Chem. Soc.*, **76**, 5692 (1954). Only nortricyclyl chloride and the *exo*-2-*syn*-7-dichloride were reported as products by these workers. In a very recent study, M. L. Poutsma [*ibid.*, **87**, 4293 (1965)] found the reaction to be more complex and to follow ionic and radical pathways concurrently. Under various conditions isomeric 2,3-dichloronorbornanes and 5-chloronorbornenes accompany the two products previously described.

(33) Framework molecular orbital.

(34) (a) D. H. R. Barton and E. Miller, *J. Am. Chem. Soc.*, **72**, 370 (1950). (b) S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *ibid.*, **78**, 4939 (1956); R. K. Summerbell and H. E. Lunk, *ibid.*, **79**, 4802 (1957).

(35) *exo*,*cis*- and *trans*-2,3-dichloronorboranes were obtained in the reaction of norbornene with iodobenzene dichloride (M. L. Poutsma[32]).

(36) Compare the *cis*-2,3-dichloronorbornanes:[35] the 2,3-*endo* protons of the *exo* chloride show a doublet (J = *ca.* 2 cps) at 242 cps; the 2,3-*exo* protons of the *endo* chloride show a triplet at 259 cps.

(37) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **80**, 1723 (1958).

(38) G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **38**, 2736 (1963).

(39) K. Tori, R. Muneyuki, and H. Tanida, *Can. J. Chem.*, **41**, 3142 (1963).

in the presence of *cuprous* chloride. Use of the prescribed[40] *cupric* salt failed to yield **4**. The cuprous salt was reduced to finely divided copper *in situ* which then catalyzed the addition of hydrogen from the expected *exo* side, presumably *via* diimide as the hydrogen donor. A recent report in fact mentions the effect of copper metal on hydrazine decompositions to diimide.[41] Reduction of a vinyl halide with diimide has been reported to fail,[42] but another study under other conditions claimed diimide reductions were relatively insensitive to inductive effects and that such halides could be saturated.[43] The structure of **4** seemed certainly established by the nmr spectrum. Analysis of the spectrum was facilitated by the fortuitous separation of all aliphatic protons. A doublet of triplets centered at 264 cps was due to the *exo*-2 proton. Analysis of the splitting was possible on the basis of a 9-cps coupling of this proton to the vicinal *exo*-3 proton and equal couplings of 4 cps between the *exo*-2 proton and the vicinal *endo*-3 and bridgehead (C-1) protons. The appearance of the *exo*-2 proton of **4** some 36 cps downfield from that of the *endo*-2 proton of **3** is in keeping with known *endo,exo* isomers.[23] The bridge methylene protons of **4** exhibited an AB pattern (J = 9.2 cps). The low field-resonance at 107 cps was ascribed to the *syn*-7 proton in the light of accumulated data which indicated additional coupling with the bridgehead protons (J = 1.5 cps) and the *endo*-3 proton (J = 4 cps). This large long-range coupling constant was found when either chlorine or hydroxyl was *endo* at C-2. With these J values the splitting found, a ten-line doublet of doubled triplets with the center lines overlapped in each half could be theoretically matched. The high-field resonance at 89 cps was ascribed to the *anti*-7 proton. This was a doublet of triplets, indicating couplings to the bridgehead and geminal protons only. The shielding effect of the aromatic ring on protons above or below its plane is well established and the downfield position of the *syn*-7 proton relative to the *anti*-7 proton in **4** is anomalous, but not without precedent.[44] This phenomenon is not restricted to **4**, because *endo*-2-benzonorbornenol (**8**) exhibited an analogous nmr spectrum, though the chemical-shift difference between the *syn* and *anti* bridge protons was somewhat smaller here (12 *vs.* 18 cps in **4**). It has been suggested[24b] that the *anti*-7 proton is more sensitive to the stereochemistry of the C-2 substituent than is the *syn*-7 proton. The present data support this view in that the variation in chemical shift for the *anti* proton is greater over the series of compounds studied (Table I). In the infrared spectrum **4** had several differences from **3**, but the absorptions at 9.11 and 10.48 μ were most useful.

