Bridged Polycyclic Compounds. XLVIII. The Proton Magnetic Resonance Spectra and Mass Spectra of Some Disubstituted Benzonorbornenes and Monosubstituted Benzonorbornadienes[1]

STANLEY J. CRISTOL AND GUENTER W. NACHTIGALL

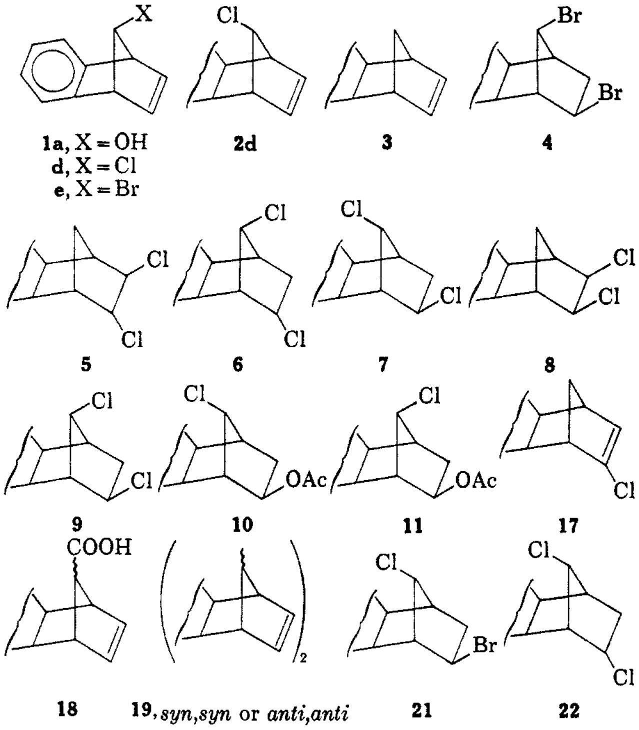
Department of Chemistry, University of Colorado, Boulder, Colorado 80302

Received May 9, 1967

This paper deals with the pmr and some mass spectral aspects of benzonorbornene and benzonorbornadiene derivatives, the preparation and some of the chemistry of which are described in a concurrent paper.[1] Chemical shifts and spin–spin coupling constants have been determined for all compounds having spectra amenable to a first-order analysis. The spectra of isomeric and other closely related benzonorbornene derivatives form internally consistent sets and are presented as further evidence for the structures assigned in the concurrent paper. For benzonorbornadiene derivatives, only certain ones of the coupling constants could be assigned on a first-order basis, but assignment of chemical shifts presented no problems. The pmr spectra of both types of derivatives are closely analogous to those of the norbornyl and dehydronorbornyl systems, with which they are compared. Mass spectrometry of dihalobenzonorbornenes has proved extremely useful in establishing the presence or absence of a halogen (chlorine or bromine) substituent at the 7 position. Strong peaks due to fragments corresponding to the isoindene cation radical (substituted or unsubstituted) appear to arise by a retro Diels–Alder fragmentation of the molecular ion. These peaks were found to be of diagnostic value in distinguishing rearranged from unrearranged halogen adducts of benzonorbornadiene. Other characteristic features of the mass spectra are discussed in terms of the fragmentation patterns likely to be involved. Relatively strong molecular ion peaks were observed in all cases and these as well as structural information from the spectra further support the structures assigned in the concurrent paper.

In connection with the work reported in ref 1, we have made use of both pmr and mass spectrometry to aid in the elucidation of structures. The nature of the spectral data that we acquired is such as to be discussed best not in conjunction with each single structure, but rather as a whole because we were largely dealing with either isomeric (epimeric) or closely related compounds differing only in the nature of the substituents. The pmr as well as the mass spectral data form internally consistent sets and, in the case of the pmr spectra, the structural assignments on the basis of what is known about the norbornyl and dehydronorbornyl systems are reinforced by the mutual exclusiveness of the spectra of isomeric or epimeric compounds. To facilitate reference to the concurrent paper, we will use here the same numbering of structures that was assigned there. Mass and/or pmr spectra for compounds 2d, 21, and 22, which were obtained in small quantities in separate, unpublished work,[2] are included for comparative purposes. The structures for all compounds treated are listed in Chart I. While all structures assigned appear to be firmly established, some ambiguities remain for the spin–spin coupling constants of benzonorbornadiene derivatives. We are hoping to clear these up by a computer analysis of the spectra involved.

CHART I
SOME DERIVATIVES OF BENZONORBORNENE AND BENZONORBORNADIENE (BENZENE RINGS OMITTED)



Proton Magnetic Resonance Spectra.—All pmr spectra were recorded on a Varian A-60 spectrometer in carbon tetrachloride solution, unless indicated otherwise. Chemical shifts with respect to tetramethylsilane internal standard are listed in Table I. "Observed" coupling constants are listed in Table II for all cases in which they could be determined by a first-order analysis. The protons are designated as indicated on p 3740.

