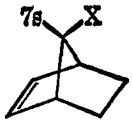
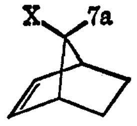


XI
anti



XII
syn

the above equation that the 7-*syn* proton experiences a paramagnetic shift of +5 Hz. Since the X-ray analysis of the corresponding *syn* compound (XII, X = *p*-bromobenzoate) has not yet been accomplished, it is impossible to calculate the effect of the double bond on the *anti*-7 proton (7a). Nevertheless the results do qualitatively show that only small perturbations are necessary to alter the geometry of the norbornenyl system to effect either paramagnetic or diamagnetic shifts on the bridge protons. Finally, support of the geometric interpretation over an electronic interpretation resides in Tanida's work on ring-substituted benzonorbornenes in which the relative chemical shift differences between the 7s and 7a protons remained invariant over a wide range of electron-donating to electron-attracting substituents.[23]

Experimental Section

Nmr spectra and proton decoupling experiments were performed on a Varian Associates HA-100 spectrometer. Deuterium decoupling experiments were performed on a Varian Associates A-60 spectrometer. Spectra were determined in carbon tetrachloride solution using tetramethylsilane as an internal standard.

exo,exo-5,6-Dideuterionorbornene (X) was prepared by published synthetic procedures.[11,12] The mass spectrum determined by the chemical ionization method[13] indicated a deuterium content of 95% d_2 and 5% d_1. The electron-impact spectrum gave an analysis of 99% d_2 and 1% d_1.

The X-ray data for *anti*-7-norbornenyl *p*-bromobenzoate[22] was utilized to calculate θ_1 and θ_2 for this compound; the value of θ computed from these data was 50° 40′. The chemical shift observed for the 7-*syn* proton in the *p*-bromobenzoate[24] was δ = 4.58 ppm.

Acknowledgment. The authors are indebted to Dr. F. H. Field of these laboratories for determining the mass spectral data.

(23) N. Inamota, S. Masuda, K. Tori, K. Aono, and H. Tanida, *Can. J. Chem.*, **45**, 1185 (1967).

(24) We wish to thank Dr. R. E. Pincock of the University of British Columbia for a sample of *anti*-7-norbornenyl *p*-bromobenzoate.

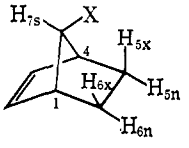
On the Question of Bridge-Proton Absorptions in the Nuclear Magnetic Resonance Spectra of Norbornene and Related Systems

Alan P. Marchand and Joseph E. Rose

Contribution from the Department of Chemistry, The University of Oklahoma, Norman, Oklahoma 73069. *Received January 8, 1968*

Abstract: *anti*-7-Deuterionorbornene has been synthesized stereospecifically. Comparison of its 100-MHz nmr spectrum with that of norbornene reveals that the *anti*-bridge proton (7a) absorbs at higher field (lower δ) than does the *syn*-bridge proton (7s). This result serves to substantiate unequivocally conclusions concerning this point which have been arrived at more recently upon reexamination of the nmr spectrum of norbornene.[6,8] The usefulness of the vinyl proton–*anti*-bridge proton long-range coupling in assigning the relative positions of bridge proton absorptions (AB pattern) is demonstrated through examination of the nmr spectra of several systems which are structurally related to the familiar insecticides aldrin (VIII) and isodrin (IX). The usefulness of coupling constant and chemical shift information as criteria for assigning stereochemical configuration in substituted norbornenes is assessed.

Analysis of the nmr spectrum of norbornene (Ia) has been a subjct of interest in recent years.[1–9] The 7-*syn* (7s), 7-*anti* (7a), 5,6-*endo* (5n,6n), and 5,6-*exo* (5x, 6x) protons absorb over a relatively narrow spectral range; assignment of the various absorption peaks arising from these protons has been facilitated by the advent of the 100-MHz nmr spectrometer. Assignments of the 5n,6n and 5x,6x absorption patterns, respectively, have been made on the basis of empirical observations[10] and on theoretical grounds.[11] The 7s and 7a



Ia, $X = H_{7a}$
b, $X = D$

---

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

(2) K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji, and H. Tanida, *ibid.*, **42**, 926 (1964).

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

(4) P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964), and references cited therein.

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

(6) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Letters*, 9 (1966).

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

(8) B. Franzus, W. C. Baird, Jr., N. F., Chamberlain, T. Hines, and E. I. Snyder, *J. Am. Chem. Soc.*, **90**, 3721 (1968).

(9) R. V. Moen and H. S. Makowski, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, No. Q9.

(10) *E.g.*, the nmr spectrum of 5,6-*exo,exo*-dideuterionorbornene has been studied: (a) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965); (b) W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *ibid.*, **89**, 410 (1967); (c) ref 8.

(11) (a) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962); (b) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963).

Table I. Norbornene Chemical Shifts and Coupling Constants (CCl_4 Solution)

Chemical shift, ppm	This work	Ref 2	Ref 8
$\delta_{2,3}$	5.93	5.98	5.92
$\delta_{1,4}$	2.82	2.85	2.80
$\delta_{5x,6x}$	1.59	1.60	...
δ_{7s}	1.33	1.33[a]	1.32
δ_{7a}	1.06	1.08[a]	1.03
$\delta_{5n,6n}$	0.96	...	0.93

Coupling constants, Hz	This work	Ref 1[b]	Ref 4[c]	Ref 5[c]	Ref 7[c]	Ref 8[b]
$J_{1,7a} = J_{4,7a}$	1.5	1.5[a]	(<1.3–1.5)[c]	1.3–1.4	1.5–1.7	1.5–1.6
$J_{1,7s} = J_{4,7s}$	1.8	1.8[a]	(1.5–2.0)[c]	1.8–1.9	1.7–2.3	2.0–2.2
$J_{5n,7s} = J_{6n,7s}$	2.2[f]	...	(2.0–3.1)[c]	2.8–3.1	2.1–2.5	2.0–2.4
$J_{2,7a} = J_{3,7a}$	~0.5[e]	...	(<0.5)[b,c]	<0.3–0.85	~0.8	0.5–0.6
$J_{2,7s} = J_{3,7s}$	...	...	...	...	...	0.20–0.35
$J_{7s,7a}$	7.7	8.2	(8.5–9.5)[c]	8.4–8.8	8.9–9.7	7.9–8.0
$J_{1,2} = J_{3,4}$	2.0[d]	3.2	2.95[b] (2.7–3.0)[c]	2.6–3.0	3.6–3.8	2.0–2.2
$J_{2,3}$	*d*	6.0	5.80[b]	5.6–5.9	5.6–5.9	...
$J_{1,3} = J_{2,4}$	...	1.2	0.55[b] (0.55–0.95)[c]	0.5	...	1.6–1.7
$J_{1,6n} = J_{4,5n}$	0	...	~0	0	≃0	0
$J_{1,6x} = J_{4,5x}$	3.5	...	(3.2–3.9)[c]	3.5–3.6	2.9–4.3	...
$J_{1,4}$	...	...	0	0	~1.0	0
$J_{5n,6n}$	...	...	...	4.4–5.6	6.8	...
$J_{5x,6x}$	...	...	(7.5–9.2)[c]	8.0–9.1	7.4–7.8	...
$J_{5n,6x} = J_{5x,6n}$	4.4[f]	...	(2.1–4.6)[c]	3.0–4.2	2.3–2.5	...
$J_{5n,5x} = J_{6n,6x}$	10.6[f]	...	(12.0–13.2)[c]	11.5–12.5	...	...

