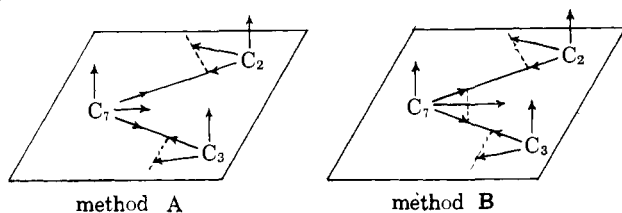


The in-plane components of the  $C_2$ ,  $C_3$  p-orbitals are then resolved along their respective internuclear lines with  $C_7$ . The question now remains regarding the proper vectorial decomposition of the  $C_7$  in-plane component with regard to the two internuclear lines. One can project the in-plane component onto one of the internuclear lines, obtain the magnitude of this component, and then repeat this operation along the other internuclear line (method A).

Alternately, one can require that the vector sum of the components along the two internuclear lines be equal to the original in-plane component (method B). These two procedures are compared in the figures below.



[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

## Analysis of the Nuclear Magnetic Resonance Spectra of Norbornene Derivatives<sup>1</sup>

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Nuclear magnetic resonance spectra of norbornene derivatives can be "deceptively simple," making a full analysis difficult. By the use of  $^{13}\text{C}$ -satellites and of selective solvent shifts, we have been able to assign all proton resonances and to measure all chemical shifts and coupling constants for several norbornene derivatives (I-VIII). "Virtual coupling" is shown to be effective in decreasing the amount of useful information obtainable from the regular spectrum alone. The vicinal coupling constants are found not to depend exclusively on the respective dihedral angles. Evidence for long-range coupling between the *syn*-7 proton  $H_a$  and the *endo*-5 and *endo*-6 protons  $H_i$ ,  $H_j$ , and between the *anti*-7 proton  $H_b$  and olefinic protons 2( $H_d$ ) and 3( $H_e$ ), is presented. The allylic 1,3( $J_{ce}$ ) and the olefinic 1,2( $J_{cd}$ ) coupling constants were found to have the same sign. The magnitudes of  $^{13}\text{C}$ -H coupling constants for C-CHCl-C and C-CH=C groupings were found to vary regularly with the value of the internal C-C-C angle.

The study of nuclear magnetic resonance chemical shifts and coupling constants is facilitated by rigid molecules, of known and fixed geometry. For this reason bicyclo[2.2.1]heptane ring systems (norbornane and norbornene derivatives), readily available as natural products or from the Diels-Alder reactions of cyclopentadiene, are of continuing interest to n.m.r. spectroscopists.

The initial investigations<sup>3-21</sup> assigned certain chemical shifts and established the applicability of the well

- (1) Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963, Abstracts, p. 3T.
- (2) (a) On leave, Faculté des Sciences, University of Paris, Paris, France; (b) Alfred P. Sloan Research Fellow.
- (3) G. V. D. Tiers, Tables of  $r$ -Values, Minnesota Mining and Mfg. Co., St. Paul, Minn., 1958.
- (4) W. D. Kumler, J. N. Shoolery, and F. V. Brucher, Jr., *J. Am. Chem. Soc.*, **80**, 2533 (1958).
- (5) W. H. Bradshaw, H. E. Conrad, E. J. Corey, I. C. Gunsalus, and D. Lednicer, *ibid.*, **81**, 5507 (1959).
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- (8) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).
- (9) M. M. Anderson and P. M. Henry, *Chem. Ind. (London)*, 2053 (1961).
- (10) H. E. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961).
- (11) (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).
- (12) N. O. Brace, *J. Org. Chem.*, **27**, 3027 (1962).
- (13) M. Green and E. A. C. Lucken, *Helv. Chim. Acta*, **45**, 1870 (1962).
- (14) R. W. King and P. E. Butler, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962, Abstracts, p. 84Q.
- (15) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).
- (16) J. Paasivirta, *Suomen Kemi.*, **B36**, 76 (1963).
- (17) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, **No. 4**, 185 (1963).
- (18) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961); P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **84**, 4876 (1962); P. R. Story, L. C. Snyder, D. C. Douglass, E. W. Anderson, and R. L. Kornegay, *ibid.*, **85**, 3630 (1963).