Not all compounds were available in a pure state. It was nevertheless possible to recognize the resonances associated with the major component and make assignments. In the cases of compounds 7 and 10, a com-

---

(1) Previous paper in series: S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3727 (1967).

(2) (a) Both **2d** and **22** were isolated in small amounts from attempts to dehydrosulfonoxylate *exo*-5-(*syn*-7-chloro)benzonorbornenyl *p*-bromobenzenesulfonate to **2d** by prolonged heating in *sym*-collidine. Compound **22** appeared to be the result of S_N2 displacement by chloride ion (from dissociation of **2d**) of the *exo*-5-sulfonoxy group. The structure of **22** was assigned on the basis of its mass spectrum (*vide infra*), which is that of a 5,7-dichlorobenzonorbornene, and of its infrared spectrum, which was clearly different from those of the remaining three 5,7-dichlorobenzonorbornenes, **6**, **7**, and **9**, which had already been identified. The practical preparation of **2d** from the sulfonate ester has been perfected since this paper was written. It, as well as the solvolytic behavior of **2d**, will be the subject of a forthcoming paper. (b) Crystalline **21**, mp 79–80°, was obtained in about 25% yield from the treatment of *syn*-7-chloro-*exo*-5-benzonorbornenol with triphenylphosphine dibromide in acetonitrile according to a published procedure (see G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964), and G. A. Wiley, B. M. Rein, and R. L. Hershkowitz, *Tetrahedron Letters*, 2509 (1964)). Its structure is assigned by pmr and mass spectra (*vide infra*) as well as by satisfactory elemental analysis.

TABLE I

NMR SPECTRA OF BENZONORBORNENES AND BENZONORBORNADIENES
(CHEMICAL SHIFTS IN τ UNITS, TMS REFERENCE)

Compound[a]	H-1	H-4	H-5x	H-5n	H-6x	H-6n	H-7a	H-7s	Aromatic protons	Other
					Benzonorbornenes					
6	6.55 bm[e]	6.33 nm	Br	6.30 4 d	7.16 2 t	7.89 2 d	Br	5.94 qui	2.88 s	
9	6.60 bm	6.46 nm	Cl	6.27 4 d	7.33 2 t	7.93 2 d	Cl	6.03 qui	2.88 s	
11	6.63 bm	6.48 nm	OAc	5.44 4 d	7.64 2 t	8.09 2 d	Cl	6.02 qui	2.91 s	$-CH_3$, 8.00 s
7	6.65 bm	6.51 nm	Cl	6.24 2 d	~7.75 2 t	~8.0 2 d	5.33 t	Cl	2.92 s	
21	6.62 bm	6.40 nm	Br	6.22 2 d	7.60 2 t	7.94 2 d	5.26 t	Cl	2.87 s	
10	6.68 bm	6.57 nm	OAc	5.37 2 d	7.85–8.40 (complex pattern)		5.50 t	Cl	2.87 s	$-CH_3$, 8.02 s
6	6.72[b] bm	6.53 bm	5.17 2 t	Cl	7.12 4 d[c]	8.72 4 d	Cl	6.06 qua	2.83 s	
5	~6.62 (overlapping m)	~6.62	5.56 2 d	Cl	Cl	6.38 t	7.67 2 t	7.94 2 qua	2.83 s	
8	6.55 t	6.55 t	Cl	6.01 d	Cl	6.01 d	7.47 2 t	8.01 2 qui	2.87 A_2B_2	
					Benzonorbornadienes					
				H-5	**H-6**					
3 (neat)	6.41 qui	6.41 qui		3.44 t	3.44 t		7.93 sm	7.93 sm	3.13 A_2B_2	
1e	6.00 qua	6.00 qua		3.28 sm	3.28 sm		Br	5.68 7-lm	2.87 A_2B_2	
1d	6.10 qua	6.10 qua		3.42 sm	3.42 sm		Cl	5.85 7-lm	2.98 A_2B_2	
1a	6.23 qua	6.23 qua		3.39 sm	3.39 sm		OH	6.11 m	2.97 A_2B_2	–OH, 6.94 s
2d	6.18 qua	6.18 qua		3.27 t	3.27 t		5.58 t	Cl	2.92 A_2B_2	
18[g]	5.83 qua	5.83 qua		3.25 it	3.25 it		(COOH) ↔	6.72 it	2.90 A_2B_2	–COOH, 0.3–0.6, br band
19[h]	6.35 t	6.35 t		3.44 it	3.44 it		7.13 ↔ s	(7-b)[d]	2.97 A_2B_2	
17	6.16 bm	6.35 nm		Cl	3.55 2 t		7.47 2 t	7.76 6 d	2.90 im	

