ate solution, and water. The solution was dried over calcium chloride and distilled through a 30-cm. glass-helix-packed column to give **3**, b.p. 54–55° (16 mm.), $n^{25}D$ 1.4826 (lit. b.p. 54–55° at 16 mm.,[22] $n^{20}D$ 1.4842,[22] $n^{25}D$ 1.4823[23]).

endo-**2-Chlorobicyclo[2.2.1]heptane** (**4**) was prepared according to the procedure of Roberts and Bennett.[24] The crude product after distillation was freed of *exo* contaminant by partial solvolysis at room temperature for 4 hr. in 95% acetone–water containing 60% of the requisite silver nitrate for complete destruction of the chloride. The organic chloride was isolated and resolvolyzed in the same manner. After reisolation, the organic chloride had b.p. 73–73.5° at 40 mm. (lit.[24] b.p. 75° at 41 mm.). Infrared and n.m.r. analysis showed that less than 5% *exo* isomer was present. G.l.c. on several columns failed to separate the *endo* and *exo* isomers.

1-Chlorobicyclo[2.2.1]heptane (**5**) was prepared according to the procedure of Wiberg[25] and purified by an initial distillation through a 90-cm. tantalum-wire column followed by an additional distillation through a 90-cm. spinning-band column, b.p. 146–148° (lit.[25] b.p. 148–154°). Analysis by g.l.c. indicated *ca.* 98% peak purity.

7-Chlorobicyclo[2.2.1.]heptadiene-2,4 was prepared according to the procedure of Story[26] and purified by distillation through a 90-cm. tantalum-wire column, b.p. 68° at 41 mm. (lit.[26] b.p. 77.5° at 63 mm.). Analysis by g.l.c. showed >99% peak purity.

7-Chlorobicyclo[2.2.1]heptane (**6**) was prepared by hydrogenation of the above diene in cyclohexane over platinum oxide at room temperature. The catalyst was removed by filtration and the organic chloride was isolated by distillation through a 90-cm. tantalum-wire column to give **6** (81% yield), b.p. 73° at 41 mm., m.p. 41–42°. Analysis by g.l.c. showed >99% peak purity. The infrared spectrum of **6** was in accord with that published by Roberts, *et al.*[27]

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[22] H. Kwart and R. K. Miller, *J. Am. Chem. Soc.*, **78**, 5010 (1956).

[23] L. Schmerling, *ibid.*, **68**, 195 (1946).

[24] J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954).

[25] K. B. Wiberg, B. R. Lowry, and T. H. Colby, *ibid.*, **83**, 3998 (1961).

[26] P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

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Nuclear Magnetic Resonance Studies of 5,6-Dihalo-2-norbornenes and 2,3-Dihalonorbornanes

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The n.m.r. spectra of several 5,6-dihalo-2-norbornenes and 2,3-dihalonorbornanes have been examined with the aid of specific deuterium labeling and double resonance. Chemical shifts and many coupling constants have been evaluated. New evidence for long-range coupling between (1) *endo* protons and *anti* 7-protons, (2) vinyl protons and *anti* 7-protons, and (3) the two bridgehead protons has been obtained. Confirmation of the requirements for "virtual coupling" is also presented. Good stereochemical correlations may be made, and the utility of measurements in aromatic solvents is discussed.

Stereochemical assignments in substituted bicyclic systems have been confronted with difficulties despite the rigid geometries involved. The obvious method of dipole moment measurements (where applicable) is often ambiguous primarily because of the lack of precise information of contributions by the basic ring system. For example, in the case of the isomeric 2,3-dibromonorbornanes, the configuration of only the *trans* isomers could be assigned unequivocally by dipole moment data. A distinction between the *endo*- and *exo-cis* compounds was impossible.[2] Of the physical methods available, the most promising approach would seem to be the application of proton magnetic resonance spectral data. Numerous publications have appeared in recent years describing either detailed analyses of the n.m.r. spectra of norbornene (and sometimes norbornane) derivatives[3] or analyses of such spectra for structural and stereochemical assignments. Some ambiguities still remain.

We have accumulated an extensive series of 5,6-dihalo-2-norbornenes and 2,3-dihalonorbornanes and have examined the n.m.r. spectra in detail, utilizing double resonance techniques and deuterium labeling in many cases. The results appear very interesting. Because the structural modifications do not involve large changes in substituent electronegativities, the observed spectra provide data which can be interpreted without recourse to electronegativity differences.

The compounds that were examined are listed in Chart I (p. 2627). Series I consisted of norbornene derivatives; II refers to dihalonorbornanes. Chemical shifts for the various protons of these compounds are given in Tables I and II. Values are recorded in cycles per second downfield from tetramethylsilane. In the case of an unresolvable multiplet, the center is denoted. For those protons where an AB pattern occurs, the resonances for each A and B species have been identified in most cases, and the chemical shifts were calculated from the measured values and coupling constants. Similar calculations were made with the AB portion of a recognizable ABX spectrum.

Many of the various coupling constants were easily recognized and were measured directly from carefully calibrated spectra. With the AB portions of an ABX pattern, only J_{AB} could be obtained by direct measurement; the values of $^1/_2(J_{AX} + J_{BX})$ were calculated from measured distances. A combination of measurements including the separation of extreme peaks in a multiplet, the spectra of specific deuterium-labeled analogs, and nuclear magnetic double resonance were applied to extract various coupling constants. The J values thus obtained are tabulated in Table III.

Chemical shifts in aromatic solvents were measured for most of these compounds. Inasmuch as this was a secondary source of information, a comprehensive study was not attempted. The concentration dependence in aromatic solvents is significant. The present limited study has indicated several trends useful for stereo-

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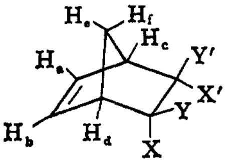
[1] Alfred P. Sloan Foundation Fellow, 1961–1965. To whom communications regarding this article should be directed.

[2] N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 623 (1960); N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *ibid.*, **85**, 3199 (1963).

[3] P. Laszlo and P. v. R. Schleyer, *ibid.*, **86**, 1171 (1964). This article cites a rather extensive list of pertinent references.

TABLE I
CHEMICAL SHIFTS OF NORBORNENES[a]



Compd.	Solvent	$H_{a,b}$	$H_{c,d}$	H_e	H_f	X	Y	X′	Y′
Ia	CCl_4	374 t	195 m	108 dt	88 dbr	. . .	267 t	. . .	= H_y
		(6.23)	(3.25)	(1.80)	(1.47)		(4.45)		
	PhH	366	162	71	36	. . .	228	. . .	. . .
	$CDCl_3$	377	197	108	90	. . .	268	. . .	. . .
Ib	CCl_4	374 t	196 m	104 dt	83 dbr	. . .	. . .	. . .	. . .
Ic	CCl_4	374 t	193 m	106 dt	85 dbr	. . .	265 q	. . .	= H_y
		(6.23)	(3.22)	(1.77)	(1.42)		(4.42)		
Id	CCl_4	374 t	193 m	105 dt	88 dbr	. . .	257 q	. . .	270 q
		(6.23)	(3.22)	(1.75)	(1.47)		(4.28)		(4.50)
	PhH	368	165	76	44	. . .	230	. . .	238
	$CDCl_3$	376	197	104	87	. . .	257	. . .	270
Ie	CCl_4	371 m	190 m	110 dqu	137 dbr	244 d	. . .	= H_x	. . .
		(6.18)	(3.17)	(1.83)	(2.28)	(4.07)			
	PhH	335	169	91	139	219	. . .	= H_x	. . .
If	CCl_4	373 t	179 m	108 m	135 dbr	233 q	. . .	242 q	. . .
		(6.22)	(2.98)	(1.80)	(2.25)	(3.88)		(4.03)	
	PhH	332	161	87	132	206	. . .	217	. . .
Ig	CCl_4	374 m	183 m	111 dq	124 dbr	. . .	263 dd	223 t	. . .
		(6.23)	(3.05)	(1.85)	(2.07)		(4.38)	(3.72)	
	PhH	362	171	93	108	. . .	258	221	. . .
Ih	CCl_4	373 m	185 m	105 dt	123 dbr	. . .	. . .	. . .	. . .
Ii	CCl_4	376	179 (2.98), 186	107	120	. . .	255	216	. . .
		(6.27)	(3.10)	(1.78)	(2.00)		(4.25)	(3.60)	
Ij	CCl_4	375	187 m	106	123	. . .	266 q	214 t	. . .
		(6.25)	(3.12)	(1.77)	(2.05)		(4.43)		
	PhH	344 or 356	155	82	100	. . .	254	205	. . .
Ik	CCl_4	375	187 m	106	123	225 t	. . .	. . .	251 q
		(6.25)	(3.12)	(1.77)	(2.05)	(3.75)			(4.18)
	PhH	344 or 356	155	82	100	216	. . .	. . .	238
III	CCl_4	355 d, 371 q	184 m[b]	98 dd	86 dbr	. . .	270 q	. . .	244 d
							(4.50)		(4.07)
V	CCl_4	357 d, 374 q	174 m[c]	101 dt	117 dbr	224 t	. . .	. . .	240 d
						(3.73)			(4.00)
VIa	$CDCl_3$	384 m	212 m	108 dt	93 dbr	. . .	216 m	. . .	= H_y
		(6.40)	(3.53)	(1.80)	(1.55)		(3.60)		
	PhH	352	171 dbr	66	40	. . .	165	. . .	. . .
VIb	$CDCl_3$	388 t	209 m	101 dbr	89 dbr	181 d	. . .	= H_x	. . .
		(6.47)	(3.48)	(1.68)	(1.48)	(3.02)			
	PhH	332	173	59	59	129	. . .	= H_x	. . .
VII	$CDCl_3$	210 sbr	169 m	84 dt	53 dbr	. . .	271 q	. . .	= H_y
							(4.52)		
	PhH	198	136	70 dt	0	. . .	220	. . .	= H_y