Method A gives results virtually identical with the procedure described by Roberts,<sup>24</sup> but method B gives different values. Using Kopineck's tables,<sup>26</sup> at a  $C_2$ - $C_7$  distance of 2.296 Å.,  $S_{27}$  is 0.0792 and 0.0641 for methods A and B, respectively, which compare to  $S_{27} = 0.0802$  quoted by Roberts. In order to bracket  $\beta_{27}$  the secular equation was solved for  $\beta_{27} = 0.3394$  (ref. 24) and  $\beta_{27} = (0.0641/0.28)\beta = 0.2289\beta$  (method B). The values of the carbonyl oxygen coulomb integral ( $\alpha + 2\beta$ ) and C=O exchange integral ( $\beta$ ) were those listed by Streitwieser.<sup>27</sup>

The energy,  $E^n$ , of the nonbonding (n) orbital of oxygen is assumed to be independent of the environment of the carbonyl group. Since the energy of the  $n \rightarrow \pi^*$  transition is  $E^{n \rightarrow \pi^*} = E^{\pi^*} - E^n$ , the difference in  $n \rightarrow \pi^*$  transition energies is then dependent upon only the relative energy levels of the first antibonding orbital,  $E_{(1)}^{n \rightarrow \pi^*} - E_{(2)}^{n \rightarrow \pi^*} = E_{(1)}^{\pi^*} - E_{(2)}^{\pi^*}$ . Transition energies for the  $\pi \rightarrow \pi$  transition are the difference between the lowest antibonding and the highest bonding orbital.

(26) H. J. Kopineck, *Z. Naturforsch.*, **5a**, 420 (1950).

(27) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 135.

known Karplus relationships between vicinal coupling constants and dihedral angles ( $\phi$ )<sup>22</sup> to these systems, chiefly for the purpose of determining structure and stereochemistry. More recent work has demonstrated a linear variation of the magnitudes of the vicinal coupling constants and of the internal chemical shifts with substituent electronegativities in norbornene derivatives.<sup>23,24</sup> These bicyclic systems provided critical tests for theories to account for the observed phenomena of magnetic shielding and spin-spin coupling. For example, it has been shown<sup>15,16</sup> that the chemical shifts of 2-norbornenes substituted at the 5- and 6-positions were consistent with the anisotropy of the double bond, as postulated by Jackman.<sup>25</sup> Similar considerations apply also to 7-oxabicyclo[2.2.1]heptene derivatives.<sup>26,27</sup> Musher<sup>28</sup> has commented recently on three unusual features found in the n.m.r. spectra of some bicyclo[2.2.1]heptanols: (a) relatively large  $^4J$ 's; (b) unequal  $J_{endo-endo}$ 's and  $J_{exo-exo}$ 's despite equal  $\phi$ 's ( $0^\circ$ ); and (c) unusual magnetic shieldings. We wished to see whether these anomalies occurred in the spectra of norbornene

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- (22) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).
- (23) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963).
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- (25) L. M. Jackman, "Applications of Nuclear Magnetic Resonance to Organic Chemistry," Pergamon Press, London, 1959.
- (26) M. P. Kunstmann, D. S. Tarbell, and R. L. Autrey, *J. Am. Chem. Soc.*, **84**, 4115 (1962).
- (27) F. A. L. Anet, *Tetrahedron Letters*, **No. 25**, 1219 (1962).
- (28) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963).

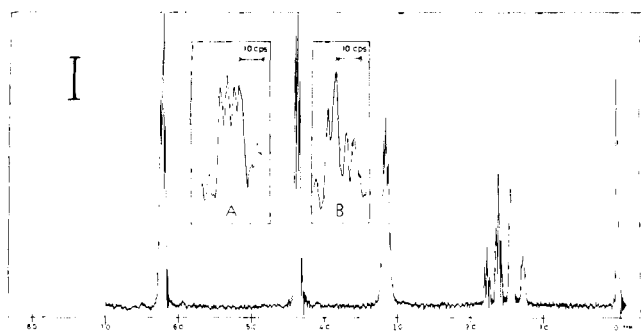
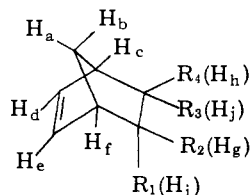


Fig. 1.—Spectrum of compound I in  $\text{CCl}_4$  solution (bottom trace): box A,  $^{13}\text{C}$  pattern relative to the olefinic protons; box B,  $^{13}\text{C}$  pattern relative to the methylene protons on chlorine-bearing carbons.

derivatives and to provide a complete analysis of their spectra. Interest in the sign and magnitude of allylic coupling constants,<sup>29,30</sup> in the magnitude of *cis*-olefinic  $J$ 's in cyclic alkenes,<sup>30–33</sup> in C–Cl bond anisotropy effects<sup>34</sup> and in long-range coupling in these systems<sup>8,10,11,14,18,21</sup> prompted our detailed examination of norbornadiene (VII),<sup>7</sup> norbornene (V), and six of its derivatives (I–IV, VI, VIII).