The addition of bromine to **2** was mentioned by Wittig and Knauss.[3] Other than its being a dibromide, no definite structure was ascribed to the adduct. Meinwald and Wiley[30] reported the formation of *exo*-2-*anti*-7-dibromo-3′,6′-diacetoxybenzonorbornene upon bromination of 3′,6′-diacetoxybenzonorbornadiene. Addition of bromine in carbon tetrachloride to **2** itself gave only *exo*-2-*anti*-7-dibromobenzonorbornene (**12**). A dibromide of this structure was mentioned also by Cristol and Caple.[7b] Though its mode of formation was not reported it was probably made in the same way as our sample. The nmr spectrum of **12** was in accord with its structure and was very much like that of **9**. Details may be found in the tables. The pathway followed in the formation of **12** is undoubtedly the same as that for the formation of **9** given earlier. Because the dibromides from norbornadiene are toxic,[45] **12** was tested on mice intravenously as a suspension at dosages as high as 200 mg/kg. After twelve hours no overt effects were seen. Dehydrobromination of **12** was achieved only after several attempts. Use of potassium *t*-butoxide in dimethyl sulfoxide at 125° under nitrogen gave *anti*-7-bromobenzonorbornadiene (**13**). The nmr spectrum of **13** showed two vinyl protons as multiplets centered at 402 cps. Only the vinyl proton–bridgehead proton coupling was determined (J = 3.5 cps). Two bridgehead protons at 243 cps were doubled doublets, evidence of coupling to the vinyl protons and the *syn*-7 proton (J = 1.5 cps). The latter was an envelope at 261 cps. The infrared spectrum had a strong band at 14.4 μ characteristic of an unsubstituted norbornene-type double bond. Catalytic hydrogenation of **13** produced *anti*-7-bromobenzonorbornene (**14**). The nmr spectrum of **14** was consonant with its structure but was clouded with multiplets, largely insufficiently resolved for accurate J value determination. The *endo*-2,3 protons were, however, well separated from their geminal protons (74 *vs.* 140 cps, respectively). Both types were doubled doublets ($J_{endo,exo}$ = 10 cps) but most of the other couplings remained obscure. The *trans* vicinal coupling appeared to be *ca.* 3 cps. Two bridgehead protons were present at 202 cps, each coupled to its *exo* vicinal proton (J = 4 cps) and the *syn*-7 proton (J = 1.5 cps). This latter was an envelope at 237 cps consisting of five lines as expected for small couplings (*ca.* 1–1.5 cps) to the two bridgehead and two *endo* protons. One of the aims of this study was the preparation of a variety of *anti*-7 substituted benzonorbornadienes and benzonorbornenes. It was believed that organometallic derivatives of **13** and **14**, or displacement reactions on them, would be an opportune start. However, no organometallic was produced (as evidenced by attempted carbonation to an acid) from **14** on treatment with any of several metals in any of several solvents. Likewise, **13** failed in one attempt to form a Grignard reagent. Displacements with cyanide salts on **14** under a variety of conditions left **14** largely unchanged, a curious result in view of the successful reaction of sodium cyanide with *anti*-7-chloronorbornene.[46] The resistance of **14** to S$_N$2 displacement by cyanide is possibly the result of the small $C_1C_7C_4$ angle.[16] In the activated complex for the S$_N$2 process this angle should widen to *ca.* 120°. The rigidity of **14** precludes this and consequently retards reaction, but why the S$_N$1 route earlier invoked[46] failed here is not known. The reaction of **14** with magnesium under several sets of conditions led to the coupling product **15**, although its structure must be considered provisional. The nmr spectrum of **15**

(40) E. J. Corey, W. L. Mock, and D. J. Pasto, *Tetrahedron Letters*, 347 (1961).

(41) J. Wolinsky and T. Schultz, *J. Org. Chem.*, **30**, 3980 (1965).

(42) E. E. VanTamelen, M. Davis, and M. F. Dean, *Chem. Commun.*, 71 (1965).

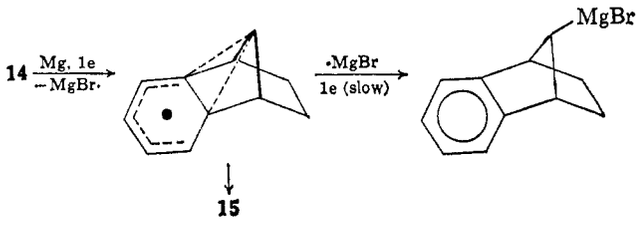
(43) J. W. Hamersma and E. I. Snyder, *J. Org. Chem.*, **30**, 3985 (1965).