[a] Chemical shifts are reported as cycles per second downfield from tetramethylsilane; values in parentheses refer to δ in parts per million for easy reference. The designations for peak patterns are d = doublet; t = triplet; q = quartet; qu = quintet; m = multiplet; dt = doublet of triplets; dbr = doublet of broad multiplets; dd = doublet of doublets; dq = doublet of quartets; dqu = doublet of quintets; sbr = broad singlet; mbr = broad multiplet. [b] Bridgehead C–CH_3, 82 c.p.s. [c] Bridgehead C–CH_3, 81 c.p.s.

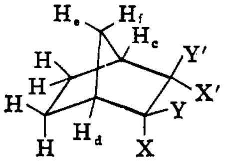
chemical correlations. The chemical shifts in benzene are included in Tables I and II, and the differences from the corresponding values in carbon tetrachloride or deuteriochloroform are given in Table IV. The resonances of all the protons were found to be shielded in benzene solution relative to those in carbon tetrachloride or deuteriochloroform.

Double irradiation measurements were performed with the three 5,6-dibromo-2-norbornenes (Ia, e, and g), *endo-cis*-5-bromo-6-chloro-2-norbornene (Id), and the mixture of *trans*-5-bromo-6-chloro-2-norbornenes (Ij and k). The observations are summarized in Table V and the spectra are reproduced in Figures 1–4. [The numbers given at the bottom of the figures represent the separation of the respective peaks in cycles per second downfield from tetramethylsilane. The inserts represented as A show that portion of the double resonance spectra corresponding to the given proton absorption during irradiation with an external radiofrequency. The letters and numbers in parentheses denote the decoupled proton(s) and the separation in cycles per second of these protons from the proton(s) observed (*e.g.*, the frequency of the external radiofrequency).]

For the compounds whose spectra were too complex for a simple analysis, an approximation was attempted

TABLE II

CHEMICAL SHIFTS OF NORBORNANES[a]



Compd.	Solvent	$H_{c,d}$	X	Y	X'	Y'
IIa	CCl_4	149 m (2.48)	...	268 mbr (4.47)	...	= H_y
	$CDCl_3$	149 m	...	272 mbr	...	= H_y
IIb	CCl_4	147 m	...	...	...	...
IIc	$CDCl_3$	148 m	...	...	...	270 m (4.50)
IId	CCl_4	147 m	...	258 mbr (4.30)	...	= H_y
IIe	CCl_4	148 m	...	257 q (4.29)	...	267 q (4.45)
	PhH	121 m	...	228	...	238
IIf	CCl_4	147 m	...	...	...	267 m
IIg	CCl_4	160 m	249 d (4.15)	...	= H_x	...
	$CDCl_3$	...	252 d	...	...	...
IIh	CCl_4	152 m	240 d (4.00)	...	250 dd (4.17)	...
	PhH	134 m	215	...	225	...
IIi	CCl_4	148 m	...	266 m (4.44)	231 t (3.85)	...
	PhH	121 m	...	257	221	...
IIj	CCl_4	149 m	...	...	...	...
IIk	CCl_4	149 m	...	...	230 d (3.83)	...
	PhH	119 m	...	...	222	...
IIl	CCl_4	150 m	...	265 d (4.42)	...	...
IIm	CCl_4	150 m	...	263 m (4.38)	221 t (3.68)	...
	PhH	129 m	...	258	217	
IIn	CCl_4	149 m	...	...	221 d	...
IIo	CCl_4	153 m	228 t (3.80)	...	...	256 mbr (4.27)
	PhH	127 m	208	...	...	236
IIp	CCl_4	...	237 m (3.95)	...	...	...
IIq	CCl_4	...	227 m (3.78)	...	...	...
IV	CCl_4	146 m	...	265 dd (4.42)	...	241 dd (4.02)

[a] See footnote *a* of Table I.

TABLE III

SPIN–SPIN COUPLING CONSTANTS FOR 5,6-DIHALONORBORNENES (I) AND 2,3-DIHALONORBORNANES (II)

Protons	J_I, c.p.s.	Compd. I, J, c.p.s.	J_{II}, c.p.s.	Compd. II, J, c.p.s.
yc	$\simeq 0$	g, e, f, j, k		
yd = y'c	2.9–4.3	a, 3.3; g, 2.9; j, 4.3; c, 3.6; k, 3.5; III, 3.7		
ec = ed	1.7–2.3	a, ~2.1; b, 2.1; d, 1.9; e, 1.7; f, 1.9; g, 2.1; III, 2.3		
fc = fd	1.5–1.7	a, ~1.5; e, ~1.7		
ef	8.9–9.7	a, 9.6; b, 9.6; d, 9.4; e, 8.9; f, 9.2; g, 9.7; III, 9.2; V, 9.5		
cd	~1.0	a, ~1.0		
af	~0.8	a, ~0.8		
xe = x'e	2.1–2.5	e, 2.1; g, 2.5; j, 2.3; k, 2.4; V, 2.4	2.1–2.9	g, 2.9; h, 2.1; i, ~2.9; k, 2.8; m, 2.6; n, 2.9
x'y	2.3–2.5	g, 2.5; j, 2.3; k, 2.4; V, 2.4	2.6–2.9	i, 2.9; m, 2.6
ab	5.6–5.9	g, ~5.9; III, 5.6; V, 5.8		
yy'	7.4–7.8	d, 7.4; III, 7.8	9.5	e, 9.5; IV, 9.3
xx'	6.8	f, 6.8	6.8	h, 6.8
ac + ad + af	~4.5	a, ~4.5		
bd	3.6–3.8	III, 3.8; V, 3.6		
ce + de	~3.5	g, ~3.5		
$^1/_2$(y'c + yd)	~2.9	d, 2.9		
$^1/_2$(xe + x'e)	~2.1	f, 2.05		
yd + yb			5.0	l, 5.0

in the following manner.[4] The widths of broad, unresolvable multiplets were measured at heights corresponding to the assumed number of spins involved; S represents the separation between the outside pair of bands of a resolved pattern, and the subscripts refer to the proton concerned. The sum rules employed above are not theoretically rigorous and the treatment assumes the same sign for all coupling constants. Nevertheless, utility is gained in approximating unmeasurable constants and justification rests in the close agreement of the values so obtained with those that have been recorded.[3] A typical calculation for *endo-cis*-5,6-dibromo-2-norbornene (Ia) is given below.

$$S_y = J_{yd} + J_{yc} = 3.2 \text{ c.p.s.} \qquad (1)$$

$$J_{yc} = 0, \; J_{yd} = 3.2 \text{ c.p.s.} \qquad (2)$$

$$S_a = J_{ad} + J_{bd} + J_{af} = 3.9 \text{ c.p.s.} \qquad (3)$$

$$W_d[1/7h] = J_{yd} + J_{ad} + J_{bd} + J_{ed} + J_{fd} + J_{cd} \cong 10.9 \text{ c.p.s.} \qquad (4)$$

$$W_f[1/5h] = 2J_{cf} + 2J_{af} = 4.7 \text{ c.p.s., or } J_{cf} + J_{af} = 2.3 \text{ c.p.s.} \qquad (5)$$

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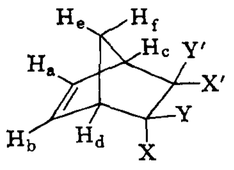
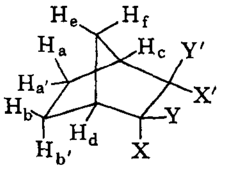
(4) *Cf.* E. I. Snyder and B. F. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964).