- I,  $R_1 = R_3 = \text{Cl}$  (*cis-endo*)  
 II,  $R_1 = R_4 = \text{Cl}$  (*trans*)  
 III,  $R_1 = R_2 = \text{Cl}$  (*gem*)  
 IV,  $R_1 = \text{Cl}$  (*endo*)  
 V,  $R_1 = R_2 = R_3 = R_4 = \text{H}$  (norbornene)  
 VI,  $R_1 = R_2 = R_3 = R_4 = \text{CN}$   
 VII,  $R_1 = R_2 = R_3 = R_4 = \text{—CH=CH—}$  (norbornadiene)  
 VIII,  $R_1 = \text{CH}_3$ ,  $R_2 = \text{COOH}$

**Spectral Analysis.**—The analysis of 5-substituted 2-norbornenes, studied earlier,<sup>24</sup> was facilitated by the large separations in position of the different types of hydrogens present; simple first-order theory provided many of the spectral features. 5,6-Disubstituted 2-norbornenes, such as *cis-endo*-5,6-dichloro-2-norbornene (I), give n.m.r. spectra (Fig. 1) which, either through symmetry or accidental equivalence, are “deceptively simple.”<sup>35</sup> Compound I possesses five different types of protons; the resonances of all are well separated in the n.m.r. spectrum (Fig. 1 and Table I). The only difficulty in chemical shift assignment is in distinguishing the  $H_a$  resonance from  $H_b$ , although it is clear that they are coupled to each other strongly,  $|J_{ab}| = 9.1 \pm 0.1$  c.p.s., and more weakly to other protons in the molecule. The signals from the other protons show degrees of multiplicity (Table I) difficult to understand from first-order theory. Full analysis of the spectrum is possible by observation of  $^{13}\text{C}$ -satellites and of selective solvent shifts.

**Use of  $^{13}\text{C}$ -Satellite Patterns.**—Examination of  $^{13}\text{C}$  side bands due to spin–spin interaction with  $^{13}\text{C}$  in natural abundance allows easy measurement of the

(29) D. J. Collins, J. J. Hobbs, and S. Sternhell, *Tetrahedron Letters*, **No. 4**, 197 (1963); **No. 16**, 1072 (1963).

(30) J. T. Pinhey and S. Sternhell, *ibid.*, **No. 4**, 275 (1963).

(31) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2017 (1963).

(32) G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963).

(33) O. L. Chapman, *ibid.*, **85**, 2014 (1963).

(34) R. C. Fort, B. C. Taylor, and G. W. H. Cheeseman, to be published; G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **38**, 2736 (1963).

(35) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

TABLE I  
SUMMARY OF THE N.M.R. SPECTRUM OF COMPOUND I

Proton type	Chemical shifts, c.p.s. <sup>a</sup>	Multiplicity <sup>b,c</sup>
Olefinic ( $H_d, H_h$ )	376	III, $S = 3.5$
$\text{CHCl-CHCl}$ ( $H_g, H_h$ )	264	III, $S = 3.25$
Bridgehead ( $H_e, H_f$ )	192	VII, $S = 10.0$
Bridge ( $H_a, H_b$ )	$\alpha^d$ 101 $\beta^d$ 85	d of t; $ J_1  = 9.1, J_2 = 2.0$ d; $ J_1  = 9.1, w_h = 3.0^e$

<sup>a</sup> All  $\pm 1$  c.p.s. <sup>b</sup> All values in c.p.s.; error  $\pm 0.1$  c.p.s. <sup>c</sup> A multiplet, when it arises from coupling of a given nucleus with one or more magnetically equivalent nuclei, is “regular” and is usually described as d = doublet, t = triplet, etc., and the separation between consecutive lines of this regular multiplet is the coupling constant,  $J$ . Other multiplets, arising from coupling of a given nucleus with two or more nonmagnetically equivalent nuclei, are “irregular” even though they may fortuitously have an appearance similar to “regular” multiplets. We introduce here the additional convention that such “irregular” multiplets be described by Roman numerals, III, IV, etc., to indicate the number of lines. In this latter case, “S” is the separation between the two outer lines of the irregular multiplet. <sup>d</sup> Not assignable directly, see text. <sup>e</sup> Band width at half-height.