(44) Laszlo and Schleyer[24b] have reported such a "reversal" for the bridge protons in *endo*-5-chloronorbornene.

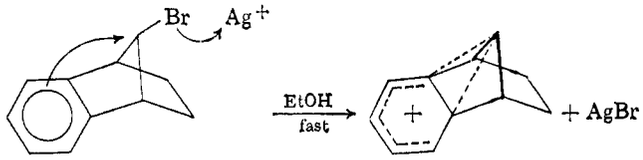
(45) S. Winstein, *J. Am. Chem. Soc.*, **83**, 1516 (1961).

(46) H. Tanida and Y. Hata, *J. Org. Chem.*, **30**, 977 (1965).

(Table I) was an array of multiplets. Identical coupling behavior has been recently reported for 7-chloronorbornadiene.[47] This coupling reaction of **14** could be the result of an especial stability in the radical formed first through reaction with the magnesium. Such a radical might have the second electron



donation to it be rather slow and, as the radical concentration on the metal surface is high, undergo dimerization instead. The resistance to organometallic formation by **13** and **14** and (the apparent) lack of SN2 reactivity by **14** is not matched in solvolytic reactivity. Ethanolic silver nitrate afforded a precipitate at 25° quickly with **13**, as well as **12**. Although **14** was much slower at this temperature, warming readily precipitated silver bromide.[20] The reactivity of the 7-bromides is analogous to the reactivity of the *anti*-7 brosylate.[9] The greater reactivity of **13** compared to **14** may be ascribed to the presence of the double bond, a known rate-enhancing structural feature.[9] Both **13** and **14** probably involve a push-pull mechanism as shown. The reactivity of **12** (and **9**) in this process



leads one to wonder which halogen is more reactive. On the basis of the reactivity of **3** and **14**, and the known superiority of the σ route over the π route for aromatic anchimeric participation,[9] the *exo*-2 halogen is predicted to be more labile. The quantitative determination of these reactivities as well as other transformations of these halides will constitute portions of later papers in this series.

Experimental Section

Melting and boiling points were not corrected for stem exposure. The former were taken on a Fisher-Johns block or in a Thomas-Hoover melting point apparatus. Spectra were determined on Perkin-Elmer Model 21 Infracord, Beckman IR-5A (infrared) and DK-2 (ultraviolet), and Varian Associates A-60 and A-60A (nmr) instruments. Only medium to strong infrared bands are given. Those in italics were most useful in the differentiation of isomers. Glpc was performed on a Wilkens Aerograph A-90P instrument. Analyses were performed by Micro-Tech Laboratories, Skokie, Ill., and by Abbott Laboratories, North Chicago, Ill.

Benzonorbornadiene (**2**) was prepared by the methods of Wittig and Knauss[3] and (better) Friedman and Logullo:[48] 31–64%, bp 55–56° (0.5 mm) and 64–68° (4.0 mm), n^{26}D 1.5620; lit. bp 88–89° (19 mm[9]) and 82.5–83° (12 mm[3]); λ^{neat} (μ), 3.26, 3.36, 3.43, 3.50, 6.38, 6.74, 6.88, 6.93, 7.69, 8.18, 9.94, 12.05, 13.22, 13.73, 14.35; $\lambda^{max}_{methanol}$ (mμ), 261 (ϵ 440), 267 (525), 275 (461); nmr spectrum in agreement with that published.[49]

Benzonorbornene (**1**) resulted from **2** by hydrogenation over a palladium-on-charcoal catalyst at ambient temperature: 90%, bp 67–70° (1 mm), n^{26}D 1.5491; lit. bp 80–82° (10 mm[50]) and 78–79° (12 mm),[3] n^{21}D 1.5545;[3] λ^{neat} (μ), 3.29, 3.31, 3.40, 3.50, 6.79, 6.85, 6.90, 7.78, 8.65, 9.00, 9.85, 10.51, 11.49, 12.05, 12.32, 13.35, 14.04; $\lambda^{methanol}_{max}$ (mμ), 258 (ϵ 619), 264 (957), 270 (1051); nmr spectrum in accord with the literature.[49]