CHART I

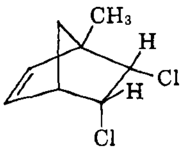


I

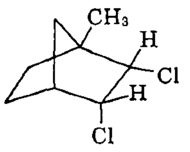


II

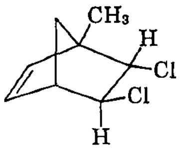
Ia, $X = X' = \mathrm{Br};\ Y = Y' = \mathrm{H}$
b, $X = X' = \mathrm{Br};\ Y = Y' = \mathrm{D}$
c, $X = X' = \mathrm{Cl};\ Y = Y' = \mathrm{H}$
d, $X = \mathrm{Cl};\ X' = \mathrm{Br};\ Y = Y' = \mathrm{H}$
e, $X = X' = \mathrm{H};\ Y = Y' = \mathrm{Br}$
f, $X = X' = \mathrm{H};\ Y = \mathrm{Cl};\ Y' = \mathrm{Br}$
g, $X = Y' = \mathrm{Br};\ X' = Y = \mathrm{H}$
h, $X = Y' = \mathrm{Br};\ X' = Y = \mathrm{D}$
i, $X = Y' = \mathrm{Cl};\ X' = Y' = \mathrm{H}$
j, $X = \mathrm{Cl};\ Y' = \mathrm{Br};\ X' = Y = \mathrm{H}$
k, $Y = \mathrm{Cl};\ X' = \mathrm{Br};\ X = Y' = \mathrm{H}$
IIa, $X = X' = \mathrm{Br};\ Y = Y' = \mathrm{H}$
b, $X = X' = \mathrm{Br};\ Y = Y' = \mathrm{D}$
c, $X = X' = \mathrm{Br};\ Y = \mathrm{H};\ Y' = \mathrm{D}$
d, $X = X' = \mathrm{Cl};\ Y = Y' = \mathrm{H}$
e, $X = \mathrm{Cl};\ X' = \mathrm{Br};\ Y = Y' = \mathrm{H}$
f, $X = \mathrm{Cl};\ X' = \mathrm{Br};\ Y = \mathrm{D};\ Y' = \mathrm{H}$
g, $X = X' = \mathrm{H};\ Y = Y' = \mathrm{Br}$
h, $X = X' = \mathrm{H};\ Y = \mathrm{Cl};\ Y' = \mathrm{Br}$
i, $X = Y' = \mathrm{Br};\ X' = Y = \mathrm{H}$
j, $X = Y' = \mathrm{Br};\ X' = Y = \mathrm{D}$
k, $X = Y' = \mathrm{Br};\ X' = \mathrm{H};\ Y = \mathrm{D}$
l, $X = Y' = \mathrm{Br};\ X' = \mathrm{D};\ Y = \mathrm{H}$
m, $X = \mathrm{Cl};\ Y' = \mathrm{Br};\ X' = Y = \mathrm{H}$
n, $X = \mathrm{Cl};\ Y' = \mathrm{Br};\ X' = \mathrm{H};\ Y = \mathrm{D}$
o, $X = Y' = \mathrm{H};\ X' = \mathrm{Br};\ Y = \mathrm{Cl}$
p, $Y = \mathrm{Br};\ X = X' = Y' = \mathrm{H}$
q, $Y = \mathrm{Cl};\ X = X' = Y' = \mathrm{H}$



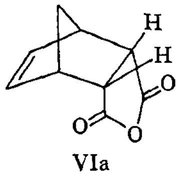
III



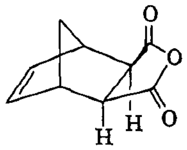
IV



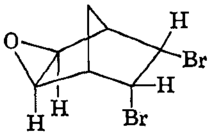
V



VIa



VIb



VII

From eq. 3 and 5

$$J_{\mathrm{ad}} + J_{\mathrm{bd}} - J_{\mathrm{cf}} = 1.6 \text{ c.p.s.} \tag{6}$$

From eq. 6 and 4

$$J_{\mathrm{yd}} + J_{\mathrm{ed}} + J_{\mathrm{cd}} + 2J_{\mathrm{cf}} = 9.3 \text{ c.p.s.} \tag{7}$$

but $J_{\mathrm{ce}} = J_{\mathrm{de}} = 2.1$ c.p.s. from direct measurement

$$J_{\mathrm{cd}} + 2J_{\mathrm{df}} = 4.0 \text{ c.p.s.} \tag{8}$$

From the double resonance spectrum

$$J_{\mathrm{df}} = 1.5 \text{ c.p.s.} \tag{9}$$

and from eq. 8 and 9

$$J_{\mathrm{cd}} \cong 1.0 \text{ c.p.s.} \tag{10}$$

J_{af} is estimated as *ca.* 0.8 c.p.s. from eq. 5 and 10, whereas from 6 and 10 we find $J_{\mathrm{ad}} + J_{\mathrm{bd}} = J_{\mathrm{ac}} + J_{\mathrm{ad}} =$ 3.1 c.p.s. From the spectrum of *endo-cis*-5,6-dibromo-2-norbornene-5,6-d_2 (Ib), S_{c} is measured as 6.9 c.p.s., S_{a} = 4.8 c.p.s., S_{e} = 4.3 c.p.s., $J_{\mathrm{ce}} = J_{\mathrm{de}}$ = 2.1 c.p.s., and J_{ef} = 9.6 c.p.s. Coupling constants estimated in this manner are included in Table III.

TABLE IV

CHEMICAL SHIFT DIFFERENCES IN BENZENE FROM CARBON TETRACHLORIDE–DEUTERIOCHLOROFORM

Compd.	$H_{a,b}$	$H_{c,d}$	H_e	H_f	X	Y	X′	Y′
Ia	8	33	37	52	..	39	...	$= H_y$
Id	6	28	29	44	..	27	...	32
Ie	36	21	19	0	25	..	$= H_x$	...
If	41	18	21	3	27	..	25	...
Ig	12	12	18	16	..	5	2	...
Ij	31 or 19	32	24	23	..	12	9	...
Ik	31 or 19	32	24	23	9	..	...	13
VIa	32	41	42	53	..	51	...	$= H_y$
VIb	56	36	42	30	52	..	$= H_x$	...
VII	12	33	14	53	..	51	...	$= H_y$
IIe	...	..	..	..	..	29	...	29
IIf	...	..	..	..	..	..	...	34
IIh	...	..	..	..	30	..	30	...
IIi	...	27	..	..	..	6	8	...
IIk	...	24	..	..	..	..	6	...
IIm	...	..	..	..	..	5	4	...
IIn	...	..	..	..	..	..	5	...
IIo	...	..	..	..	13	..	...	18

Discussion

Chemical Shifts.—A distinguishable feature in the spectra of the saturated and unsaturated dihalo compounds is that the *endo* α-proton resonance occurs at a higher field than that of the *exo*. *endo* α-protons are invariably characterized by sharp resonance peaks. The magnitude of this relative chemical shift difference varies between 17 and 40 c.p.s. For example, the *endo* 5,6-protons of *exo-cis*-5,6-dibromo-2-norbornene (Ie) occur at 23 c.p.s. higher field (0.38 p.p.m.) than those of the *endo* isomer Ia. With the bromochloro-2-norbornenes, the *endo* hydrogen atoms of If are 24 and 28 c.p.s. at higher field than the *exo* protons of Id. In the saturated series, the differences are 19 c.p.s. for the IIa–IIg pair and 17 c.p.s. for the IIe–IIh pair. The *trans*-dihalides, which allow intramolecular comparisons, show a much greater separation. The magnitudes are 40 c.p.s. (0.67 p.p.m.) for Ig, 39 c.p.s. for Ii, and 35 c.p.s. for IIi. Comparisons with the *trans*-5,6-bromochloro-2-norbornenes (Ij, Ik, IIm, and IIo) are complicated by other factors, and discussion of the chemical shifts for these compounds will be deferred. The anisotropy of the C-1–C-2 (C-3–C-4) bond in norbornenes and the C-1–C-6 (C-4–C-5) bond in norbornanes is usually considered to be the origin of the primary effect as noted by many workers.[5–8]

The variations in magnitude may be accounted for in terms of the magnetic anisotropies of the double bond[9,10] and the carbon–halogen bonds.[8b] The influence of the former will be discussed in greater detail below. Appreciation of the latter becomes important when one considers the large intramolecular differences given above and the observations that *both* protons in the *trans*-dihalides occur at higher fields than the corresponding protons of the two *cis* isomers (*cf.* Ig, *exo*, 263 c.p.s., *endo*, 223 c.p.s. *vs.* Ia, 267 c.p.s.,

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[5] W. D. Kumler, J. N. Shoolery, and F. V. Brutcher, Jr., *J. Am. Chem. Soc.*, **80**, 2533 (1958).

[6] F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

[7] H. E. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961).

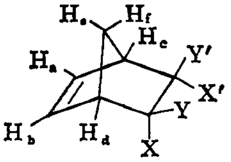
[8] (a) W. F. Erman and T. J. Flautt, *J. Org. Chem.*, **27**, 1526 (1962); (b) T. J. Flautt and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 3212 (1963).

[9] R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

[10] J. Paasiverta, *Suomen Kemi*, **B36**, 76 (1963).