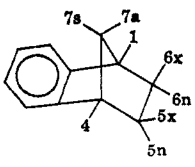
[a] Grouped according to substituent position to facilitate intercomparison. Substituents are indicated in the corresponding column. Solvent is indicated if other than CCl_4. [b] H-1 and H-4 assigned on the basis of chemical shift. [c] A seven-line pattern; four doublets with two lines coinciding. [d] 7-b = 7-benzonorbornadienyl. [e] s, singlet;[f] d, doublet; t, triplet; qua, quartet; qui, quintet; m, multiplet; nm, narrow multiplet; bm, broad multiplet; sm, symmetrical multiplet; 7-lm, 7-line multiplet; im, irregular multiplet; it, irregular triplet; ↔, relative assignment uncertain. [f] In the case of aromatic protons, the resonance is not a true singlet. Low-intensity irregular side bands are present. The chemical shift refers in these cases to the position of the intense, singletlike line. [g] Solvent was acetone-d_6. [h] Solvent was deuteriochloroform.

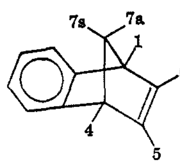
TABLE II

COUPLING CONSTANTS IN SOME DISUBSTITUTED BENZONORBORNENES
(CYCLES PER SECOND)

Coupled protons	Compound **4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**21**
1–6x	3.5	...	4.0	*a*	...	4.0–4.5	*a*	3.7	3.6–3.7
4–5x	...	4.8	3.7	...	...	...	...	...	...
1–7a ≅ 4–7a	...	1.4	...	1.7	1.6	...	1.7	...	1.6–1.7
1–7s ≅ 4–7s	1.2–1.4	1.8	1.7–1.8	...	1.6	1.3–1.4	...	1.3–1.4	...
5x–6n	...	2.4	3.7	...	...	...	...	...	...
5n–6x	4.5	...	...	4.3[b]	...	4.5	4.2[b]	3.7	3.7–3.8
5x–6x	...	...	9	...	...	...	...	...	...
5n–6n	8	...	...	7.0[b]	*a*	8	6.6[b]	7.6	8.0
5n–7s	1.2–1.4	...	...	...	1.9	1.2–1.3	...	1.3–1.4	...
6n–7s	1.2–1.4	2.4	2.0	...	1.9	1.2–1.3	...	1.3–1.4	...
6n–6x	13	...	13	*a*	...	13	*a*	13.0	13.7
7a–7s	...	9.8	...	...	10.0	...	...	...	...

[a] Not determined—no coupling because of substitution. [b] Measured only in the H–5n resonance.





plete first-order analysis was not possible because in the former the splitting pattern due to the methylene protons was obscured by the presence of *trans* dichloride **5** and in the latter case this splitting pattern was not clearly recognizable owing to the apparent closeness in chemical shift of the two protons and complications by overlap with the signal of the acetoxy methyl group.

The pmr data obtained for benzonorbornene and benzonorbornadiene derivatives are, not unexpectedly, closely analogous to the corresponding spectral features of the norbornyl and dehydronorbornyl systems. Assignments in the benzo systems are facilitated by the absence of protons at the 2 and 3 positions. A distinction between the remaining five positions, particularly in disubstituted benzonorbornenes, was generally easily accomplished on the basis of chemical shifts and characteristic splitting patterns. Unambiguous assignments could be made even when the spectra were somewhat clouded by the presence of isomeric compounds.

Orientational assignments of 7 substituents were made on the basis of the presence or absence of long-range coupling for the 7 proton. Thus, as is observed for the corresponding protons in the norbornyl and dehydronorbornyl systems,[3-7] H-7s couples with H-5n and H-6n, but not with the *exo* protons. For H-7a no such coupling is observed. In the present series of 7-substituted benzonorbornenes the H-7s coupling is of approximately the same magnitude as the coupling between the 7 protons and the bridgehead protons. Hence, H-7a is easily recognized as a downfield triplet (coupled only to H-1 and H-4) whereas H-7s may either be a quartet or a quintet, depending on whether or not an *endo* substituent is present. The additional splittings observed for H-7s are repeated in the resonances for H-5n and/or H-6n, but are absent if H-7s is substituted, thus confirming the assignment. With this initial assignment the analysis of the remaining resonances led in each case to an internally consistent correlation, further confirmed by the observed magnitudes of vicinal coupling constants, which ranged from 6.6 to 8 cps for *endo–endo* coupling and amounted to 9 cps for *exo–exo* coupling in **6**. That *exo–exo* coupling constants are larger than the *endo–endo* ones in the norbornyl and dehydronorbornyl systems has been reported.[5,8] *endo–endo* coupling constants of 7 and 6.6 cps, respectively, have been demonstrated in trimethylenenorbornane derivatives.[9]

The 5,6 dichlorides were initially recognized as such by dehalogenation with zinc–copper couple to give benzonorbornadiene.[1] The pmr spectra then readily enabled us to assign the *exo,cis* and *trans* structures, on the basis of which the spectra can be convincingly explained. For details refer to the tables.