Radical chlorination of 1 was carried out with one-half the stoichiometric amount of chlorinating agent to avoid polychlorination. Compound **1** (5.3 g, 36 mmoles) was heated at reflux for 2 hr with sulfuryl chloride (freshly distilled, 1.48 ml, 18 mmoles) and a few crystals of benzoyl peroxide. The mixture was washed with sodium bicarbonate solution and twice with water. Distillation afforded a colorless product (2 g, 67%, bp 64° at 0.35 mm, n^{26}D 1.5657) that was shown by glpc and nmr to contain 92–93.5% of **3** and 6.5–8% of **4**. A small amount of **11** was also observed in glpc, but no vinyl protons were seen in the nmr spectrum. It is believed that some contaminating **10** (or other dichloride) eliminated hydrogen chloride under the glpc conditions to account for this. An analytical sample was collected by glpc.

Anal. Calcd for $C_{11}H_{11}Cl$: C, 73.95; H, 6.20; Cl, 19.85. Found: C, 73.93; H, 6.21; Cl, 19.81.

A similar reaction run for 35 min showed 14% product by glpc. No difference in composition was detected. The product gave an immediate positive test with alcoholic silver nitrate at room temperature. The presence of both **3** and **4** could be seen also in the infrared spectrum, but quantitative determinations were not done. Similar results were obtained with trichloromethanesulfonyl chloride[5] and benzoyl peroxide under the above conditions. Use of chlorine and ultraviolet light was more difficult to control. Polychlorination appeared to occur (products with long retention times were observed), but the monochloride again was largely the *exo* epimer **3**. Dehydrochlorination was achieved by refluxing a mixture of the chlorides (0.5 g, 2.8 mmoles) under nitrogen for 3 days with potassium *t*-butoxide (13 mmoles) in dry *t*-butyl alcohol (25 ml). Processing the reaction *via* glpc showed that **2** was formed to the extent of 84%, with the remainder being unchanged starting material.

***exo*-2-Chlorobenzonorbornene** (**3**) was prepared by the addition of dry hydrogen chloride gas to **2** (9 g, 64 mmoles) in anhydrous ether (100 ml) at 0°. After saturation the solution was allowed to stand overnight. Dilute sodium bicarbonate was added with stirring and the mixture was extracted with ether. The ether solution was dried and distilled to obtain **3** as a colorless oil: 6.35 g, 70%, bp 66° (0.75 mm), n^{26}D 1.5641; lit.[7b] bp 55° (0.2 mm), n^{25}D 1.5664; λ^{neat} (μ) 3.31, 3.40, 3.51, 6.87, 6.94, 7.71, 7.81, 7.91, 8.02, 8.62, 9.35, 9.88, 10.10, *10.28*, 10.70, 10.90, 11.28, 11.40, 11.90, 12.20, 13.30, *13.80*, 14.10, 15.10; $\lambda^{methanol}_{max}$ (mμ), 259 (ϵ 660), 265 (1023), 272 (1121); nmr spectrum in Table I. **3** was also prepared by the addition of *exo*-2-benzonorbornenol (**5**,[9] 2.2 g, 13.8 mmoles) in ether (50 ml) to a solution of thionyl chloride (4 ml) in further ether (50 ml) at −80°.[26] After the addition hydrogen chloride was removed under vacuum and the solution was kept overnight. Dioxane (250 ml) was added and the solution was refluxed under nitrogen until no further sulfur dioxide was evolved. The material was poured into water and extracted with several portions of ether. The dried ether solution was distilled to afford **3** in 89% yield.

***exo*-2-*anti*-7-Dichlorobenzonorbornene** (**9**) was prepared by portionwise addition of an equivalent of chlorine dissolved in chloroform to **2** (37.9 g, 0.267 mole) with stirring at 0°. The chloroform was removed on a rotary evaporator and the residue was distilled to give recovered **2** (30.5%) and **9** as a colorless oil: 25.1 g, 64% based on consumed **2**, bp 100–115° (0.75 mm); lit.[7b] bp 86° (0.2 mm), mp 50–51°; λ^{neat} (μ) 3.4, 6.86, 7.72, 7.87, 10.3, 10.73, 11.17, *11.68*, *12.0*, 12.52, *12.85*, 13.2, 13.5, 13.8, *15.25*; nmr spectrum in Table I. The spectra of this material matched those of the lower-boiling product obtained in the reaction of **2** with iodobenzene dichloride (see below).