TABLE V

DOUBLE RESONANCE STUDIES OF 5,6-DIHALO-2-NORBORNENES



Compd.	Proton(s) observed	Proton(s) saturated	Original pattern[a]	Resulting pattern[a]	Remarks
Ia	$H_{e,f}$	$H_{a,b}$	dbr (H_f)	dt (H_f)	Small J_{af}
(X = X′ = Br)	$H_{c,d}$	$H_{a,b}$	mbr	mbr	
	Y,Y′	$H_{a,b}$	t (dd)	n.c.	
	$H_{a,b}$	$H_{c,d}$	t	sbr	
	Y,Y′	$H_{c,d}$	t (dd)	s	Presence of J_{yd}
	$H_{c,d}$	Y,Y′	mbr	m (simp)	
Ie	H_f	$H_{a,b}$	dbr	dt	Small J_{af}
(Y = Y′ = Br)	$H_{c,d}$	$H_{a,b}$	qu	t	
	$H_{a,b}$	$H_{c,d}$	tbr	sbr	
	$H_{c,d}$	X,X′	qu	qu	No significant J_{xd}
	X,X′	H_e	d	s	Long-range J_{ex}
	$H_{a,b}$	H_f	tbr	t	
Ig	H_f	$H_{a,b}$	dbr	dt	Small J_{af}
(X = Y′ = Br)	$H_{c,d}$	$H_{a,b}$	mbr	m (simp)	
	X′	$H_{a,b}$	t	n.c.	
	$H_{a,b}$	$H_{c,d}$	m	q	
	Y	X′	t	d	
	H_e	X′	dq	dbr	
	X′	H_e	t	d	
	Y	H_e	dd	n.c.	
Id	H_f	$H_{a,b}$	dbr	dt	
(X = Br, X′ = Cl)	Y,Y′	$H_{c,d}$	o	AB (q)	
	$H_{c,d}$	Y,Y′	mbr	m (simp)	
Ij + Ik	218 c.p.s.	$H_{a,b}$	t	n.c.	
	230 c.p.s.	$H_{a,b}$	t	n.c.	
	214 c.p.s.	266 c.p.s.	t	d	

[a] n.c. = no change; m (simp) = simplified multiplet; tbr = broad triplet; o = octet; for the meaning of the other abbreviations see footnote *a* of Table I.

and Ie, 244 c.p.s.). The facts indicate increased shielding of an eclipsed β-C–H by a carbon–halogen bond suggesting a *positive* magnetic anisotropy for the carbon–halogen bond. A calculation of the sign (and magnitude) of the carbon–chlorine bond anisotropy[8b] employing an equation proposed by Zürcher[11] gave a positive value. With the present series of dihalides, a C-2 halogen atom (whether *exo* or *endo*) should shield a *cis*-C-3 hydrogen (vicinal, eclipsed) and have little effect (possibly slightly deshielding) on a *trans* vicinal hydrogen atom. Although both α-methine protons of the *trans* isomers are shielded relative to the stereochemically equivalent protons of the *cis*-dihalides by this mechanism, the *endo* protons are affected to a greater extent. This we designate as the "*endo* effect" apparently arising because of differing magnitudes of C–X bond anisotropies depending upon whether the halogen substituent is *endo* or *exo*. We have no way of evaluating the extent of contribution of a small π character in these ring systems[12] or the effect of a lower dipole moment characteristic of the *trans*-dihalides. A study of the bicyclo[2.2.2]octyl analogs will be helpful in resolving some of the remaining questions. The additional point may be made that positive magnetic shielding by eclipsed vicinal chlorine is larger than that by eclipsed vicinal bromine.

A comparison of the two *exo*-monohalonorbornanes IIp and IIq shows that a proton α to chlorine absorbs at about 10 c.p.s. higher field than the corresponding proton α to bromine. The very same trend may be observed by comparing the spectra of the dibromo- and dichloronorbornenes and -norbornanes, and is in agreement with data from α-halocamphors.[5] From considerations based only upon electronegativity differences, the opposite might be expected. This topic has been examined rather extensively, and several rationalizations have been put forth.[13,14] It has been repeatedly pointed out that the absolute chemical shifts for given protons in simple halides is misleading, and the internal chemical shift differences ($\delta_{H\alpha} - \delta_{H\beta}$) usually show good correlation with electronegativities.[15]

Nevertheless, the chemical shift comparisons given above for the halo- and dihalonorbornenes and -norbornanes are *normal* for secondary halides, despite the presence of a vicinal (and complicating) halogen atom. On this basis, the report that the 5-proton of *endo*-5-bromo-2-norbornene absorbs at higher field than the 5-proton of the chloro analog is confusing.[15b] Perhaps the chemical shift data were accidentally reversed.

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[11] R. F. Zürcher, *J. Chem. Phys.*, **37**, 2421 (1962).

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

[13] J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1094, 1099 (1961).

[14] A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **80**, 1728 (1958).

[15] See for example (a) K. L. Williamson, *ibid.*, **85**, 516 (1963); (b) P. Laszlo and P. v. R. Schleyer, *ibid.*, **85**, 2709 (1963).

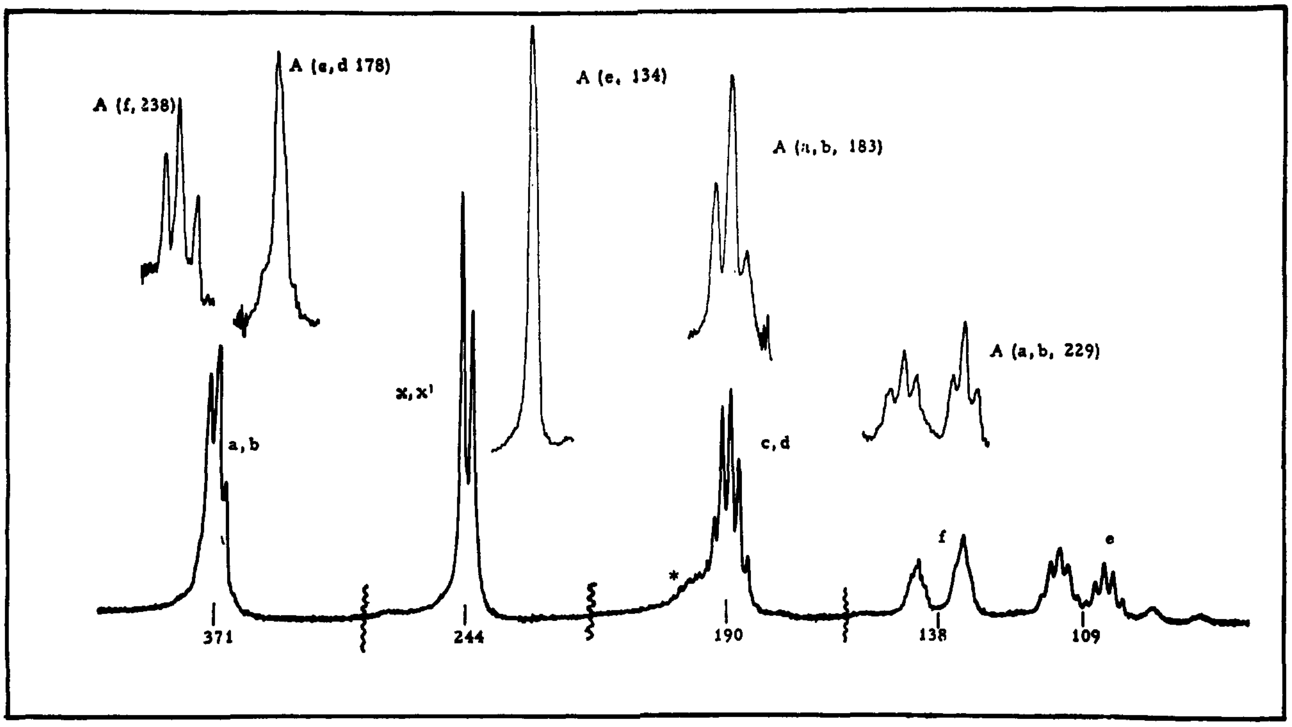


Figure 1.—N.m.r. spectra of *exo-cis*-5,6-dibromo-2-norbornene (* = trace impurity).