coupling constant between isochronous nuclei (those with the same chemical shifts)<sup>36</sup> and simplifies complicated interactions.<sup>37</sup> A practical drawback to this method is the difficulty of observing  $^{13}\text{C}$  patterns in anything but pure liquid samples or very concentrated solutions. Much easier observation, even for relatively dilute samples, is possible through time integration achieved with a Varian A-60 n.m.r. spectrometer adapted with a Mnemotron CAT digital computer.<sup>38</sup>

$^{13}\text{C}$  side bands were observed as the multiplets predicted by first-order theory. For example, the low-field satellite of the main  $H_g$  and  $H_h$  resonance peaks consists of four moderately sharp ( $w_h = 1.5 \pm 0.1$  c.p.s.) lines, part of an AA'XY spectrum (A, A'  $\equiv H_g, H_h$ ; X  $\equiv H_f$ ; Y  $\equiv ^{13}\text{C}$ ). Analysis readily yields the coupling constants

$$J_{^{13}\text{C}-H_h(H_g)} = 155 \pm 1 \text{ c.p.s.}, J_{gb} = 7.5 \pm 0.1 \text{ c.p.s.}$$

$$J_{fg} = J_{ch} = 3.2 \pm 0.1 \text{ c.p.s.}, J_{cg} = J_{fh} \cong 0$$

These data provide an explanation for the triplet appearance of the 264 c.p.s.  $H_h, H_g$  resonance (Fig. 1). These protons are magnetically equivalent<sup>36</sup> so that, even though they are strongly coupled, this coupling cannot be evaluated from the ordinary spectrum alone.<sup>36</sup> Nevertheless, this coupling affects the appearance of the ordinary spectrum significantly by a process elegantly described by Musher and Corey<sup>39</sup> and termed “virtual coupling” by them.  $H_g$  and  $H_h$  are each coupled or virtually coupled to *two* other protons, giving rise to the “triplet” 264 c.p.s. band. For example,  $H_g$  is coupled directly with  $H_f$  ( $J_{fg} = 3.2 \pm 0.1$  c.p.s.) and virtually coupled with  $H_c$  ( $J_{cg} \cong 0$ ) through the strong coupling of  $H_g$  with  $H_h$ . According to Musher and Corey,<sup>39</sup> the separation between the outer lines (“S,” Table I) of this “triplet” should be equal to the algebraic sum  $J_{fg} + J_{cg}$ . This is indeed the case, since the latter sum is equal to  $3.2 \pm 0.1$  c.p.s. and  $S$  is equal to  $3.25 \pm 0.1$  c.p.s. This correspondence justifies *a posteriori* our conclusion, based on the observed sharpness of the  $^{13}\text{C}$  side band lines, that  $J_{cg}$  (and any other

(36) A. Abragam, “Principles of Nuclear Magnetism,” Oxford University Press, Oxford, England, 1961, p. 480.

(37) A. D. Cohen, N. Sheppard, and J. J. Turner, *Proc. Chem. Soc.*, 118 (1958); N. Sheppard and J. J. Turner, *Proc. Roy. Soc. (London)*, **A262**, 506 (1959); G. S. Reddy and J. H. Goldstein, *J. Am. Chem. Soc.*, **84**, 583 (1962).

(38) This technique has been described elsewhere: P. Laszlo, L. C. Allen, P. von R. Schleyer, and R. M. Erdahl, Abstracts, Fourth Omnibus Conference on the Experimental Aspects of Nuclear-magnetic-resonance Spectroscopy (4th OCEANS), Mellon Institute, Pittsburgh, Penna., March 2, 1963; L. C. Allen and L. F. Johnson, *J. Am. Chem. Soc.*, **85**, 2668 (1963); also see ref. 31.

(39) J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

long range couplings involving  $H_g$  and  $H_h$ ) must be very small.