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

(48) This method employed either benzenediazonium carboxylate or *o*-carboxybenzenediazonium chloride as the benzyne precursor used to adduct with cyclopentadiene. We thank Dr. Friedman (Case Institute) for unpublished directions for both of these preparations. *Cf.* L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963).

(49) K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji, and H. Tanida, *Can. J. Chem.*, **42**, 926 (1964).

(50) P. Bruck, *Tetrahedron Letters*, 449 (1962).

Chlorination of 2 with iodobenzene dichloride was performed in ethylene chloride[51] (500 ml) containing the hydrocarbon (15.1 g, 0.106 mole) and the chlorinating agent (freshly made,[52] 60 g, 0.218 mole) by slowly heating to reflux with stirring. The solution became homogeneous as it was heated for a further 30 min. The solvent was removed and the residue fractionated. Iodobenzene was first obtained, followed by a mixture of dichlorides as a pale yellow oil, 21 g, 93%, bp 89–91° (0.25 mm).

Anal. Calcd for $C_{11}H_{10}Cl_2$: C, 62.00; H, 4.72. Found: C, 62.12; H, 5.01.

A comparison of spectra showed that this product was mainly **9** (*ca.* 65%), with some **10** (*ca.* 30%), and a very small amount (*ca.* 5%) of a third, unidentified (and presumably isomeric) compound. A subsequent redistillation of a portion of this mixture from another preparation afforded a lower-boiling fraction of essentially pure **9** [bp 96–99° (0.35 mm), infrared and nmr spectra identical with those obtained earlier (see above)], followed by a higher boiling, minor fraction of nearly pure *exo,cis*-2,3-dichlorobenzonorborene (**10**): bp 107–110° (0.3 mm), solidified on standing; λ^{neat} (μ) 3.38, 6.82, 7.71, 7.8, 7.92, 10.3, *11.02*, 11.15, 12.42, 12.53, 13.17, 13.56, *14.95*; nmr spectrum in Table I.

2-Chlorobenzonorbornadiene (**11**) was obtained from the mixture above (21 g, 98.6 mmoles) by treatment with potassium *t*-butoxide (20 g, 0.18 mole) in *t*-butyl alcohol (250 ml) under reflux with stirring for 4 days (shorter times were ineffective). Most of the solvent was removed on a rotary evaporator and the residue was taken up in ether, filtered through Celite, decolorized with charcoal, dried, and distilled to give **11** as a pale yellow oil: 6 g, 34.5%, bp 62–64° (0.7 mm), $n^{7}D$ 1.5803; λ^{neat} (μ) 3.31, 3.40, 3.45, 3.52, 6.36, 6.93, 7.88, 8.11, 8.38, 8.79, 9.61, 10.0, 11.3, 11.9, 12.5, 12.75, 13.3, 13.9, 15.9; nmr spectrum given in Table I.

Anal. Calcd for $C_{11}H_9Cl$: C, 74.79; H, 5.14. Found: C, 74.93; H, 5.16.

A higher boiling fraction [*ca.* 50%, bp 92–94° (0.3 mm)] of essentially pure **9** was recovered.

endo-**2-Chlorobenzonorbornene** (**4**) was made at 25° by allowing an air stream to bubble into a stirred solution of hydrazine (95%, 9 g) and **11** (4.5 g, 25.5 mmoles) in ethanol (95%, 200 ml) containing suspended cuprous chloride (freshly made, 0.5 g). The initially white cuprous salt turned brown and then black as the reaction was continued for 48 hr. The material was filtered, freed of ethanol by flash evaporation, and taken up in ether. The ether solution was washed, dried and then distilled through a small Vigreux column to afford first some unreacted **11** and then **4** as a colorless oil: 1.01 g, 22.2%, bp 66–68° (0.45 mm), $n^{9}D$ 1.5730, free of **11** by glpc; λ^{neat} (μ) 3.42, 3.52, 6.88, 6.93, 7.61, 7.8, 7.89, 8.47, 8.80, 8.88, *9.11*, 9.88, 10.1, *10.48*, 10.7, 10.85, 11.5, 12.03, 13.3, 14.16, 15.05; nmr spectrum given in Table I.