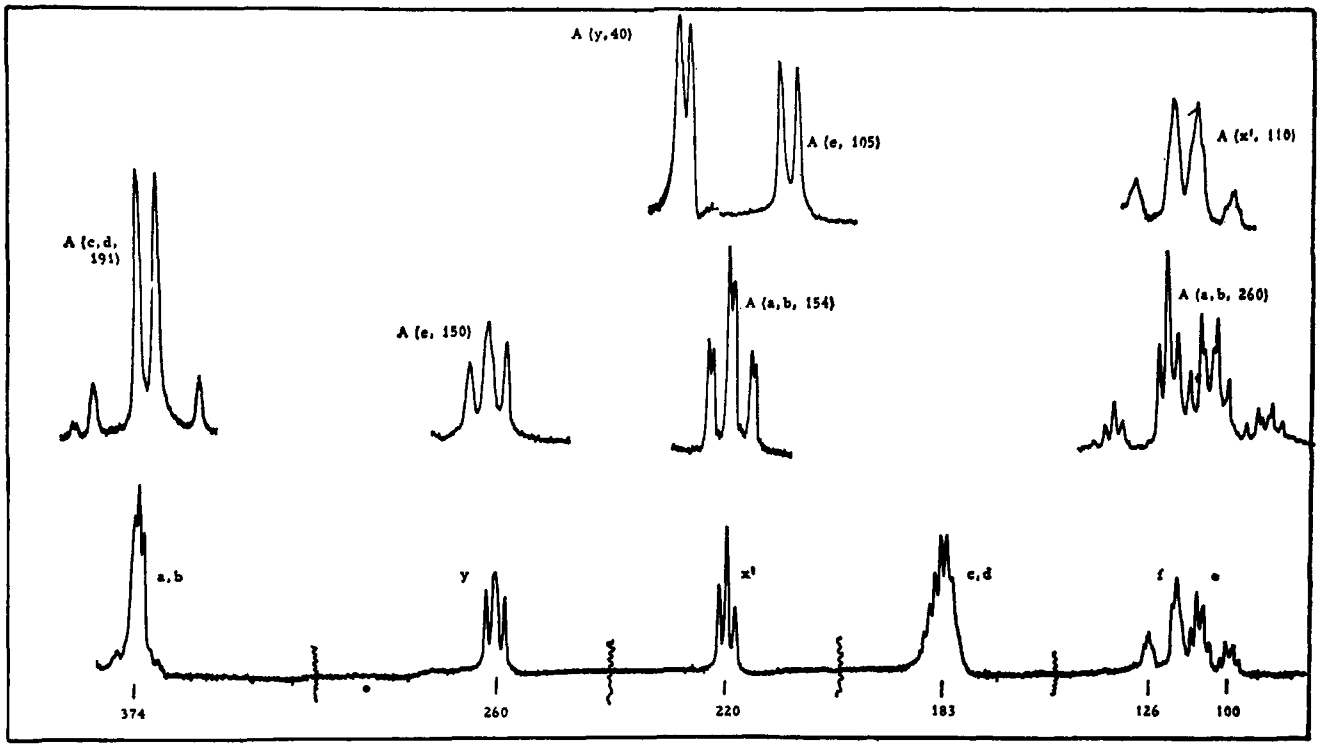


Figure 2.—N.m.r. spectrum of *trans*-5,6-dibromo-2-norbornene.

With the experimentally verified observations that (1) *endo* protons absorb at higher field than *exo* protons, (2) protons α to chlorine normally absorb at higher field than those α to bromine, and (3) vicinal β-halogen substituents cause shielding of *cis* (eclipsed) α-protons, with the effect of chlorine being larger than that of bromine and *endo* protons being more sensitive than *exo* protons; attention may now be turned to the *trans*-5-bromo-6-chloro-2-norbornenes and the *trans*-2-bromo-3-chloronorbornanes. Only one of the compounds, IIm, was obtained pure, and the chemical shift assignment to the two methine protons was confirmed by a study of the *exo*-monodeuterated derivative IIn. From these data, chemical shift assignments for the isomer IIo could be unambiguously made from the spectrum of the mixture of IIm and IIo. The spectrum of the mixture of Ij and Ik showed four multiplets corresponding to protons α to halogen atoms: two *exo* protons at low field and two *endo* protons at high field. Double resonance work clearly showed that the protons at 266 and 214 c.p.s. were coupled and hence in the same molecule (Figure 4). By analogy with the

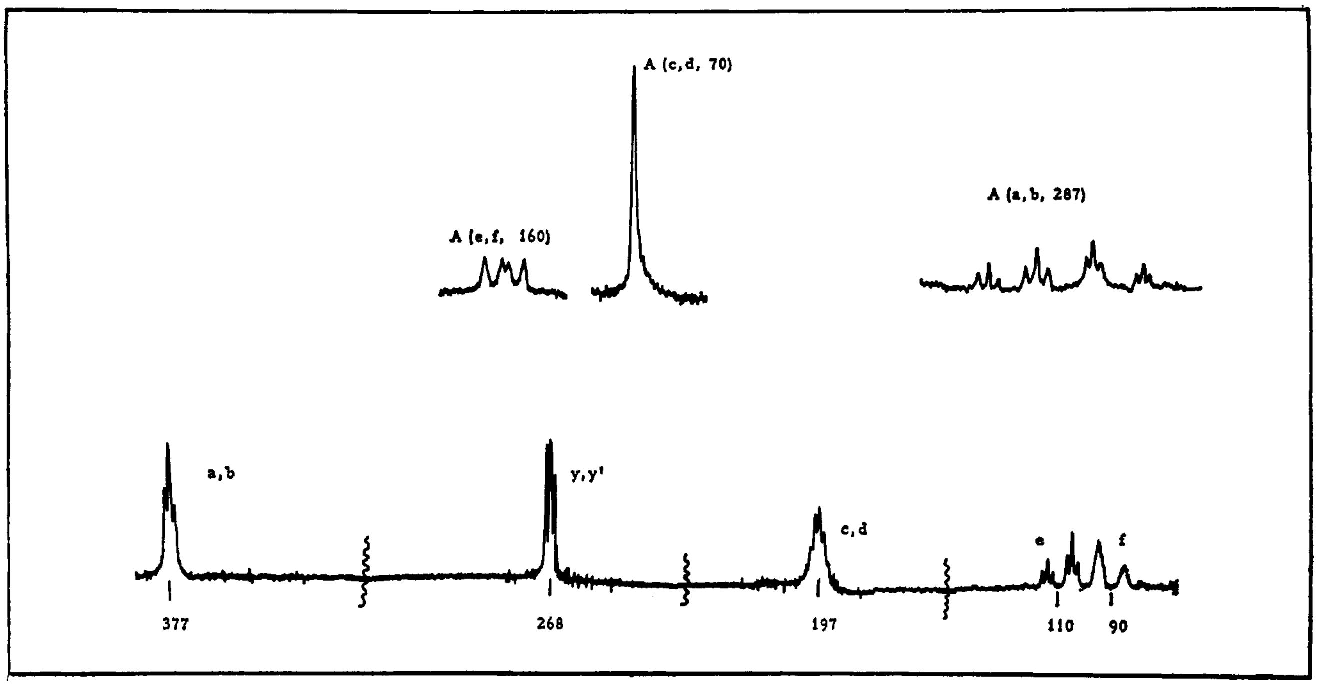


Figure 3.—N.m.r. spectra of *endo-cis*-5,6-dibromo-2-norbornene (in deuteriochloroform).

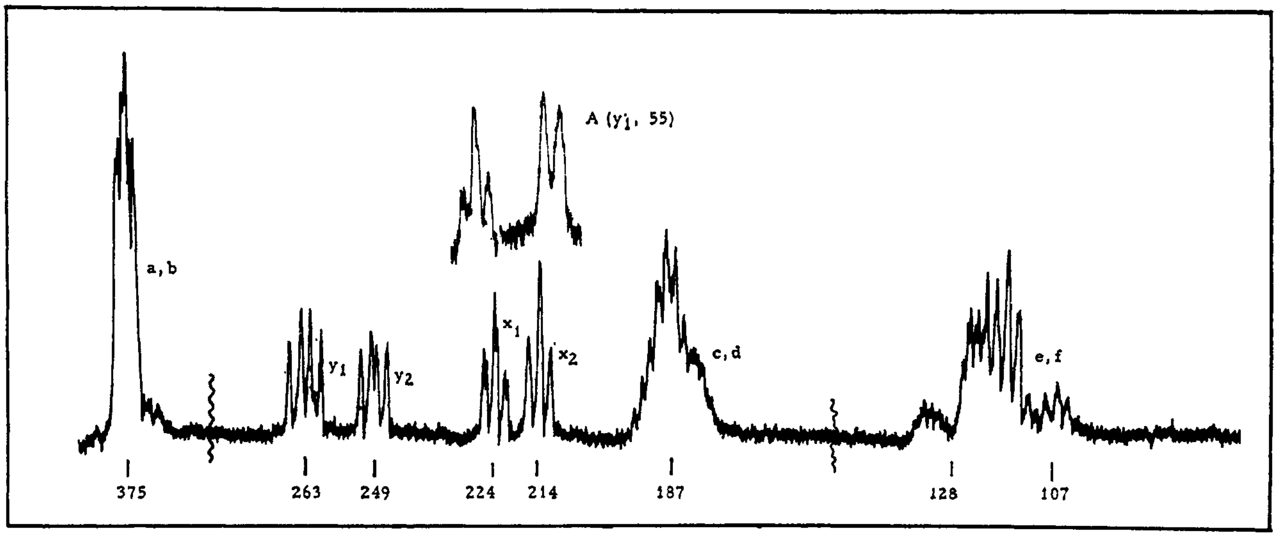


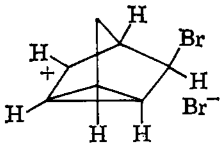
Figure 4.—N.m.r. spectra of a 1:1 mixture of *exo*-5-bromo-*endo*-6-chloro-2-norbornene and *endo*-5-bromo-*exo*-6-chloro-2-norbornene.

saturated analog, these were assigned as characteristic resonances of *exo*-5-bromo-*endo*-6-chloro-2-norbornene (Ij). The isomer *endo*-5-bromo-*exo*-6-chloro-2-norbornene (Ik) showed absorption at 251 and 225 c.p.s.