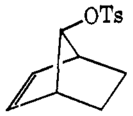
[a] The assignments for δ_{7s} and δ_{7a}, and values for $J_{1,7s}$ and $J_{1,7a}$ given in ref 1 and 2, are in the reverse order of those presented here. [b] J's measured for unsubstituted (or deuterium-substituted) norbornene. [c] J's measured for a number of 5- and 5,6-substituted 2-norbornenes. [d] $J_{2,3} = 5.1–6.0$; $J_{1,2} = 2.2–3.3$ Hz; P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2017 (1963). [e] See text. [f] $J_{5n,5x} = J_{6n,6x} = 11.1–11.6$; $J_{5n,6x} = J_{5x,6n} = 3.4–5.0$; $J_{5n,7s} = 2.2–2.6$ Hz (ref 9).

protons, however, have been a source of some controversy. In 1964, Tori and his coworkers[2] assigned the multiplet centered at δ 1.08 to the 7s proton and the δ 1.33 multiplet to the 7a proton on the basis of the anticipated diamagnetic shift of 7s relative to 7a due to the anisotropy of the $\Delta^{2,3}$ double bond. This assignment was later reversed[6] when long-range coupling between the δ 1.33 multiplet and the 5n,6n protons were observed; stereospecific coupling between the 7s proton and the 5n,6n protons, in accord with the familiar "W-letter" rule,[12] suggested this reassignment. More recently, this reassignment has been confirmed by Franzus and coworkers,[8] who performed extensive decoupling studies on 5,6-*exo*,*exo*-dideuterionorbornene.

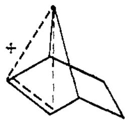
It appeared to us that this question could be resolved unequivocally through analysis of the nmr spectrum of a 7-monodeuterionorbornene. Accordingly, we have stereospecifically synthesized *anti*-7-deuterionorbornene and have examined its 100-MHz nmr spectrum. The nmr spectra of a number of norbornene derivatives have been examined with an eye toward generalizing the conclusions which arise from the study of the spectrum of *anti*-7-deuterionorbornene.

Discussion

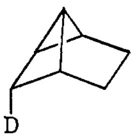
Norbornene and *anti*-7-Deuterionorbornene. Stereospecific synthesis of *anti*-7-deuterionorbornene (Ib) was accomplished *via* solvolysis of *anti*-7-norbornenyl tosylate (II) in 65% aqueous diglyme in the presence of sodium borodeuteride (method of Brown and Bell[13]). The basis of this method is to trap the intermediate ion III produced in this solvolysis with borodeuteride ion; as in other solvolysis reactions of II, attack by the nucleophile at the 7 position must occur stereospecifically from the direction *anti* to the double bond to form Ib, or at the 2 or 3 positions from the *endo* side to form the tricyclic compound, IV.[14] Separation of Ib from the major by-products, IV and V, was readily effected by preparative vpc techniques.



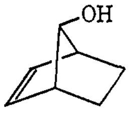
II



III



IV



V

Chemical shift and coupling constant data for Ia and Ib, obtained at 100 MHz, are shown in Table I. The agreement between the values obtained in this work and the corresponding values obtained by previous investigators appears to be satisfactory.

Direct comparison between the normal 100-MHz spectra of Ia and Ib is afforded by Figure 1. Inspection of Figure 1 reveals that substitution of D for the 7a proton produces three important changes in the nmr spectrum of norbornene: (1) reduction in the multiplicity of the absorption pattern centered at δ 2.82; (2) reduction in the multiplicity and pronounced broadening of the absorption pattern extending from δ 1.23 to 1.42; (3) disappearance of peaks in the region δ 1.05–1.13 ppm. Of these three points, the latter two offer salient evidence to bear on the question of the relative absorption positions of the 7s and 7a protons. The δ

---

(12) (a) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, 83, 2769 (1961); (b) for a review, see S. Sternhell, *Rev. Pure Appl. Chem.*, 14, 15 (1964).

(13) H. C. Brown and H. M. Bell, *J. Org. Chem.*, 27, 1928 (1962).

(14) (a) H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, 85, 2324 (1963); (b) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, 85, 2324 (1963).

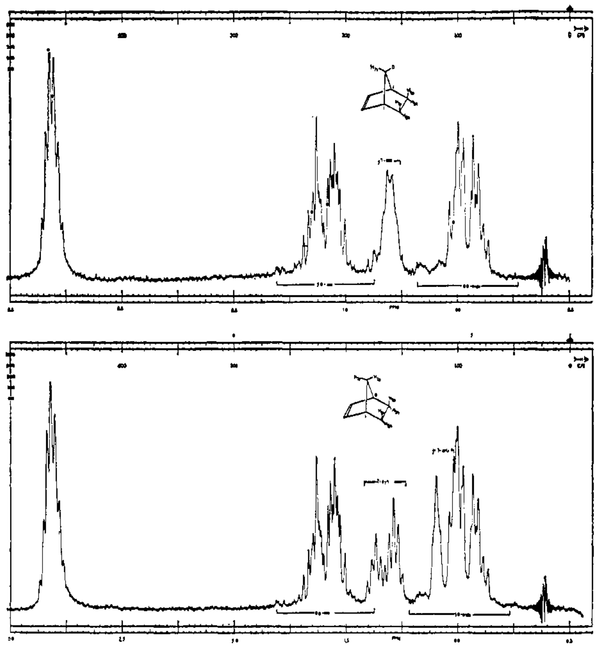


Figure 1. Top, normal nmr spectrum of Ib at 100 MHz (250-Hz sweep width); bottom, normal nmr spectrum of Ia at 100 MHz (250-Hz sweep width).