Anal. Calcd for $C_{11}H_{11}Cl$: C, 73.95; H, 6.20. Found: C, 74.00; H, 6.24.

Compound **4** failed to give a precipitate with alcoholic silver nitrate even on heating 15 min. Other attempts to synthesize **4** merit a mention. Reaction of *endo*-2-benzonorbornenol (**8**)[9] with thionyl chloride and dioxane exactly as described above for the *exo* epimer lost sulfur dioxide slowly and incompletely and produced a sulfurous-smelling oil, apparently a mixture of benzonorbornenone (**7**, infrared spectrum 5.82 μ, 2,4-DNP mp 173–174°, mixture melting point with authentic sample undepressed), starting alcohol (infrared spectrum 3.0 and 9.5 μ) and perhaps a sulfite ester (infrared spectrum 8.3–8.6 μ br). Reaction of 1, 3-dibromoindan (mp 108–109°, lit.[29b] mp 110°) with zinc dust and gaseous vinyl chloride in dimethylformamide (DMF) or the same in liquid vinyl chloride gave only indene as an identifiable product.

Glpc retention times (in minutes) of the various monochlorides were determined on a Reoplex 400 column (20% on 60–80 Chromosorb P, 5 ft × 0.25 in.) at 172° with a helium flow of 60 ml/min. The times follow: **11**, 9.6; **3**, 10.5; **4**, 15.3.

Solvolysis Studies. All kinetic runs were made at 104 ± 0.5° using *ca.* 0.04 *M* substrate plus 2 equiv of sodium acetate dissolved in 80:20 ethanol–water (v/v) using the sealed ampoule technique. Chloride ion release was followed by the Volhard method, plotting ln milliliters of SCN^- *vs.* time. The reactions were followed to 65–75% completion. Solvolysis of pure **3** had $k_1 = 1 \times 10^{-3}$ min^{-1} while pure **4** was inert. The radical chlorination of **1** gave a product with $k_1 = 0.9 \times 10^{-3}$ min^{-1}.[53] Omission of sodium acetate and rate determination by pH gave erratic results. Collected material from several solvolyses was separated by glpc and found to be *exo*-2-benzonorbornenol (**5**) and its ethyl ether **6** in the expected ratio of 1:4 by comparison with authentic samples. *exo*-**2-Ethoxybenzonorbornene** (**6**) was prepared for this purpose from **5** using sodium hydride in benzene followed by ethyl sulfate: 43%, bp 93° (0.25 mm), $n^{26}D$ 1.5660; λ^{neat} (μ) 3.3, 3.43, 6.77, 6.82, 7.27, 7.7, 7.77, 7.93, 8.90, 9.00, 9.15, 13.3; $\lambda_{max}^{methanol}$ (mμ) 258 (ϵ 752), 265 (912), 271 (912); nmr spectra (cps) 73 t (CH_3CH_2O), 90–140 m (ring CH_2), 190–240 m (CH_3CH_2O at 205 q, the remainder being the bridgehead and >C*H*-OEt protons), and 425 m (Ar-H).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.50. Found: C, 82.98; H, 8.80.

exo-2-*anti*-**7-Dibromobenzonorbornene** (**12**) was prepared by the dropwise addition of bromine (24 g, 0.3 mole) in carbon tetrachloride (175 ml) to a stirred solution of **2** (20 g, 0.14 mole) in further carbon tetrachloride (75 ml) with cooling such that the temperature remained under 10°. After the addition the solution was stirred for 1 hr as it came to room temperature. The solvent and excess bromine were evaporated under vacuum and the oily residue was taken up in hot ethanol (95%, 100 ml) and clarified with charcoal. After standing overnight in the refrigerator the solution deposited **12** as white crystals: 36 g, 87.5%, mp 76–77°; λ^{CHCl_3} (μ) 3.32, 6.89, 6.96, 7.75, 7.85, 8.0, 8.7, 8.81, 8.91, 9.89, 10.4, 10.8, 11.23, 11.9, 12.1, 14.1; nmr spectrum given in Table I.

Anal. Calcd for $C_{11}H_{10}Br_2$: C, 43.74; H, 3.33. Found: C, 43.97; H, 3.12.