Some significant comparisons may be made. The *exo* proton (α to chlorine) of Ij absorbs at 3 c.p.s. lower field than that of Ig (both β-substituents are bromine). Similarly, the *endo* proton of Ik (225 c.p.s.) occurs at lower field than the *endo* proton of Ig (223 c.p.s.), whereas the *exo* proton of Ik and the *endo* proton of Ij (251 and 214 c.p.s., respectively, both β substituents chlorine) appear at slightly higher field than the analogous protons in Ii (255 and 216 c.p.s.). This trend is the reverse of that which occurs in the *cis* compounds. That eclipsed vicinal chlorine is more shielding than eclipsed vicinal bromine can easily be seen by comparison of Ij and Ik. The *exo* proton of Ij (α to chlorine, β to bromine) is some 15 c.p.s. lower field than the *exo* proton of Ik (α to bromine, β to chlorine); the corresponding value for the *endo* protons is 9 c.p.s., with that of Ik (α to chlorine, β to bromine) at lower field. Similar conclusions are evident upon examination of the data for the saturated isomers II.

The vinyl proton resonances are the least affected by the 5,6 substituents, regardless of stereochemistry. This precludes any significant electronegativity effect by the substituents on the remote double bond. This result may be contrasted to the report[10] that 5-*endo* substituents caused a greater downfield shift in the position of the olefinic proton resonances than did corresponding 5-*exo* substituents.

The bridgehead proton(s) resonances were very complex owing to spin–spin interactions with many vicinal and allylic hydrogen atoms, and were consequently not amenable to an analysis. However, by measuring the position of the center of the broad multiplet it was observed that an *exo*-5-halogen substituent in the norbornenes exerted a shielding effect of approximately 10 c.p.s. relative to an *endo*-5-halogen atom (*cf.* Ia–Ie, Ia–Ig, Id–If, Id–Ij, Id–Ik, Ic–Ii). From an examination of models one finds that (1) the *exo*-halogen–bridgehead proton distance is shorter than the corresponding *endo*-halogen–bridgehead proton distance; and (2) the *exo*-bridgehead dihedral angle is ~40°, whereas the *endo*-bridgehead angle is ~80°. This minor shielding influence might be attributed to C–X bond anisotropy which affects the bridgehead protons to different degrees depending upon the *exo* or *endo* orientation of the halogen atoms. Surprisingly, the *exo*-halogen substituent effect is small for the saturated analogs, and is in the opposite direction. It could well be that this latter is the normal situation, and the anomaly with the norbornenes is brought about by resonance contributions from forms such as VIII. Such "homoallylic resonance" would be important only for *exo* substituents.



VIII

Each of the methylene bridge (C-7) protons of the compounds I (also III and VI) showed a characteristic pattern distinct from that of the other proton. The over-all appearance was that of an AB quartet; the two lines corresponding to one of the protons had well-defined fine splitting, whereas the other pair were broadened. The proton H_e, *syn* to the double bond, always absorbed at approximately the same field position. Proton H_f, *anti* to the double bond, showed resonance which was highly dependent on the orientation of the C-5,C-6 substituents. When the halogen substituents were *exo*, the proton H_f was highly deshielded. A smooth trend toward lower field can be observed in going from the *endo-cis* isomer to the *trans*-dihalide (*cf.* Ia–Ig = −31 c.p.s., Id–Ij = −37 c.p.s., Ic–Ii = −35 c.p.s.) to *exo-cis*-dihalide (*cf.* Ia–Ie = −50 c.p.s., Id–If = −44 c.p.s.). That H_f was the proton whose resonance position was altered was unequivocally demonstrated by double resonance experiments. This deshielding is probably due to anisotropy effects; a steric argument has little to recommend it. The deshielding is much smaller with the anhydride VIa (relative to VIb), possibly because the deshielding of Hf by the electronegative substituents in the *exo*-anhydride VIb is partially offset by the fact that this proton is situated in the diamagnetic shielding region above the carbonyl groups of the anhydride.

It has been reported that the methylene-bridge proton when *syn* to the double bond in a norbornene absorbs at higher field because it resides in the diamagnetic region of the double bond.[4,16] Such is *not* the situation with the 5,6-dihalo-2-norbornenes. In the *endo-cis* derivatives, the proton H_e (*syn* to the double bond) actually absorbs at lower field than the proton H_f. It might be argued that the two highly polar *endo* substituents affect the molecular moments of the compounds in such a way as to alter the electronic distribution about the C-7 protons and overcome the anisotropy effect of the double bond. However, the original generalization[4] was made with 7-substituted norbornenes, and it is more reasonable to assume that 7-substituents are responsible for the effect rather than the remote double bond. The final answer to the problem must await a complete analysis of the norbornene spectrum.

Little information can be obtained from the resonance absorptions of protons H_e and H_f in the spectra of the saturated compounds because the peaks overlap with those of the other methylene protons.

In compound VII (*exo*-2,3-epoxy-*endo*-5,6-dibromonorbornane), the protons H_e and H_f absorb at 84 and 53 c.p.s. The pattern is consistent with those of the unsaturated dihalides. Since the epoxide is *exo*, a small deshielding of the *syn* proton (H_e) would be intuitively expected. The proton H_f would be unaffected by the vicinal *endo* bromine atoms. The observation is that both protons are considerably shielded relative to Ia, and one can delineate a significant ring current anisotropy that would shield both the proton *syn* to the epoxide and the proton *anti* to it unlike that postulated with other bicycloalkene oxides.[17]

It has been postulated that the 5- and 6-*exo* protons in *endo*-substituted 2-norbornenes lie in the deshielding region of the double bond.[9] The *exo* proton should, therefore, move upfield upon removing the anisotropy by hydrogenation of the double bond. The opposite effect is expected for the *endo* protons. This trend is, in general, observed with the compounds studied in this work. However, it should be pointed out that both the magnitude and the direction of this shift are dependent upon the nature of the substituents. The shifts observed for the dihalonorbornenes are recorded in Table VI. Inconsistencies with Fraser's correlation are noted for *exo* protons.

TABLE VI

CHEMICAL SHIFT DIFFERENCES OF α-PROTONS OF 5,6-DIHALO-2-NORBORNENES AND 2,3-DIHALONORBORNANES

Unsaturated compd.	Saturated compd.	Δ, c.p.s.[a]	
		H_{exo}	H_{endo}
Ia	IIa	−1	...
Ic	IId	+5	...
Id	IIe	0, +3	...
Ie	IIg	...	−5
If	IIh	...	−7, −8
Ig	IIi	−3	−8
Ii	IIm	+3	−7
Ik	IIo	−3	−5

[a] + signifies a shift to higher field, and − a shift to lower field.

Coupling Constants. A. Geminal Coupling.—The geminal coupling in the absence of substituent effects is dependent on the geminal angle. In the disubstituted 2-norbornenes examined in this study, the only geminal coupling present is the one at C-7 corresponding to a C-1–C-7–C-4 angle ≃96.5°.[18] Based upon available literature data, a coupling constant intermediate between those observed in cyclobutyl and cyclohexyl systems was anticipated. Values of the observed geminal coupling constants are included in Table III and are consistently found to lie between 8.9 and 9.8

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(16) K. Tori, *et al.*, *Can. J. Chem.*, **42**, 926 (1964).

(17) K. Tori, *et al.*, *Tetrahedron Letters*, 559 (1964).

(18) D. A. Brueckner, T. A. Hamor, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.*, 799 (1962).

c.p.s. No significant 5,6-substituent effect was expected or noticed. These values are in good agreement with those reported.[3,12] This coupling constant could not be evaluated with certainty for the saturated compounds (II) owing to overlap of these peaks with those of the other methylene peaks.

B. Vicinal Coupling.—Analysis afforded considerable information about vicinal couplings in the 5,6-dihalo-2-norbornenes and 2,3-dihalonorbornanes. Certain trends relating spin–spin coupling constants with dihedral angles and electronegativity are evident, but even more subtle factors can be seen to play a part.

The vinyl proton ($H_{a,b}$) resonance in the compounds I were quite complex. With *cis*-dibromides or -dichlorides, the patterns occur as irregular triplets, and these have been adequately accounted for[3] in terms of "virtual coupling,"[19] an explanation readily verified by the double resonance work (see entry 4, Table V and Figure 3). With the *trans*-dihalides and the *cis*-bromo chlorides the pattern becomes that of a complex multiplet because the protons H_a and H_b are no longer isochronous. Evaluation of J_{ab} for *trans*-5,6-dibromo-2-norbornene by double resonance—which simplified the multiplet to a clean AB quartet—led to a value of 5.9 c.p.s. The corresponding coupling for III could be measured directly and was determined to be 5.6 c.p.s. These numbers are in close agreement with the value reported[3] (note also, *cis* coupling in cyclopentenes is of the order of 5.1–5.4 c.p.s.[20]).