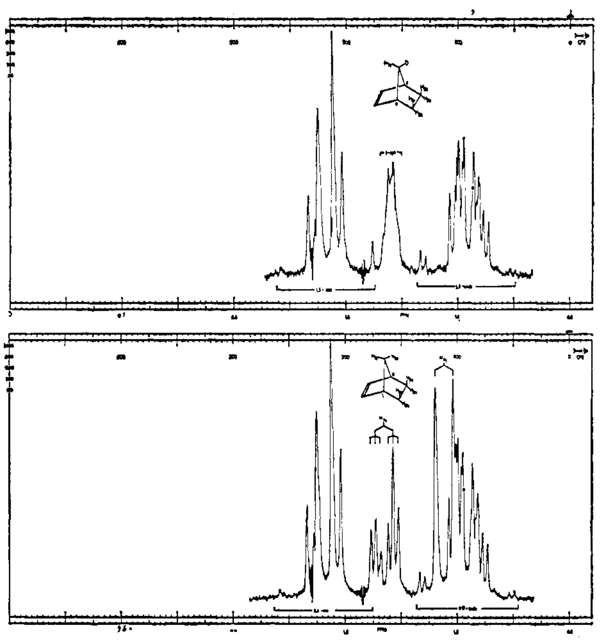


Figure 2. Top, nmr spectrum of Ib at 100 MHz (250-Hz sweep width), bridgehead (1,4) protons decoupled (irradiated 283 Hz from TMS); bottom, nmr spectrum of Ia at 100 MHz (250-Hz sweep width), bridgehead (1,4) protons decoupled (irradiated 283 Hz from TMS).

1.23–1.42 multiplet is assigned to the 7s proton, the broadening of this pattern in the nmr spectrum of Ib resulting from coupling of this proton with the nuclear quadrupole of the geminal deuterium atom. Signals present in the nmr spectrum of Ia in the region δ 1.05–1.13 which are not present in the corresponding region of the spectrum of Ib must be due to the 7a proton. Cursory inspection, therefore, reveals that Tori's reassignment[6] of the 7a,7s proton resonance positions, confirmed by Franzus and coworkers,[8] is indeed the correct interpretation.

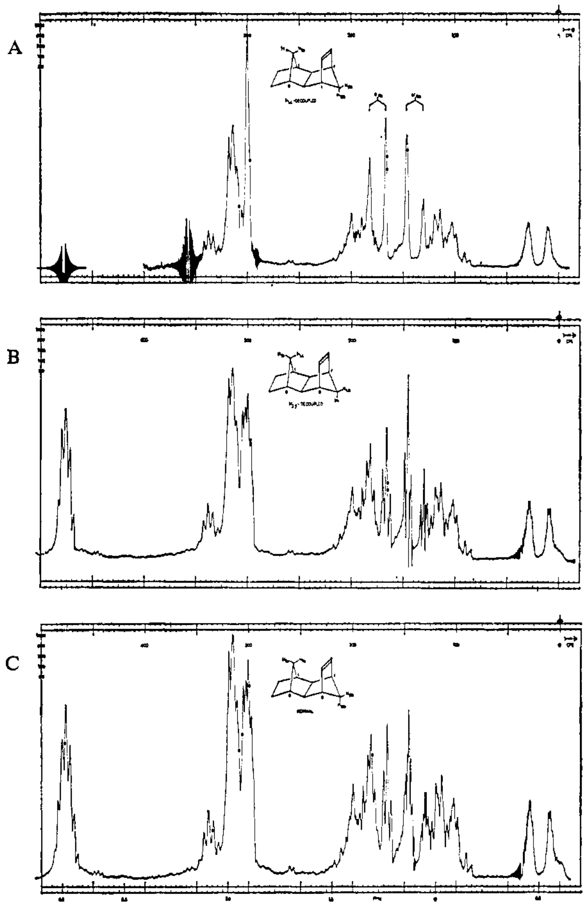


Figure 3. A, nmr spectrum of VI at 100 MHz (250-Hz sweep width), bridgehead (1,4) protons decoupled (irradiated 279 Hz from TMS); B, nmr spectrum of VI at 100 MHz (250-Hz sweep width), vinyl (2,3) protons decoupled (irradiated 587 Hz from TMS); C, normal nmr spectrum of VI at 100 MHz (250-Hz sweep width).

The AB pattern generated by the 7a,7s protons is more clearly seen in Figure 2; here, the bridgehead (1,4) protons have been decoupled. The 7s proton (the "A" part of the AB system) generates two peaks, each of which is further split into a triplet due to stereospecific long-range coupling ("W-letter rule"[5,8]) with the 5n, 6n protons ($J_{5n,7s}$ = 2.2 Hz). The 7a-proton resonance signals in Ia appear as two rather sharp singlets (width at half-height = W_H = 1.55 Hz) at δ 1.10 and 1.02; this is consistent with the small stereospecific coupling, $J_{2,7a}$ = 0.5–0.6 Hz, reported by Franzus and coworkers.[8]

Comparison of Figures 1 and 2 reveals that the bridgehead (1,4) protons are strongly coupled to the 5x,6x protons ($J_{1,6x}$ = 3.5 Hz).[15] However, the absorption pattern corresponding to the 5n,6n protons is identical in the normal and decoupled spectra of Ia and Ib, indicating that $J_{1,6n}$ = 0, in agreement with observations noted by other investigators in their studies of the nmr spectra of substituted norbornenes.[5,8]

Substituted Norbornenes. The nmr spectra of compounds VI–X have been examined. Each of these in turn may be regarded as a substituted norbornene (*e.g.*, compound VI can be considered as a norbornene

---

(15) This value for $J_{1,6x}$ was obtained by directly measuring the difference, $\Delta\nu$, between the outermost members of the 5x,6x multiplets in the normal spectrum of Ia (Figure 1, bottom) and in the bridgehead (1,4) proton decoupled spectrum of Ia (Figure 2, bottom). The double difference thus obtained corresponds to $J_{1,6x}$; see ref 3 and 4.