Compound **12** reacted quickly at 25° with alcoholic silver nitrate.

anti-**7-Bromobenzonorbornadiene** (**13**) resulted from the portionwise addition of **12** (9 g, 0.03 mole) in dimethyl sulfoxide (freshly distilled from lithium aluminum hydride, 15 ml) to a solution of potassium *t*-butoxide (freshly made, 3.3 g, 0.03 mole) in further dry dimethyl sulfoxide (70 ml) with stirring at 125° under nitrogen. After the addition heating was continued for 15 min. The cooled solution was poured into water and extracted with three 50-ml portions of chloroform. The dried extracts were distilled to afford **13** as a pale yellow oil that readily solidified: 3.3 g, 67%, bp 94–96° (1 mm), mp 53–54°; λ^{CHCl_3} (μ) 3.22, 3.3, 6.9, 7.7, 8.3, 11.12, 11.5, 12.0, 14.4; nmr spectrum given in Table I.

Anal. Calcd for $C_{11}H_9Br$: C, 59.75; H, 4.10; Br, 36.14. Found: C, 59.64; H, 4.32; Br, 36.34.

Compound **13** reacted immediately at 25° with alcoholic silver nitrate. When potassium t-butoxide was employed in t-butyl alcohol at reflux or in dimethyl sulfoxide at 55° recoveries of 89 and 83.5%, respectively, of **12** were obtained.

anti-**7-Bromobenzonorbornene** (**14**) was the product of the catalytic hydrogenation at 55° of **13** (3.33 g, 15 mmoles) in ethanol (95%, 100 ml) using palladium-on-charcoal catalyst (5%, 0.35 g). Isolation in the usual way gave **14** as a colorless oil which eventually solidified: 3.3 g, 95%, bp 107–108° (2.5 mm), mp 33–34°; λ^{CHCl_3} (μ) 3.33, 6.85, 7.8, 7.97, 8.66, 9.0, 9.9, 10.8, 11.4, 11.86, 12.22, 14.2; nmr spectrum given in Table I.

Anal. Calcd for $C_{11}H_{11}Br$: C, 59.22; H, 4.97; Br, 35.81. Found: C, 59.34; H, 5.25; Br, 35.77.

Compound **14** was slow to react at 25° with alcoholic silver nitrate. Gentle warming, however, readily developed a precipitate.

Bis(*anti*-**7-benzonorbornene**) (**15**) formed when a mixture of **14** (4.4 g, 0.02 mole), magnesium turnings (1.5 g, 0.06 g-atom), and a crystal of iodine in dry ether (200 ml) was refluxed with stirring under nitrogen for 2 hr. The reaction was quenched with aqueous, saturated ammonium chloride solution and the precipitate was collected and recrystallized from 95% ethanol. Compound **15** formed a white crystalline mass: 2.4 g, 83.5%, mp 173–174°; λ^{CHCl_3} (μ) 3.26, 3.4, 3.5, 6.84, 6.9, 7.88, 8.0, 8.7, 9.1, 9.9, 11.45, 12.4; nmr spectrum given in Table I.

Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.01; H, 7.82.

(51) The method of B. S. Gravey, Jr., L. F. Halley, and C. F. H. Allen, *J. Am. Chem. Soc.*, **59**, 1827 (1937).

(52) H. J. Lucas and E. R. Kennedy, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 482.

(53) Cristol and Caple[7b] report a somewhat faster k_1 for **3** (2.2×10^{-5} sec^{-1}) at 103.5° under these conditions with no drift in rate to beyond 90% reaction.

Similar results were found with several variations of this procedure and also when tetrahydrofuran was the solvent. Bromide **14** was recovered from attempts to treat it with ethereal *n*-butyllithium at −40, 0°, or 25° (59, 59, and 64.5% recovery, respectively); with *t*-butyllithium in ether at −80 or 0° (57 and 67% recovery); with lithium ribbon under reflux in any one of ether, tetrahydrofuran, or cyclohexane solvents (73, 68, and 66% recovery); with lithium shot in the presence of sodium in hot cyclohexane (68% recovery); with magnesium turnings and tetrahydrofuran under reflux in either toluene (79% recovery) or xylene (78% recovery). No other organic products could be isolated from these attempts upon carbonation and work-up. An attempt to prepare the Grignard reagent from **13** exactly as described for the preparation of **15** led to recovered **13** (74%).