The vinyl–bridgehead coupling constant, $J_{ac} = J_{bd}$, may be measured directly from the spectra of the 1-methyl derivatives III and V and shows a value of 3.6–3.8 c.p.s. This value is somewhat higher than those previously reported (2.8–3.0 c.p.s.[3]). The vinyl proton pattern for V shows six lines each somewhat broadened; the high-field proton (C-6 H) shows two lines corresponding to one-half of an AB quartet, whereas the low-field proton (C-5 H) shows four lines corresponding to coupling with the bridgehead proton (C-4 H). Allylic coupling between the C-6 and C-4 proton must be 0.8 c.p.s. since the lines for the C-6 proton are not appreciably broadened (W_h = 1.65 c.p.s.). From measurements of the separation of the outerlines of the vinyl proton "triplet" of Ia (*endo-cis*-dibromide), a value, $S = 4.5 = J_{ac} + J_{ad} + J_{af}$, was obtained. Assuming the allylic coupling (J_{ad}) to be +0.8 c.p.s.,[3,4,21] and the long-range coupling (J_{af}) to be 0.8 c.p.s. (*vide infra*), a value for $J_{ac} = J_{bd} = 2.9$ c.p.s. can be estimated.

An analysis of the AB quartet of the *exo* protons of *endo-cis*-5-bromo-6-chloro-2-norbornene (Id) gave a value of 7.4 c.p.s. for the *exo–cis* coupling constant ($J_{yy'}$). A similar value (7.5 c.p.s.) had been reported earlier for *endo-cis*-5,6-dichloro-2-norbornene.[3] The corresponding coupling for 1-methyl-*endo-cis*-5,6-dichloro-2-norbornene (III) was observed to be 7.8 c.p.s. For the saturated analogs IIe and IV, the values for $J_{yy'}$ were found to be much higher, 9.5 and 9.3 c.p.s., and are nearly the same as that found for the norborneols[12] despite the absence of a vicinal electronegative substituent in the latter.

exo-cis-5-Bromo-6-chloro-2-norbornene is an ideal compound for evaluation of the *endo-cis* coupling constant. A value of 6.8 c.p.s. was obtained for $J_{xx'}$, and is smaller than the *exo–cis* coupling constant by 0.6 c.p.s. Preliminary examination of the spectrum of 1-methyl-*exo-cis*-5,6-dichloro-2-norbornene shows $J_{xx'}$ = 7.1 c.p.s. This unique variation is surprising because, in both cases, the dihedral angles and substituent effects are identical. This decrease, though smaller in magnitude, is in the same direction as that observed by Musher.[12] No significant variation was noticed for the *endo-cis* coupling between the norbornenes and norbornanes. A $J_{yy'}$ of 6.8 c.p.s. was measured for compound IIh.[22]

The results given here, coupled with numerous literature reports, indicate a wide variation in *exo–exo* and *endo–endo* coupling constants of norbornanes and norbornenes depending upon the nature of the substituents. Nevertheless, with identical substituents $J_{endo\text{-}endo}$ does not vary significantly from saturated to unsaturated systems, whereas $J_{exo\text{-}exo}$ increases by at least 2 c.p.s. when a norbornene is hydrogenated to a norbornane. This large *exo–exo* coupling constant has been referred to as "anomalous."[12] Essentially the question revolves around whether the *exo–cis* coupling is abnormally large in the saturated series or abnormally small in the unsaturated analogs. The latter might be explained on the basis of partial overlap of the back lobes of the *exo* C-5 H and C-6 H bonds with the π orbital of the double bond causing a decrease in the magnitude of the coupling. A rationale for the former might cite steric restrictions involved with placing a substituent(s) *endo* in a norbornyl system as perturbing the *exo* hydrogen atoms and enhancing coupling. The data is insufficient to distinguish between the alternatives, and we contemplate X-ray crystallographic work.

An unusual feature in the spectrum of *endo*-5,6-dibromo (and dichloro)-2-norbornene is that the *exo*-proton(s) resonance occurs as a quartet (or unsymmetrical triplet).[3] It may be argued that the pattern arises from interaction with both the bridgehead and the vinyl protons. The latter is not warranted because irradiation of the vinyl resonance leaves the quartet unaltered. Irradiation at the resonance frequency of the bridgehead proton(s), however, cause the quartet to degenerate into a sharp singlet. This allows the conclusion that there is interaction between the *exo* proton and *both* bridgehead protons, despite ample evidence in this and other work[3] that J_{yc} ($= J_{y'd}$) = 0. The explanation is qualitatively given in the terminology "virtual coupling"[19] resulting from the (nearly) isochronous, strongly coupled, vicinal *exo* proton. Treating the observed pattern of this symmetrical molecule as the A portion of a limiting A_2X_2 system ($J'_{AX} = J_{yc} = 0$, $J_{AA} = J_{yy'} = 7.4$ c.p.s., and $J_{XX} = J_{cd} \cong 1.0$ c.p.s., we would expect an irregular triplet with the separation between the outer lines equal to $J_{AX} = J_{yd}$ (3.3 c.p.s., Table III). The fact that some splitting of the center line of the triplet is observed suggests that the two *exo* protons may have slightly different chemical shifts. *endo-cis*-5-Bromo-6-chloro-

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

[20] (a) G. V. Smith and H. Kriloff, *J. Am. Chem. Soc.*, **85**, 2016 (1963); (b) O. L. Chapman, *ibid.*, **85**, 2014 (1963); (c) P. Laszlo and P. v. R. Schleyer, *ibid.*, **85**, 2017 (1963).

[21] See also, E. W. Garbisch, Jr., *ibid.*, **86**, 5561 (1964).

[22] Values for the *endo-cis* coupling constants for the *exo-cis* oxymercuration products of norbornadiene and norbornene have been reported as 5.9 and 6.6 c.p.s., respectively: F. A. L. Anet, *Tetrahedron Letters*, 3399 (1964).

2-norbornene (Id) does not appear to exhibit this unique splitting; probably because the protons α to the halogen substituents are no longer isochronous ($\nu_y - \nu_{y'} =$ 15 c.p.s.) and $J_{yc} = J_{y'd} = 0$. A symmetrical eight-line pattern for the AB portion of an ABXX′ spectrum was observed and analyzed. The broad multiplet for the *exo* protons of the saturated *endo–cis* analogs are less amenable to analysis; contributing interactions are J_{yd}, J_{yc} (virtual coupling), and J_{yb} (long-range coupling).

Very little variation was noticed for the *trans* coupling ($J_{xy'}$) in all the cases investigated. Values obtained varied between 2.3 and 2.5 c.p.s. This value is not much at variance with the coupling constant expected from dihedral angle considerations alone. In the saturated series (II), a slight increase in the *trans* coupling constant was observed (IIi, 2.9 c.p.s.; IIm, 2.6 c.p.s.). Comparative literature values vary between 2.2 and 2.3 c.p.s.[3] The value is generally higher (3.2 c.p.s.) in monohalonorbornanes because of electronegativity effects.

On the basis of an assumption that J_{yd} and $J_{y'c}$ have the same value (within experimental error) for 5,6-dihalonorbornenes, a large range (2.9–4.3 c.p.s.) in the *exo*–bridgehead coupling constant has been detected. The reported values vary from 3.2 to 3.9 c.p.s.[12] With the saturated analogs, experimental measurements yield only ($J_{yd} + J_{yb}$). In most cases the *exo* proton is a broad multiplet, and consequently a precise evaluation of coupling constants becomes an arduous task. If 2-*exo*–6-*exo*- or 3-*exo*–5-*exo* coupling constants are assumed to be $\simeq$1.5 c.p.s.,[12] the *exo*–bridgehead coupling constant in IIl could be calculated to be $\simeq$3.5 c.p.s. This value is again slightly higher than the value for the unsaturated compound. A small error in this value is to be expected, because a slight broadening due to the vicinal deuterium substituent may be present.

From the pattern of the resonance peak of proton $H_{e,f}$ in compounds Ia and Ib, a value of 2.1 c.p.s. was obtained for J_{ec} ($= J_{ed}$) (reported 2.0 c.p.s.).[12] However, when the substituents are *exo* (Ie), a small decrease in the value (1.7 c.p.s.) was seen. For *trans*-2,3-dibromo-2-norbornene (Ig) only an approximate estimate could be obtained because the proton H_e appears as a quartet due to coupling with the different bridgehead protons—probably with unequal coupling constants—and with the *endo* proton. A rough calculation gave $J_{ec} \simeq 2.1$ c.p.s.

Because of the obscured pattern in the H_f resonance peak, J_{fc} and/or J_{fd} could not be easily evaluated. One of the reasons for this complex pattern is a small, but significant, long-range coupling with the vinyl protons. On removal of this interaction by decoupling of the vinyl proton resonance, the H_f peak is found to appear as a defined set of two triplets. Analysis of this set afforded a value of 1.5–1.7 c.p.s. for J_{fc} ($= J_{fd}$). This J_{fc} coupling is obviously lower than that of J_{ec}. A possible explanation for this behavior is the electronic interaction between H_f and the *exo*-oriented electronegative halogen atoms which decreases the electron density around H_f. A similar decrease in vicinal coupling with increasing electronegativity of the substituent has been noted. The more remote proton H_e again is affected very little.