The chemical shifts of H-1 and H-4 (when different) were assigned on the basis of peak width. The wider resonance was assigned to H-1, for which line broadening due to H-6x was to be expected. This led in all cases in which H-5x was substituted to the H-4 resonance being the one at lower field, consistent with deshielding by the neighboring substituent. The H-1 and H-4 resonances generally appeared as poorly resolved, sometimes partially overlapping patterns not suitable for direct measurement of the splittings (these were obtained from the coupling partners). We observed, however, that the peaks were of somewhat greater widths than could be accounted for on the basis of assignable couplings, possibly an indication that an H-1–H-4 long-range coupling may be present. Such couplings have not been observed generally, but examples in the norbornene system are known.[6,10]

Of particular interest in connection with the pmr spectra of dihalobenzonorbornenes have been the pmr studies reported for 5,6-dihalo-2-norbornenes and 5,6-dihalonorbornanes.[6] Distinguishable features for the chemical shifts in these compounds are repeated in the benzonorbornene system: *e.g.*, *endo* proton resonances occur at higher field than those of the *exo*; a *cis* hydrogen (*endo* or *exo*) is shielded by a vicinal eclipsed halogen substituent while a *trans* hydrogen is affected little, possibly somewhat deshielded. *endo* protons are shielded to a larger extent than *exo* protons and the effect of eclipsed vicinal chlorine is larger than that of eclipsed vicinal bromine. A particularly large shielding by an *endo* chlorine on the vicinal *endo* proton (and deshielding on the vicinal *exo* proton) appears to be operating in **6**, for which we observe a chemical-shift difference of 1.6 ppm for the two methylene protons (H-6x and H-6n) whereas with *exo* chlorine (or bromine) this difference ranges from about 0.3 to 0.7 ppm. A similarly large difference has been reported by Wilt and co-workers for the chemical shifts of the C-6 methylene protons in *endo*- compared with *exo*-5-chlorobenzonorbornene,[11] amounting to 1.2 ppm for the *endo* compound and lying between 0 and 0.4 ppm for *exo*. The shielding effect of a vicinal, eclipsed carbon–halogen bond has been attributed to the positive magnetic anisotropy of this bond.[12] The resonances of the methylene bridge protons in norbornenes have been reported to occur at higher field for the proton *syn* to the double bond,[13] with the noted exception that in *endo,cis*-dihalonorbornenes the resonance positions are reversed.[6] *endo,cis* compounds were not encountered in the present work, but for all benzonorbornene derivatives listed in Table I, whether or not 7-substituted, the resonances of H-7s were observed at higher field than those of H-7a.

The coupling constants observed for benzonorbornene derivatives are generally in line with expectations from observations on the norbornene system.[5,6] However, long-range couplings of H-7s with the *endo* protons tend

---

[3] J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

[4] P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964).

[5] J. C. Davis, Jr., and T. V. van Auken, *ibid.*, **87**, 3900 (1965).

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

[7] E. A. Hill, *ibid.*, **31**, 20 (1966).

[8] J. I. Musher, *Mol. Phys.*, **6**, 93 (1963).

[9] S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, 185 (1963).

[10] R. W. King and P. E. Butler, Abstracts, 142nd Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1962, p 84Q.

[11] J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *J. Org. Chem.*, **32**, 893 (1967). We wish to thank Professor Wilt for making his results available to us before publication.

[12] See ref 6 and additional references given therein.

[13] E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964).

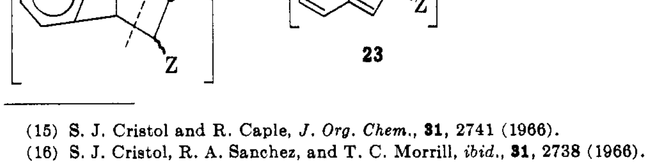
to be somewhat smaller (1.2–2.0 cps *vs.* 2.1–3.1 cps) while *trans* couplings (5n–6x, 5x–6n) tend to be larger (3.7–4.5 cps *vs.* 2.6–2.9 cps in dihalonorbornenes, 3.1–4.2 cps in other norbornene derivatives) in the benzonorbornene system. At the same time, we observed some additional broadening in the resonance lines of the *endo* protons, suggesting small couplings on the order of 0.3–0.6 cps to the adjacent bridgehead protons. These are perhaps a more likely cause for the already mentioned broadening of the bridgehead proton resonances than is the possibility of long-range coupling of the two bridgehead protons. All these differences can probably be accounted for by some difference in the geometry of the benzonorbornene skeleton *vs.* that of norbornene.