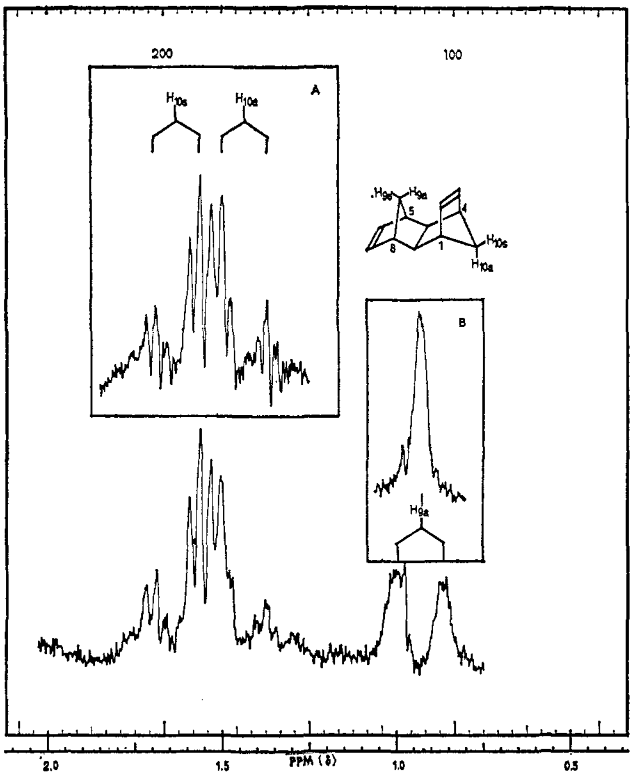


Figure 4. Normal nmr spectrum of VII at 60 MHz (250-Hz sweep width): inset A, vinyl (2,3) protons decoupled fom the 10a proton (250-Hz sweep width, difference frequency 94.5 Hz); inset B, H_{9s} decoupled from H_{9a} (250-Hz sweep width, difference frequency 276 Hz).

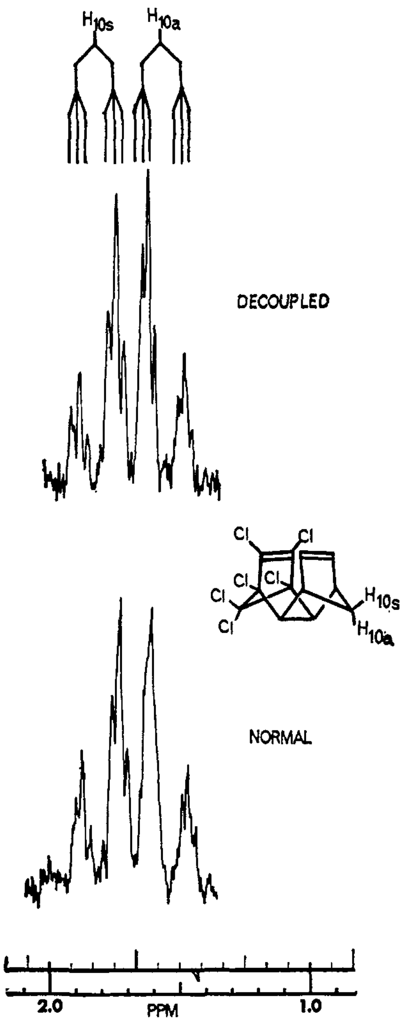
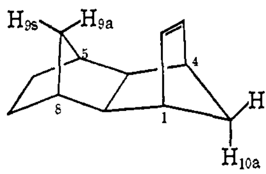
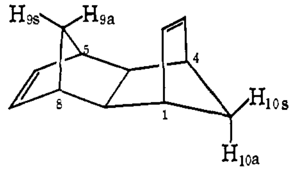


Figure 5. Top, nmr spectrum of the bridge (10s,10a) proton AB pattern of aldrin (VIII) at 60 MHz (500-Hz sweep width), vinyl (2,3) protons decoupled (difference frequency 280 Hz); bottom, normal nmr spectrum of the bridge (10s,10a) proton AB pattern of aldrin (VIII) at 60 MHz (500-Hz sweep width).

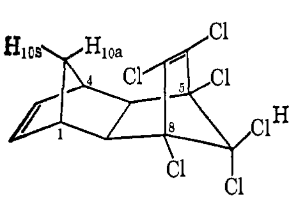
in which the 5n,6n protons have been replaced by a norbornane ring, and similarly for compounds VII–X). The normal 100-MHz nmr spectrum of VI is shown in Figure 3C. The "bridge norbornene" (10s,10a) protons are clearly visible in Figure 3A (bridgehead (1,4) protons decoupled). The assignment of the relative positions of the 10s,10a proton absorptions is made on the basis of a comparison of Figures 3B and 3C. When the vinyl (2,3) protons are irradiated, it is the *higher* field portion of the 10s,10a AB pattern which becomes more sharply defined (*i.e.*, two sets of triplets centered at δ 1.05 and 1.13 are evident in Figure 3B; in the normal spectrum (Figure 3C), further splitting of these peaks due to the stereospecific coupling $J_{2,10a}$ is evident). Our conclusion is that the *anti*-"bridge norbornene" proton (10a) absorbs at higher field than does the corresponding *syn* proton (10s).



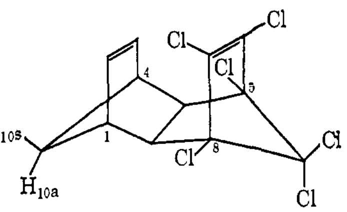
VI



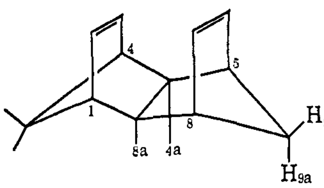
VII



VIII



IX



X

Of particular interest in the spectrum of VI is the one-proton doublet (J = 9.5 Hz) centered at δ 0.48. This is due to the 9a proton, which experiences a very strong shielding effect of the $\Delta^{2,3}$ double bond. Decoupling experiments reveal that this proton is coupled to another proton (9s) at δ 1.97. Thus, a separation of $\Delta\delta = 1.49$ ppm between the bridge protons (9s,9a) is observed in VI. Similar behavior is observed for the 9s,9a protons in VII (Figure 4); decoupling experiments (inset B) reveals $\Delta\delta = 1.58$ ppm for the separation of these two protons. These values for $\Delta\delta$ between bridge norbornene protons are unusually large; a comparable value has been noted only once before in the literature (*i.e.*, $\Delta\delta = (H_{7a} - H_{7s})$ for XI was observed to be 1.76 ppm).[16]

---

(16) M. P. Cava and F. M. Scheel, *J. Org. Chem.*, 32, 1304 (1967).