Spin–spin interaction between the *endo* protons (x,x′) and the bridgehead protons (c,d) was found to be $\cong$0 for all compounds studied.

C. Long-Range Coupling.[23]—It was mentioned earlier that the bicycloheptene skeleton, with its rigid geometry, allows certain spin–spin interaction properties such as long-range coupling, virtual coupling, etc. A small *positive* allylic coupling (J_{ad}, J_{bc}) is present in the spectra of substituted norbornenes.[3,4,21] The compounds examined here do not provide an exact value for this coupling constant, although the double resonance experiments clearly show it is present. Other J_4 couplings can, however, be evaluated. Theoretical explanations have not been satisfactorily presented for σ-bond interactions over four bonds,[24] but a rationale has been given that this phenomenon is due to interaction between the small lobes of the carbon sp^3 orbitals, situated *trans* to each other, or between the small lobe of the sp^3 orbital and sp^2 orbitals wherever geometry permits.[25]

The most significant long-range interaction in norbornenes and norbornanes is the *endo*-5H–*anti*-7H and *endo*-2H–*anti*-7H coupling (J_{xe}, $J_{x'e}$) suggested by Musher[12] and confirmed, first by *anti*-7-substitution,[26] later by C-13–H coupling measurements,[3] and in the present work by double resonance. For the unsaturated compounds I this coupling varied in magnitude from 2.1 to 2.5 c.p.s. (Ie,g,j,k). In Ie, the *endo* 5(6)-proton resonance absorption (x,x′) occurs as a sharp doublet, $J = 2.1$ c.p.s. Coupling with the adjacent bridgehead proton ($H_{c,d}$) is unlikely because the pertinent dihedral angle measures $\sim$80°. Irradiation at the absorption frequency of the *anti* 7-proton H_e caused this pattern to simplify to a sharp singlet (Figure 1). Similarly, the *endo* 5-proton resonance of the *trans*-dibromide Ig appears as a regular triplet. This triplet pattern is retained upon irradiation of the bridgehead protons $H_{c,d}$, but degenerates to a doublet upon irradiation of either the vicinal *exo*-5H or the *anti*-7H (Figure 2).

This same interaction occurs in the spectra of the saturated analogs II. It could be demonstrated by the observation that the proton $H_{x'}$ of the *exo* 6-deuterated *trans* isomer IIk appears as a doublet with a $J_{x'e} = 2.8$ c.p.s. This value may be slightly high because of the line-broadening effect of the vicinal deuterium atom; it appears to be general that J_{xe} is somewhat higher in the saturated compounds than in the norbornenes.

A long-range coupling between the vinyl protons ($H_{a,b}$) and the *anti* 7-proton (H_f) is observed in substituted norbornenes. This constant, J_{af} ($= J_{bf}$), was calculated to be in the order of 0.8 c.p.s. for compound Ia, a value in good agreement with those reported.[4] This coupling is clearly seen in the double resonance spectra (Figures 1–3). In each case the broad, two-line pattern for H_f is simplified to a pair of triplets by irradiation at the vinyl proton resonance frequency.

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(23) Good reviews of such long-range coupling are S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964); C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, **No. 34**, 115 (1962); A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, **No. 5**, 233 (1964).

(24) See, however, footnote 8a in ref. 21.

(25) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961).

(26) J. Meinwald and Y. C. Meinwald, *ibid.*, **85**, 2514 (1963).

Calculations also give evidence for a long-range coupling between the two bridgehead protons (H_c and H_d). J_{cd} seems to be in the order of 1.0 c.p.s.; a value of $\sim$1.5 c.p.s. has been reported for this type of coupling.[27]

A long-range coupling between *exo* 2(3)-protons (H_y $H_{y'}$) and the *exo* 5(6)-protons is evident in the norbornane derivatives II. The patterns for H_y and $H_{y'}$ in the spectra of these compounds show as broad multiplets with much fine splitting, and an evaluation of J_{yb} and $J_{y'a}$ is hardly worthwhile. An estimate from the spectrum of the monodeuterated *trans* isomer III allows a prediction of $J_{yb} = 2$ c.p.s., which is undoubtedly high because of the deuterium quadrupole moment.

Solvent Shifts.—The shift of the resonance absorption of the various protons when the solvent is changed from carbon tetrachloride (or deuteriochloroform) to benzene are recorded in Table IV. Each of the protons in the dihalides is shifted to higher field in benzene solution.

With *endo-cis*-5,6-dihalo-2-norbornenes, the C-7 proton H_f, *anti* to the double bond, the bridgehead protons $H_{c,d}$, and the *exo* protons $H_{y,y'}$ are highly shielded. Shielding of the *syn*-C-7 proton H_e occurs to a moderate degree, whereas the vinyl protons $H_{a,b}$ are hardly affected. A 1:1 complex of these isomers with the aromatic solvent having a specific orientation has been proposed to account for the magnitude of these shifts,[3] and our work is in general agreement.

When the substituents are both *exo* oriented (Ie,f,h), the situation is somewhat different. Again, the α-protons $H_{x,x'}$ are shielded effectively, but most affected are the vinyl protons $H_{a,b}$. The *anti*-C-7 proton H_f has little change in its resonance position. Employing considerations similar to those outlined,[3] we can conclude that the 1:1 complex of benzene with the *exo-cis*-dihalides has a probable geometry in which the aromatic ring is oriented below the norbornene skeleton parallel to the plane defined by C-1, C-2, H_x, and $H_{x'}$.

Shielding of the protons of the *trans*-5,6-dihalo-2-norbornenes by an aromatic solvent is less pronounced than with the two *cis* isomers. Both C-7 protons are appreciably shielded as are the vinyl protons. Only slight shielding of the α-protons is noted, with that of the *exo* proton being greater than that of *endo*. A possible orientation of a 1:1 complex is that in which the benzene ring is parallel to the plane defined by H_a, H_b, and H_f.

These selective solvent shifts can be used to assign stereochemistry of 2,3-disubstituted norbornanes and 5,6-disubstituted 2-norbornenes under certain circumstances.

Experimental

2-Norbornene and Norbornane Derivatives.—Syntheses of the 5,6-dihalonorbornenes (I), 2,3-dihalonorbornanes (II), and the deuterated analogs have been reported elsewhere.[2,28,29] 1-Methyl-*endo-cis*-5,6-dichloro-2-norbornene (III) and 1-methyl-5-*exo*-6-*endo*-dichloro-2-norbornene (V) were prepared by the addition of *cis*- and *trans*-dichloroethylene to commercially available methylcyclopentadiene (cracking of the dimer) by Dr. W. Redmond. Purification was effected by fractional distillation and low temperature crystallization: *cis* isomer III, m.p. 47.5–48.3°; *trans* V, b.p. 28–28.5° (0.5 mm.). *endo*-3,6-Methylene-1,2,3,6-tetrahydro-*cis*-phthalic anhydride (VIa), from maleic anhydride and cyclopentadiene, was recrystallized from petroleum ether (b.p. 40–60°), m.p. 162–163° (lit.[30] m.p. 161–162°). The *exo*-anhydride VIb was prepared by thermal isomerization of VIa and was recrystallized from benzene, m.p. 139–141° (lit.[31] m.p. 142–143°). *exo*-2-Bromonorbornane (IIp) was obtained by addition of hydrogen bromide to norbornene: b.p. 96.5–97° (45 mm.), $n^{25}\mathrm{D}$ 1.5123 (lit.[32] b.p 82° at 29 mm., $n^{25}\mathrm{D}$ 1.5126). Similarly, *exo*-2-chloronorbornane (IIq) showed b.p. 74° (21 mm.) and $n^{25}\mathrm{D}$ 1.4826 (lit.[33] b.p. 97° at 100 mm., $n^{25}\mathrm{D}$ 1.4823).

***endo-cis*-5,6-Dibromo-2-norbornene Oxide (VII).**—A solution of 1.34 g. (0.0053 mole) of *endo-cis*-5,6-dibromo-2-norbornene in 10 ml. of chloroform was cooled in an ice bath and 10.5 ml. of concentrated monoperphthalic acid solution (in ether) was added with stirring over a 45-min. period. After 24 hr. at room temperature a white precipitate had formed (phthalic acid). The solid was removed by filtration and was washed with chloroform. The weight of the residue indicated that the reaction had proceeded to 95% completion. The filtrate was washed with aqueous sodium bicarbonate solution and water and was dried over anhydrous magnesium sulfate. The solvent was removed by distillation, and the residue was crystallized from hexane to give 0.82 g. (57.3%) of the epoxide VII, m.p. 137–138.5°.

N.m.r. Measurements.—Spectra were recorded with a Varian DP-60 spectrometer. Line positions were measured by a linear interpolation of frequencies of audio side bands using an HP 200 CDR wide-range oscillator and an HP 523 CR counter. Solutions of the compounds were made up to approximately 20% w./v., except when limited by solubility, in the specified solvent. Tetramethylsilane was used as the internal standard.

Double resonance studies were carried out by employing essentially the instrumentation described by Freeman[34] and Elleman and Manatt,[35] with minor modifications (M. T. E.).

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