The pmr spectra of benzonorbornadiene derivatives are less amenable to a first-order analysis. While a distinction between the presence of a 5 or 7 substituent is, of course, readily accomplished, the assignment of a *syn*-7 substituent appears somewhat ambiguous. The olefinic H-5 and H-6 resonances in 7-substituted benzonorbornadienes occurred in most cases as complex multiplets (symmetrical or somewhat distorted), probably due to "virtual coupling"[14] involving the bridgehead and olefinic protons. 7 protons *anti* to the double bond in norbornenes are known to couple with the olefinic protons.[4–6,13] Splittings on the order of 0.8–0.9 cps were clearly observable in the olefinic resonances of some of the 7-substituted benzonorbornadienes and were repeated in the resonances assigned to H-7s. The structures **1a**, **1d**, **1e** were thereby confirmed. The seven-line multiplets observed for H-7s in **1d** and **1e** can be readily understood if $J_{1-7s} = J_{4-7s} = 2(J_{5-7s}) = 2(J_{6-7s})$. For these couplings, a seven-line multiplet with line intensities as 1:2:3:4:3:2:1 and separation J_{5-7s} ($= J_{6-7s}$) is expected, a pattern closely approximated by the H-7s multiplets. Observable splittings are 0.8–0.9 cps in the resonances for H-5, H-6, and H-7s, and 1.7–1.8 cps in the resonances for H-1 and H-4, closely approximating the conditions for the occurrence of a seven-line multiplet of the expected shape. With *syn*-7-chlorobenzonorbornadiene (**2d**), the resonance for H-5 and H-6 appears as a clean triplet, as does the resonance for H-7a. As would be expected from analogy to the norbornene system,[5] the absence of coupling between the proton *syn* to the double bond and the olefinic protons is indicated. In compounds **18** and **19** the olefinic resonances are clearly of a different nature, appearing as irregular triplets. Compound **18** shows an irregular triplet for H-7, but still a quartet for H-1 and H-4, whereas for **19** H-7 gives a sharp singlet and the resonances for H-1 and H-4 have become a triplet. The 7-7′ coupled product **19** is clearly indicated to be symmetrical, leaving a choice between the *syn,syn* and *anti,anti* configurations. The H-7 resonance not showing any signs of olefinic couplings, we tend to favor the *syn,syn* structure for **19**; yet it is not clear why an H-7–bridgehead coupling is not observed. The spectrum of the 7-carboxylic acid **18** leads to similar difficulties. Here an H-7–bridgehead coupling is clearly indicated (1.9–2.0 cps), but H-7–olefinic coupling may or may not be present. We feel that at present the information available is insufficient to base an orientational assignment for the 7 substituent in compounds such as **18** and **19** on pmr data.

The vinyl chloride **17** is clearly indicated as such by the pmr data. A small splitting of 0.9 cps in the olefinic resonance is repeated in the upfield resonance of the methylene bridge protons, making possible the assignment of this resonance to H-7s. The large splitting in the olefinic resonance (two triplets) amounts to 3.4 cps and is attributable to coupling with H-1, which shows a broad multiplet at τ 6.16. Additional splittings are seen for H-7s and H-7a and are also discernible for H-1 and H-4, indicating that both methylene bridge protons are coupled approximately equally to both bridgehead protons with a coupling constant of about 1.7 cps. The geminal coupling of the two methylene protons could be assigned with certainty and amounts to 7.3 cps. The resonance assigned to H-4, next to chlorine, appears at higher field than that of H-1. Since the chlorine substituent is nearly eclipsed with H-4, a shielding mechanism similar to that mentioned earlier for eclipsed 5,6-halogen–hydrogen interaction in benzonorbornenes may be operative.

Coupling constants for benzonorbornadiene derivatives are not included in Table II because in no single case could all of them be observed with certainty. The combined data allow the conclusion, however, that in our 5- or *anti*-7-substituted benzonorbornadienes the coupling constants appear to be on the order of $J_{5-7s} = J_{6-7s}$, 0.8–0.9 cps; $J_{1-6} = J_{4-5}$, 2–3.5 cps; $J_{1-7a} = J_{4-7a} \cong J_{1-7s} = J_{4-7s}$, 1.7–2 cps; J_{7a-7s}, 7–8 cps. Couplings between H-5 and H-6, H-1 and H-5, and H-4 and H-6 are not observable directly. It may be possible to determine these as well as better values for the remaining ones by a computer analysis of the spectral data.