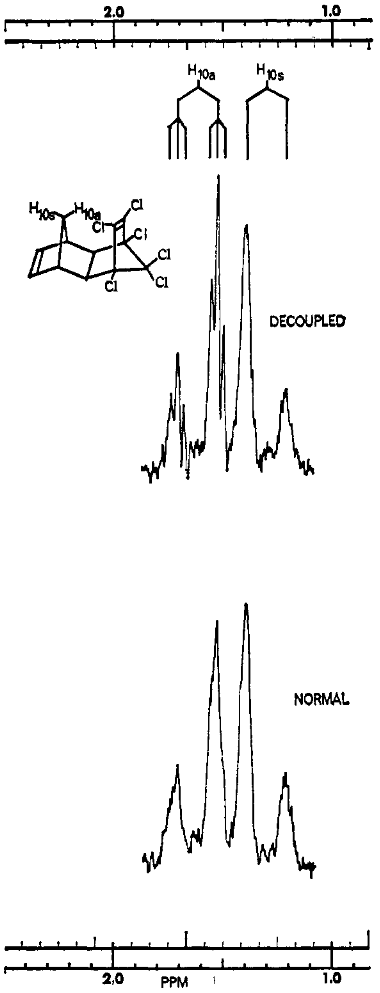


Figure 6. Top, nmr spectrum of the bridge (10s,10a) proton AB pattern of isodrin (IX) at 60 MHz (500-Hz sweep width), vinyl (2,3) protons decoupled (difference frequency 268 Hz); bottom, normal nmr spectrum of the bridge (10s,10a) proton AB pattern of isodrin (IX) at 60 MHz (500-Hz sweep width).

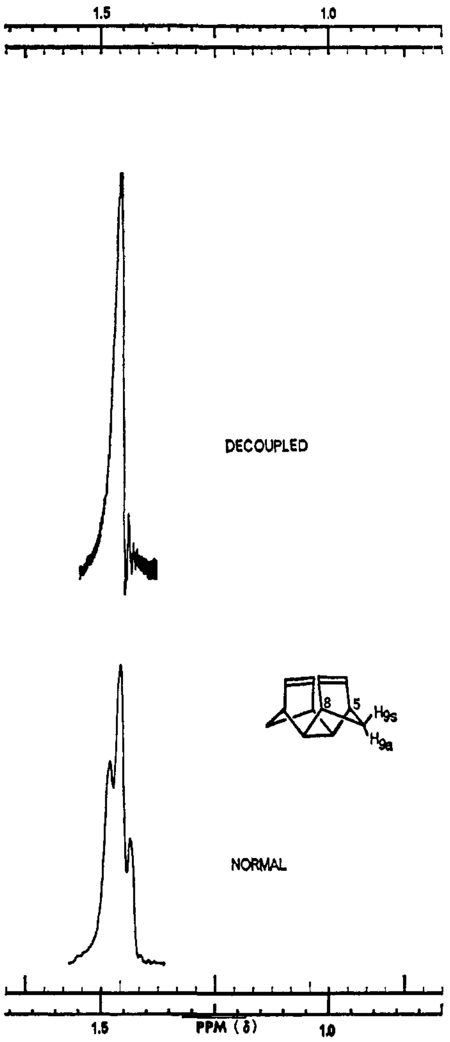
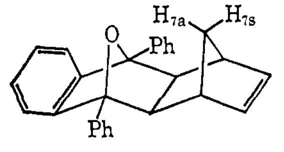


Figure 7. Top nmr spectrum (carbon tetrachloride solution) of the 9s,9a proton absorption pattern of X at 60 MHz (250-Hz sweep width), bridgehead (5,8) protons decoupled (difference frequency 67 Hz); bottom, normal nmr spectrum (carbon tetrachloride solution) of the 9s,9a proton absorption pattern of X at 60 MHz (250-Hz sweep width).

Inset A, Figure 4, reveals the alteration in the 10s, 10a AB pattern upon decoupling the vinyl (2,3) protons. The upfield portion of the AB pattern in inset A reveals two sets of triplets, resulting from the decoupling of $J_{2,10a}$; once again, it is the proton *anti* to the double bond (10a) which absorbs at higher field in the AB pattern composed of the 10s,10a protons in VII.



XI

The 60-MHz spectra of the readily available insecticides aldrin (VIII) and isodrin (IX) have also been examined (Figures 5 and 6, respectively). Interestingly, the relative positions of absorption of the 10s and 10a protons are *reversed* in these two compounds. Isodrin displays behavior consistent with the other norbornene-derived systems discussed thus far in that the *anti*-bridge proton (10a) falls at higher field than does the *syn*-bridge proton (10s). The basis for this conclusion is the observation of the stereospecific long-range coupling, $J_{2,10a}$, which results in broadening of the 10a portion of the normal AB pattern due to the 10a,10s proton absorptions. This broadening disappears when the vinyl (2, 3) protons are decoupled from this pattern (Figure 6), producing two sets of sharp triplets (due to $J_{1,10a}$) in place of the broad absorption pattern for the 10a proton in the normal spectrum.

Similar consideration of the 10s,10a proton absorption pattern of aldrin (Figure 5) leads to the conclusion that the 10a proton absorbs at *lower* field than does the 10s proton. This would appear to be due primarily to the operation of anisotropy and field effects of the vinyl (6,7) chlorine atoms in the ring adjacent (5,6-*endo*) to the norbornene ring. The magnitude of this effect can be appreciated *via* a comparison of the chemical shift values of the 10s,10a protons in VIII with the corresponding values for the 9s,9a protons in VII. The net effect of the vinyl chlorine atoms is to produce a large (0.70 ppm) paramagnetic shift of the 10a proton in VIII relative to the 9a proton in VII, and a large (1.20 ppm) diamagnetic shift of the 10s proton in VIII relative to the 9s proton in VII.

A similar comparison of the spectrum of isodrin (IX, Figure 6) with that of its dehalogenated counterpart, X

(Figure 7), both in carbon tetrachloride solution, is instructive. The net effect of the halogen atoms is to *deshield* the 10s,10a protons in IX relative to the 9s,9a protons in X; in carbon tetrachloride solution, these values are $\Delta\delta_{9s-10s} = -0.34$ ppm, $\Delta\delta_{9a-10a} = -0.04$ ppm. Of the several factors which might operate to give rise to the observed $\Delta\delta$ values, we may eliminate from consideration the σ-inductive effects of the halogen atoms and the halogenated double bond, as these groups are removed from C_{10} by more than one chemical bond.[17] The possibility that long-range magnetic effects of the carbon–chlorine bonds may be primarily responsible for the observed chemical shift differences is not dispensed with as readily. Although it is likely that long-range magnetic effects are not important due to the relatively large distances separating the C_{10}–H bonds and the various C–Cl bonds,[18] the extreme sensitivity of proton chemical shifts to long-range magnetic interactions precludes an unequivocal statement to this effect.[19] Perhaps a more satisfactory explanation for the chemical shift differences ($\Delta\delta$'s) of these protons in IX and X is that this behavior reflects the total *field effect* of all of the distant halogen atoms in IX upon the distribution and circulation of electrons in C_{10}–H_{10s} and C_{10}–H_{10a} bonds in IX.[17,20]

The nmr spectrum of X in carbon tetrachloride solution reveals an accidental degeneracy of the 9s,9a protons (Figure 7). This is demonstrated by decoupling the bridgehead (5,8) protons, which produces a singlet (W_H = 1.45 Hz). Laszlo and Schleyer[4] have employed selective solvent shifts to resolve the question of the positions of absorption of the 7s and 7a protons in 5,6-*endo*,-*endo*-dichloronorbornene (XII); this was effected by examining the solvent shifts of the various protons in benzene solution relative to chemical shift values in carbon tetrachloride solution. When this technique was applied to compound X, an AB pattern emerged in benzene solution for the previously degenerate (in carbon tetrachloride solution) 9s,9a protons (Figure 8). The results are tabulated in Table II. Decoupling experiments (Figure 8) reveal that in benzene solution, the *anti*-bridge proton (9a) absorbs at higher field than does the *syn*-bridge proton (9s).