Attempted Displacements on 14. The following reactions on **14** were attempted under reflux for 26 hr without success: potassium cyanide with a trace of potassium iodide in absolute ethanol (66% recovery of **14**); the same process in dimethylformamide (56.5% recovery); cuprous cyanide in the presence of copper bronze in dimethyl sulfoxide (53% recovery).

Registry No.—**1**, 4486-29-7; **3**, 7605-04-1; **4**, 7605-05-2; **9**, 7605-06-3; **10**, 7605-07-4; **11**, 7605-08-5; **12**, 7605-09-6; **13**, 7605-10-9; **14**, 7605-11-0; **15**, 7605-12-1; **2**, 4453-90-1; **6**, 7605-14-3.

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The Benzidine Rearrangement. VIII.[1,2] The Rearrangement and Disproportionation of 4,4′-Di-*t*-butylhydrazobenzene and 4-*t*-Butyl-4′-chlorohydrazobenzene

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The products and rates of disappearance of 4,4′-di-*t*-butylhydrazobenzene (I) at 0° and 4-*t*-butyl-4′-chlorohydrazobenzene (II) at 25° in acidic 95% ethanol have been determined. Rearrangement to an *o*-semidine, accompanied by 40–50% disproportionation, occurred in each case. Neither the rates of disappearance of I and II nor the relative amounts of rearrangement and disproportionation were affected by changing the initial concentration of the hydrazo compound. The disappearance of I is second order in acid; that of II has an order 1.9 in acid. The concentration of the acid did not seriously affect the ratio of the amounts of rearrangement and disproportionation, with the exception of an increase in the extent of rearrangement of II at the highest acid concentration used. It is concluded (1) that steric hindrance by *para* substituents is not a factor in determining the order in acid, and (2) that the role of an intermediate in the rearrangement of hydrazoaromatics cannot be ignored. The latter conclusion is discussed in the following paper (part IX).

Since Carlin and Odioso[3] showed that the rearrangement of *o*-hydrazotoluene was kinetically 1.6 order in acid, information has been slowly gathered to explain this fractional acid dependence. Other cases have come to light. Dewar and McNicoll[4] have reported 1.58 for 4-chloro-4′-methylhydrazobenzene and 1.51 for 4-*t*-butyl-4′-chlorohydrazobenzene. In a series of papers, Banthorpe, Hughes, and Ingold[5] have shown first-, second-, and varied-order acid dependences among the hydrazonaphthalenes. They have also placed on a firm footing the kinetic dichotomy of the benzidine rearrangement, first proposed by Blackadder and Hinshelwood,[6] and confirmed by White and Preisman.[7] Thus, they have shown that where fractional acid dependence prevails, the rearrangement will go toward first-order acid dependence as acidity is lowered and toward second-order as it is raised.

In spite of the settling of the kinetic features of the benzidine rearrangements it is still necessary to know why the order in acid may vary from one compound to another. Dewar[8] has proposed that steric effects owing to bulky *p*-substituents would be one of the factors leading to mixed orders in acid. The basis for this proposal is the π-complex theory of the benzidine rearrangement. In this theory a series of π complexes is proposed, each complex corresponding with a product type, *e.g.*, benzidine, semidine, diphenyline, that may arise from a hydrazobenzene. It is predicted that bulky *para* substituents would cause rotation of the π-complexed halves of the protonated hydrazo molecule to a sterically favorable configuration. The theory, which describes the interconversions of the several π complexes, also requires that such a steric effect would result in a lowering of the acid order. Dewar and McNicoll concluded that their results with 4-chloro-4′-methylhydrazobenzene and 4-*t*-butyl-4′-chlorohydrazobenzene were in accord with predictions. While recognizing that the 4-*t*-butyl-4′-chloro isomer might have special steric properties, we were unable to accept that a steric effect was responsible for the difference between the 4-chloro-4′-methyl isomer (order 1.58) and the similarly sized *p*-hydrazotoluene, for which Carlin and Wich[9] reported an acid dependence of 2, a dependence which has been confirmed.[10] There-

(1) Part VII, H. J. Shine and J. P. Stanley, *Chem. Commun.*, 294 (1965).

(2) Taken from the Ph.D. Thesis of J. T. Chamness, Texas Technological College, Aug 1963. Support from the Robert A. Welch Foundation and the National Science Foundation (Grant No. G-14551) is gratefully acknowledged.

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