Mass Spectra.—Additional evidence for the structures of the various 5,6- and 5,7-dihalobenzonorbornenes was derived from mass spectrometry. On the basis of previous results on related compounds,[15–17] we expected a major mode of fragmentation to be the retro Diels-Alder process.[18] In particular, we expected to be able to derive information as to the position of substituents from the process outlined below. That this process is indeed an important one in the fragmentations of the molecular ions derived from the dihalo compounds is borne out by the data of Table III.[19] In all four 5,7 dichlorides, the peaks at *m/e*



23

---

[14] J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

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

[16] S. J. Cristol, R. A. Sanchez, and T. C. Morrill, *ibid.*, **31**, 2738 (1966).

[17] T. Goto, A. Tatematsu, Y. Hata, R. Muneyuki, H. Tanida, and K. Tori, *Tetrahedron*, **22**, 2213 (1966).

[18] K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 102.

[19] The peak intensities are listed in $\%\Sigma_{74}$ rather than relative to the base peak. Because the ionization cross sections of isomers are equal (see ref 18, p 44) a more meaningful comparison thereby becomes possible even though peaks of *m/e* below 74 have not been included. The peak intensities for halogen-containing species are listed as the sums of intensities of the multiplets characteristic of such species. These multiplets closely approximated the expected intensity ratios in each case. Peaks due to heavy carbon and heavy hydrogen species have not been added.

TABLE III

PARTIAL MASS SPECTRA OF SOME HALOGENATED DERIVATIVES OF BENZONORBORNENE AND BENZONORBORNADIENE[a]

	Peak intensity, %Σ_{74}									
		Fragment ions (m/e)								
Compd	Molecular ion (m/e)	223 + 221	196 + 194	179 + 177	152 + 150	141	129	128	116	115
	216 + 214 + 212									
6	7.6	...	...	2.5	15.3	9.8	7.7	2.5	3.3	19.5*[b]
7	5.8	...	...	2.0	15.4	10.4	6.0	2.9	8.2	19.6*
9	7.1	...	...	2.9	13.4	9.8	14.1	2.8	3.5	19.5*
22	7.4	...	...	1.8	18.0	10.3	3.5	3.1	3.3	19.4*
5	5.6	...	...	9.4	0.4	9.3	2.3	1.8	26.5*	12.2
8	6.3	...	...	10.6	0.9	10.1	2.9	1.9	29.0*	11.7
	260 + 258 + 256									
21	7.1	0.3	0.0	7.0	9.3	19.3*	5.7	2.9	1.7	15.0
	304 + 302 + 300									
4	2.3	18.8	1.0	0.0	0.0	20.7*	4.4	0.9	2.4	19.1
	178 + 176									
1d	4.6	...	...	...	0.0	48.1*	0.0	0.8	1.1	10.9
2d	5.5	...	...	...	0.0	45.7*	1.0	1.3	1.9	9.9
17	14.8	...	...	...	0.7	32.4*	0.2	0.3	3.8	9.5
	222 + 220									
1e	5.0	...	0.0	0.0	0.0	43.9*	0.1	0.7	1.5	14.6

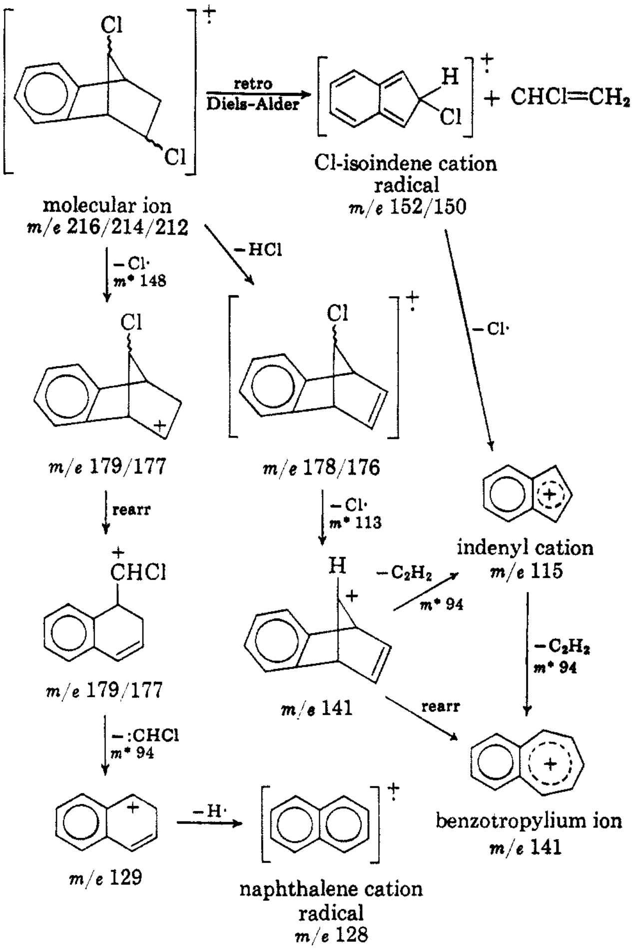
[a] All spectra were obtained on a Consolidated Electrodynamics Corp., Type 21-103 C mass spectrometer at 70 ev and 150° inlet temperature (all-glass inlet system). [b] * indicates base peak.