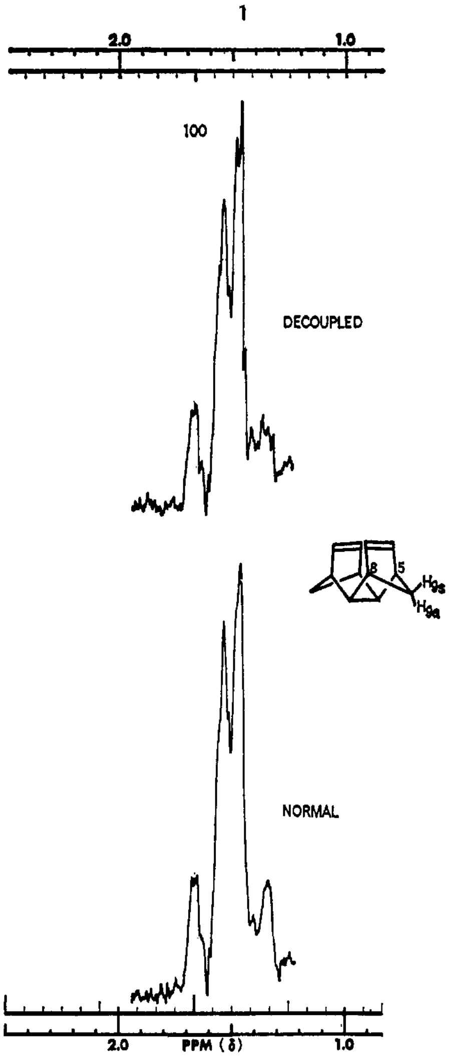


Figure 8. Top, nmr spectrum (benzene solution) of the 9s,9a proton absorption pattern of X at 60 MHz (500-Hz sweep width); vinyl (6,7) protons decoupled (difference frequency 232.5 Hz); bottom; normal nmr spectrum (benzene solution) of the 9s,9a proton absorption pattern of X at 60 MHz (500-Hz sweep width).

Table II. Proton Chemical Shifts of X in Benzene and in Carbon Tetrachloride[a]

	$\delta_{6,7}$	$\delta_{4a,8a}$	$\delta_{5,8}$	δ_{9s}	δ_{9a}
In CCl_4	314	162	155	88	88
In benzene	314	~154[c]	~150[c]	96	84
$\Delta\delta$ (Hz)[b]	0	~+8	~+5	−8	+4
$\Delta\delta$ (ppm)[b]	0	~+0.13	~+0.08	−0.13	+0.07

[a] Measured at 60 MHz with TMS internal reference. [b] Shifts are relative to resonance positions in carbon tetrachloride. Shifts are taken as positive when the resonance position in benzene is upfield of the corresponding resonance position in carbon tetrachloride solvent. [c] Protons 4a, 8a, 5, and 8 formed a complex multiplet (δ 2.4–2.7 ppm) in benzene solution.

Conclusions

The rigidity of the norbornene skeleton imposes restraints upon the allowed geometries of the various C–H bonds in the molecule. Magnetic effects which are strongly geometry dependent (*e.g.*, long-range coupling and chemical shift (anisotropy) phenomena) manifest themselves in a unique fashion under these conditions. Several of these effects have been found to be of general utility in assigning stereochemical configuration in substituted norbornenes. Those effects which have been encountered in the present work are enumerated and discussed below.

(1) The stereospecific coupling between vinyl (2,3) protons and the *anti*-bridge proton (7a) has been utilized by several investigators to assign the configuration of 7-substituted norbornenes.[4–6,8,21] Chemical shift

---

(17) (a) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3539, 3548 (1962); (b) M. J. S. Dewar and A. P. Marchand, *ibid.*, **88**, 354 (1966).

(18) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

(19) (a) H. H. McConnell, *ibid.*, 27, 226 (1957); (b) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **80**, 1728 (1958); (c) K. Ito, *ibid.*, **80**, 3502 (1958).

(20) (a) M. J. S. Dewar and A. P. Marchand, *ibid.*, **88**, 3318 (1966); (b) M. J. S. Dewar and W. Adcock, *ibid.*, **89**, 379 (1967); (c) M. J. S. Dewar and Y. Takeuchi, *ibid.*, **89**, 390 (1967).

(21) Wilcox has assigned the structure of one of the products of the zinc–acetic acid reduction of 1,2,3,4,7,7-hexachloro-2-norbornene as

information, and especially arguments based on presumed anisotropy effects of the double bond upon the magnetic environment of the 7s and 7a protons, have proved to be unreliable as criteria for assigning configuration about C_7.[4,5,8] Franzus[8] has recently reported a small but finite $J_{2,7s}$ of 0.20–0.35 Hz. This long-range coupling is so small as to have escaped notice by previous investigators. It is our opinion that the utility of the stereospecific coupling $J_{2,7a}$ in assigning stereochemical configuration about C_7 in norbornenes is not impaired by the operation of this very small $J_{2,7s}$ coupling.

(2) An attempt to utilize chemical shift information to assign configurations in substituted norbornenes is a hazardous undertaking indeed in view of the operation of anisotropy effects in the norbornene molecule which are as yet not completely understood.[5,8,11b] Nevertheless, useful correlations have been obtained. It appears to be generally true that the 5x,6x protons absorb at lower field than do the 5n,6n protons ($\Delta\delta \simeq$ 35–40 Hz at 60 MHz); the configurations of 5- and of 5,6-substituted norbornenes have been assigned, and mixtures of *exo*- and *endo*-5- and 5,6-substituted norbornenes have been analyzed quantitatively by nmr on the basis of this chemical shift criterion.[9] However, the presence of 5, 5,6, or 7 substituents has an effect upon the magnetic environment of 7a and/or 7s protons in norbornenes which has thus far defied quantitative evaluation.[4,8]

(3) Davis and Van Auken[5] have pointed out that in general, $J_{5x,6x} > J_{5n,6n}$, and that $J_{1,7s} > J_{1,7a}$. The latter inequality was observed in the present work. Utilization of these coupling constant inequalities should also prove to be of value in assigning configurations to appropriately substituted norbornenes. However, it has been pointed out[7] that substitution in the norbornene system causes the relative magnitudes of $J_{5x,6x}$ and $J_{5n,6n}$ to vary; hence, use of this inequality as a criterion for configurational assignment is tenuous, but may be acceptable as supporting evidence.[22]

(4) It is our finding that, in general, the *anti*-bridge proton absorbs at higher field than does the *syn*-bridge proton in norbornene and in substituted norbornenes, *in the absence of the complicating effects caused by the presence of highly anisotropic substituents in close proximity to the bridge protons.* Our results suggest that this generalization may best find application to purely *hydrocarbon* systems derived from norbornene.

Experimental Section

All melting points were measured on a Thomas-Hoover Uni-Melt apparatus, and are corrected. Nmr spectra (100 MHz) were obtained by Dr. LeRoy F. Johnson, Varian Associates, on the Varian HA-100 instrument operating in the frequency-sweep mode. Nmr spectra (60 MHz) were run on the Varian A-60 instrument equipped with a Varian Model V-6058A spin–spin decoupling apparatus. Coupling constant and chemical shift values are accurate to within ±0.3 Hz. Solvents (benzene, carbon tetrachloride) used to prepared solutions for nmr studies were of reagent grade quality, used as obtained from freshly opened bottles without additional purification. Norbornene (Ia), obtained commercially from Aldrich Chemical Co., was further purified by preparative vpc techniques.[23] A generous sample of technical grade aldrin (VIII) was kindly provided by Dr. J. J. Coyle, Shell Development Co., Emeryville, Calif. An analytical sample of isodrin (IX), assay 99.7%, was kindly provided by Velsicol Chemical Co., Chicago, Ill.; isodrin was also prepared by the method of Kleiman.[24]

***anti*-7-Deuterionorbornene (Ib).** 7-Ketonorbornene[25] was reduced with excess lithium aluminum hydride in ether; recrystallization of the crude product from pentane followed by sublimation afforded material melting at 111–113°. This material, which contained some *syn*-7-hydroxynorbornene, was used without additional purification.

Reaction of 3.3 g of the above material with *p*-toluenesulfonyl chloride (7.5 g) in dry pyridine (30 ml) at 0°[26] afforded in essentially quantitative yield *anti*-7-tosyloxynorbornene containing a small amount of the corresponding *syn* isomer, mp 46.5–54.5°. It should be noted that the presence of *syn* isomer caused no difficulty in the preparation of Ib, as the rate of solvolysis of *syn* isomer is negligibly slow compared with that of the *anti* isomer, and different products would be expected in each case.[27] The unreacted *syn*-tosylate was readily recoverable at the conclusion of the solvolysis reaction.

The crude tosylate was solvolyzed in 65% diglyme–35% D_2O (50 ml) containing $NaBD_4$ (7.55 g) and NaOD (2.0 g) under nitrogen for 2 hr at 55–60°.[13] Combined pentane extracts of the crude solvolysis product mixture were concentrated by careful distillation through a 24-in. vacuum-jacketed Vigreux column. Upon cooling in a freezer compartment, the concentrate afforded unreacted *syn*-7-tosyloxynorbornene (0.8 g), which was isolated by suction filtration as colorless needles, mp 65–66° (lit.[28] mp 67.5–68.5°). The desired *anti*-7-deuterionorbornene was isolated from the filtrate by preparative vpc techniques.[23]

Isotopic analysis by mass spectroscopy of the *anti*-7-deuterionorbornene thus prepared was performed by Mr. Seymour Meyerson, American Oil Co., Whiting, Ind. Mass spectra were measured with 70-V electrons on a modified[29] Consolidated Model 21-103c instrument. Isotopic composition of labeled norbornene was estimated from the parent regions of the low-voltage spectra.[30] Low-voltage measurements were carried out with the repeller plates at an average potential of 3 V; actual settings, adjusted for maximum ion current, were 3.35 V on the inner repeller and 2.65 V on the outer repeller.

The sample of labeled norbornene thus analyzed displayed a very high degree of isotopic purity (97.8 ± 0.2% norbornene-d_1, 2.2 ± 0.2% norbornene-d_0). However, peaks corresponding to norbornadiene-d_0 and norbornane-d_1 impurities were also observed, each to the extent of roughly *ca.* 5%. The presence of these impurities went undetected by nmr and hence their presence does not affect conclusions which have been based upon nmr analysis of Ib.

1,4,4a,5,6,7,8,8a-Octahydro-1,4-*exo*,*endo*-5,8-dimethanonaphthalene (VI).[31] Norbornene (20.7 g), cyclopentadiene[32] (16 g), and hydroquinone (1 g) were heated in a sealed glass bomb at 180–190° for 20 hr. The crude product was purified *via* its silver com-

---

being *syn*-1,2,3,4,7-pentachloro-2-norbornene on the basis of the observed long-range coupling, $J_{2,7a}$, in the nmr spectrum of this product. (C. F. Wilcox, Jr., and J. G. Zajacek, *J. Org. Chem.*, **29**, 2209 (1964)).

(22) We are indebted to a referee for calling this point to our attention.

(23) Wilkins A-700 Autoprep, Carbowax 20M (20%) on 60–80 mesh ABS Anachrome column (20 ft × $^3/_8$ in.), 85°, helium carrier gas (flow rate 40 cc/min). Under these conditions, both authentic norbornene and *anti*-7-deuterionorbornene had a retention time of 28 min.

(24) M. Kleiman, U. S. Patent 2,655,153 (to Arvey Corp., Oct 13, 1953); *Chem. Abstr.*, **48**, 10773*i* (1954).

(25) (a) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964); (b) P. G. Gassman and J. L. Marshall, unpublished results. We wish to thank Dr. Paul G. Gassman for providing us with a detailed experimental procedure, and for providing authentic samples and spectra of 7-ketonorbornene and *anti*-7-hydroxynorbornene.

(26) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(27) *E.g.*, the acetolysis of *anti*-7-tosyloxynorbornene at 25° occurs 10^7 times faster than does the corresponding solvolysis of the *syn* isomer. In the former case, the major product is *anti*-7-acetoxynorbornene, whereas in the latter case, the major product is 4-acetoxybicyclo[3.2.0]hept-2-ene. See S. Winstein and E. T. Stafford, *J. Am. Chem. Soc.*, **79**, 505 (1957); S. Winstein and C. Ordronneau, *ibid.*, **82**, 2084 (1960).