152 and 150, corresponding to the isoindene cation radical **23** with X = Cl, contribute from 13.4 to 18.0% Σ_{74} to the spectrum, whereas in the 5,6 dichlorides these peaks contribute less than 1% and, as expected, the m/e 116 peak, corresponding to **23** with X = H, is now a major one with a contribution of 26.5%Σ_{74} for the *trans* and 29.0%Σ_{74} for the *cis* compound. The m/e 116 peak is by far the strongest one in the spectra of the vicinal dichlorides, but for the 5,7 dichlorides the base peak corresponds to the indenyl cation, m/e 115, with abundances ranging from 19.4 to 19.6%Σ_{74}. These characteristic differences are strong evidence for either 5,6- or 5,7-dichloro substitution and corroborate our assignments on the basis of pmr and chemical evidence.

The indenyl cation does not appear to result only from loss of chlorine from the chloroisoindene cation radical. The presence of metastable peaks at or near m/e 113 and 94 suggests that it is formed as well from an intermediate species of m/e 176, even though the latter does not produce a prominent peak in the spectra of the dichlorides (but is not absent). These metastable peaks are also apparent in the spectra of the 5- and 7-chlorobenzonorbornadienes, for which the data are included in Table III.

For the 7-substituted compounds, the fragmentations can be rationalized as in Scheme I, which also shows a path leading to fragments of m/e 129 and 128. The latter two fragments are relatively important in the spectra of the benzonorbornene derivatives, but much less so in those of benzonorbornadienes. In the mass spectrum of benzonorbornene itself the m/e 129 fragment has been suggested to arise from methylene bridge elimination with migration of a hydrogen atom to eliminate a methyl radical.[17] If a corresponding mechanism applied in the case of 5,7-dichlorobenzonorbornenes, the migration of a chlorine atom would be required. While this is possible, the alternate path shown in Scheme I, leading to the elimination of a chlorocarbene fragment, appears just as reasonable. The metastable peak at m/e 94, already assigned to the process m/e 141 → m/e 115 (m^* 93.8), may also apply to m/e 177 → m/e 129 (m^* 94.0).

SCHEME I



A corresponding scheme for the 5,6 dichlorides, which show the same metastable peaks as the 5,7 compounds, will not fit so nicely. It has been pointed out that the fragmentation of polycyclic compounds may involve considerable random rearrangements of hydrogen and even of carbon atoms[20] and there may therefore be several, though perhaps less obvious, paths leading to species of the observed *m/e* values. Another oddity is the relatively large contributions of species of *m/e* 116 (indene or isoindene cation) in the case of 7-substituted benzonorbornenes. These exceed the C^{13} and H^2 isotopic contributions of the indenyl cation and the excess may be rationalized as the result of a random rearrangement in the course of fragmentation.

The spectra of the bromine-containing compounds bear out the greater probability of loss of bromine over that of chlorine.[21] In the 5,7 dibromide, **4**, the molecular ion intensity is much diminished and there is a relatively large abundance of fragments resulting from the loss of bromine ($18.8\%\Sigma_{74}$). The increased competition of bromine loss with retro Diels–Alder fragmentation has considerably diminished the contribution of **23** (with X = Br), compared with the chlorine compounds, but the contribution still appears sufficiently significant to confirm a 7-bromo substituent. Both in **4** and **21** the base peak corresponds to the benzotropylium ion, in line with the greater probability of initial loss of bromine and/or elimination of hydrogen bromide.

The spectra of all of the benzonorbornadiene derivatives show the by far most intense peak at *m/e* 141 (benzotropylium ion). The peak next in importance occurs at *m/e* 115 (indenyl cation), but peaks at *m/e* 129 and 128 are much diminished relative to the spectra of benzonorbornene derivatives. All these relative changes can again be rationalized on the basis of the corresponding part of Scheme I (starting with the *m/e* 178/176 ion for the chlorides). Now merely the loss of a single substituent is required to arrive at a fragment of *m/e* 141. The retro Diels–Alder process, requiring here the elimination of acetylene from the molecular ion, does not appear to be of any importance. The relative ease of eliminating ethylene (from benzonorbornene) over acetylene (from benzonorbornadiene) has been pointed out.[17] The formation of the *m/e* 115 fragment in the latter case has been ascribed to expulsion of acetylene from the benzotropylium ion[17] which, in view of the reluctance of the molecular ion to undergo the retro Diels–Alder process, may be a more probable process than the retro Diels–Alder process, on the 7-benzonorbornadienyl cation also included in Scheme I.