(28) W. C. Baird, Jr., *J. Org. Chem.*, **31**, 2411 (1966).

(29) H. M. Grubb, C. H. Ehrhardt, R. W. Vander Haar, and W. H. Moeller, 7th Annual Meeting of the American Society for Testing Materials Committee E-14 on Mass Spectrometry, Los Angeles, Calif., May 1959.

(30) D. P. Stevenson and C. D. Wagner, *J. Am. Chem. Soc.*, **72**, 5612 (1950).

(31) S. B. Soloway, *ibid.*, **74**, 1027 (1952).

(32) R. B. Moffett, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 238.

plex;[33] the silver complex was recrystallized from absolute ethanol to afford a colorless microcrystalline solid, mp 134.0–135.5° dec. Decomposition of the silver complex[33] afforded the hydrocarbon, which was further purified by fractional distillation; a heart cut, bp 111–114° (8 mm), gave $n^{25.5}$D 1.5231 (lit.[33] bp 86° (6 mm), $n^{22.5}$D 1.5245).

5,6,7,8,9,9-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*exo,endo*-5,8-dimethanonaphthalene (VIII, Aldrin). Technical grade aldrin was purified by elution chromatography (Florisil column, pentane eluent). Methanol recrystallization of the solid obtained from the eluate afforded colorless needles, mp 99–102° (lit.[34] mp 104.0–104.5°).

1,4,4a,5,8,8a-Hexahydro-1,4-*exo,endo*-5,8-dimethanonaphthalene (VII). Dechlorination of aldrin (25.0 g) using sodium (37.0 g)–1-butanol (54.3 ml) in tetrahydrofuran (425 ml) was effected by the method of Gassman and Marshall.[25b] A pentane solution of the crude product was concentrated, and the residue was treated with a solution of silver nitrate (35.0 g) in water (15 ml). The aqueous solution was extracted with five 50-ml portions of pentane and three 30-ml portions of ether to remove noncomplexed materials. The silver complex of VII was then decomposed according to the procedure of Stille and Witherell.[33] The crude product was purified by elution chromatography (Florisil column, pentane eluent) to remove colored impurities. The clear eluate was concentrated, and the residue was purified by preparative vpc techniques.[35] The purified hydrocarbon gave n^{25}D 1.5270 (lit.[36] n^{26}D 1.5324). The infrared spectrum of this material was consistent with that previously reported for VII:[36] nmr spectrum (carbon tetrachloride solution), δ 0.97, doublet (J = 8.0 Hz), area 1 H (9a); δ 1.45, 1.65, AB pattern, area 2 H (10s,10a); δ 2.18, multiplet, area 2 H (4a, 8a); complex multiplet with absorption maxima at δ 2.45, 2.63, area 5 H (1,4,5,8,9s); δ 5.97, triplet, area 2 H, and δ 6.12, multiplet, area 2 H (2,3,6,7).

1,4,4a,5,8,8a-Hexahydro-1,4-*endo,endo*-5,8-dimethanonaphthalene (X). Dechlorination of isodrin (25.0 g) was carried out by the same procedure described above for the dechlorination of aldrin. Work-up afforded an oil which was purified by preparative vpc.[35,37] The product thus obtained was a waxy, white solid; our purest material gave mp 69–74°. Bruck, Thompson, and Winstein[38] have reported that X is a liquid, n^{25}D 1.5303. Howe[37] has pointed out that this material was impure, almost certainly being contaminated with the rearrangement products, XIII and XIV. Howe[37] prepared X and purified it *via* its silver complex; the material thus obtained was a waxy, white solid, mp 94–96°.

The infrared spectrum of X showed strong absorption at 713 cm^{-1}, with no absorption in the 700–710-cm^{-1} region. Howe[37] indicates that absorption at 714 cm^{-1} is characteristic of X, whereas the twist monoene XIII shows strong absorption at 702 cm^{-1}; nmr spectrum (carbon tetrachloride solution), δ 1.47, triplet, area 4 H (9s,9a,10s,10a); δ 2.59, multiplet, area 4 H (1,4,5,8); δ 2.70, multiplet, area 2 H (4a,8a); δ 5.22, triplet, area 4 H (2,3,6,7).

Caution should be exercised in handling X to avoid skin contact and exposure to its vapors. Even brief contact with this material produces unpleasant physiological reactions (depression, vertigo, and headache).[37]

Acknowledgment. Partial support of this research in the form of postdoctoral fellowships (summer 1967) extended by the University of Oklahoma Alumni Development Fund (to A. P. M.) and by the University of Oklahoma Graduate College (to J. E. R.) is gratefully acknowledged. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (PRF Grant No. 1035-G1), for partial support of this work. Helpful discussions with Dr. Boris Franzus are also gratefully acknowledged. We are indebted to Dr. Franzus and his coworkers for delaying the publication of their work (ref 8) to permit simultaneous publication of these parallel studies.

---

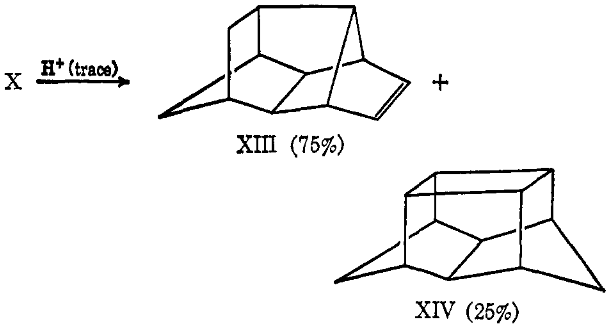
(33) J. K. Stille and D. R. Witherell, *J. Am. Chem. Soc.*, **86**, 2188 (1964).

(34) R. E. Lidov, U. S. Patent 2,635,977 (to Shell Development Co.), April 21, 1953); *Chem. Abstr.*, 48, 2769*i* (1954).

(35) Same instrument and column as described in ref 24. Column temperature, 129°.

(36) J. K. Stille and D. A. Frey, *J. Am. Chem. Soc.*, 81, 4273 (1959).

(37) Howe has indicated that careful avoidance of traces of acid in the vpc system is necessary to prevent rearrangement of X to the twist monoene, XIII, and the bird-cage hydrocarbon, XIV: K. C. Pande, unpublished results, quoted by R. K. Howe, Ph.D. Thesis, University of California, Los Angeles, 1965. We experienced no difficulty with this rearrangement under the vpc conditions employed in the present work.



(38) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.* (London), 405 (1960).