Exceptional behavior is shown by the vinyl chloride **17**. Its molecular ion peak is considerably stronger than that of the other benzonorbornadienes; yet the remainder of the spectrum is quite similar to that of the others. One might expect a relatively larger contribution of a fragment of *m/e* 177/175, corresponding to loss of a hydrogen atom and rearrangement to a chlorine-substituted benzotropylium ion. Peaks at these *m/e* values (not inclued in Table III) amount to 5.1 $\%\Sigma_{74}$ for the vinyl chloride, compared with $3.0\%\Sigma_{74}$ and $2.7\%\Sigma_{74}$ for the *anti-* and *syn-*7-chlorobenzonorbornadienes, respectively, and $0.8\%\Sigma_{74}$ at *m/e* 221/219 in the case of the *anti-*bromo compound. The fact that the vinyl chloride still has the strongest peak at *m/e* 141 indicates the importance of chlorine loss and hydrogen migration because in the benzotropylium ion (which is likely to be the major, if not the exclusive, contributor to the *m/e* 141 peak) the carbon formerly bearing the chlorine substituent must now be linked to a hydrogen.

Registry No.—**1a**, 6991-42-0; **1d**, 14362-53-9; **1e**, 7605-10-9; **2d**, 14518-75-3; **3**, 4453-90-1; **4**, 14362-55-1; **5**, 14296-33-4; **6**, 14296-34-5; **7**, 14296-35-6; **8**, 14362-56-2; **9**, 7605-06-3; **10**, 14296-37-8; **11**, 14518-76-4; **17**, 7605-08-5; **18**, 14362-57-3; **19**, 14444-29-2; **21**, 14296-39-0; **22**, 14296-40-3.

Acknowledgments.—G. W. N. is indebted to American Cyanamid Co. for support of this work by a Junior Educational Award (1964–1966). This investigation was also supported (in part) by a Public Health Service Fellowship to G. W. N. (1-F1-GM-33, 790-01) from the National Institutes of General Medical Sciences. Thanks are due to Mr. Ronald Sadecky of this department for the recording of the mass spectra.

(20) See ref 18, p 138.

(21) J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, p 417.

---

cis- and *trans-*1,4-Cyclohexadiene Dioxide[1]

THEODORE W. CRAIG,[2] GEORGE R. HARVEY, AND GLENN A. BERCHTOLD[3]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received July 13, 1967

cis- and *trans-*4,8-dioxatricyclo[5.1.0.0^{3,5}]octane have been synthesized and their ring-opening reactions have been investigated. Aqueous acid, aqueous base, aqueous hydrogen bromide, sodium bromide in dimethylformamide, dimethylamine, and ethylamine lead to 1,4 attack on the *cis* isomer and 1,3 attack on the *trans* isomer. Lithium aluminum hydride leads to 1,3 attack on the *cis* isomer and 1,4 attack on the *trans* isomer. Dimethyl magnesium, magnesium iodide, and methylmagnesium iodide result in 1,3 attack on both isomers. Hydrogen and palladium-on-carbon catalyst give a mixture of diols with the *cis* isomer and no reaction with the *trans* isomer. Sodium sulfide reacts with the *cis* isomer to produce **27**. These results are correlated. The *cis-* and *trans-*N-ethylaziridines of 1,4-cyclohexadiene were also prepared.

The chemistry of *cis-* and *trans-*4,8-dioxatricyclo-[5.1.0.0^{3,5}]octane (**1** and **2**, respectively) has been investigated to determine the stereochemical course of ring-opening reactions of the bisepoxide systems as a route to polysubstituted cyclohexanes of known stereochemistry. Bisepoxide formation from 1,4-cyclohexadiene (**3**)[4] and 1,3-cyclohexadiene[5] has been re-

(1) Supported by National Institutes of Health Grant NIH-AI-05408-MCB.

(2) National Science Foundation Predoctoral Fellow, 1963–1965.

(3) Alfred P. Sloan Fellow, 1963–1967.

(4) N. D. Zelinsky and A. N. Titowa, *Chem. Ber.*, **64**, 1399 (1931).

(5) P. Bedos and A. Ruyer, *Compt. Rend.*, **196**, 625 (1933); **195**, 802 (1932).