The "triplet" appearance of the olefinic proton  $H_d, H_e$  resonance at 376 c.p.s. (Fig. 1) is explicable similarly. The  $^{13}C$  side band for these protons consists of four individual lines, each of which is broadened appreciably. Analysis gave the following coupling constants, in c.p.s.

$$J^{13C-H_d(H_e)} = 164 \pm 1 \quad J_{de} = 5.55 \pm 0.1$$

$$J_{cd} = J_{ef} = 2.85 \pm 0.1^{31} \quad (J_{ce} = J_{df} \cong 0.65)$$

The magnitude of  $J_{ce} = J_{df}$  was deduced indirectly by the following considerations. The width of the individual satellite lines suggested a value  $>0$ , but  $<1$ , since  $w_h$  for the entire multiplet was  $10.6 \pm 0.1$  c.p.s. Each olefinic proton (as  $H_d$ ) is coupled directly to the adjacent bridgehead proton (as  $H_c$ ;  $J_{cd} = 2.85$  c.p.s.) and is virtually coupled through the adjacent olefinic hydrogen (as  $H_e$ ) to the other bridgehead proton (as  $H_f$ ). The outer line separation  $S = 3.5$  c.p.s. (Table I) for the resulting olefinic "triplet" observed should equal the sum  $J_{cd} + J_{ce}$ . Since  $J_{cd} = 2.85$  c.p.s., the value  $J_{ce} = 0.65$  c.p.s. is very likely. "Virtual coupling" once again is effective in averaging the actual coupling constants between each olefinic proton and both allylic, bridgehead hydrogens.

The remaining two protons  $H_a, H_b$  are coupled to each other  $|J_{ab}| = 9.1 \pm 0.1$  c.p.s. (Table I), but the chemical shifts remain to be assigned. The upfield ( $\alpha$ ) resonances are split into "regular" triplets with 1:2:1 intensities; this can be due only to interaction with the two equivalent bridgehead protons,  $J_{H\alpha H_c(H_f)} = 2.0 \pm 0.1$  c.p.s. The other bridge hydrogen ( $\beta$ ) gives rise to lines broadened, but not split, presumably also due to coupling with the two bridgehead protons  $H_c$  and  $H_f$ . Estimation of  $J_{H\beta H_c(H_f)}$  and an explanation for the obscuration of the details of the  $\beta$ -proton peaks, assignment of the  $H_a$  and  $H_b$  chemical shifts, and an explanation of the appearance of the 192 c.p.s. bridgehead  $H_c, H_f$  hydrogen resonance remain.

**Use of Selective Solvent Shifts.**—In order to assign  $H_\alpha$  and  $H_\beta$  resonances, the effect on the position of the various absorptions with change in solvent was examined (Table II). It is believed that polar solutes, such

TABLE II  
SOLVENT SHIFTS FOR COMPOUND I<sup>a</sup>

Solvent	$(\epsilon - 1)/(\epsilon + 1)^b$	$\Delta(H_d, H_e)$	$\Delta(H_g, H_h)$	$\Delta(H_c, H_f)$	$\Delta H_\alpha$	$\Delta H_\beta$
CCl <sub>4</sub>	0.38	0.0	0.0	0.0	0.0	0.0
C <sub>6</sub> H <sub>12</sub>	.33	-2.9	+4.6	+6.0	...	...
CS <sub>2</sub>	.45	-2.8	+1.5	+3.0	-0.5	+4.5
CHCl <sub>3</sub>	.66	-9.3	-6.0	-2.5	-2.0	+3.5
CH <sub>2</sub> Cl <sub>2</sub>	.79	-8.3	-7.0	-1.8	-1.5	+3.0
(CH <sub>3</sub> ) <sub>2</sub> CO	.90	-6.7	-16.5	-1.0	...	...
CH <sub>3</sub> CN	.95	-7.8	-12.5	-1.0	...	...
C <sub>6</sub> H <sub>6</sub>	.34	+3.2	+32.0	+29.8	+31.5	+51.5

<sup>a</sup> 5% w./v. solutions with TMS internal reference. The variations in chemical shifts with changes in solvent ( $\Delta$ , in c.p.s.) are taken as positive when the resonances move upfield, negative when they move downfield, with CCl<sub>4</sub> positions as the reference. <sup>b</sup> Dielectric constant function; see text.

as I, polarize nonaromatic solvents in such a way as to create a "reaction field" which affects the magnetic shielding of solute protons in an approximately linear way; solvent shifts are roughly in proportion to a function of the dielectric constant of the solvent,  $(\epsilon - 1)/(\epsilon + 1)$ .<sup>40, 41</sup> Inspection of Table II reveals that this is

(40) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960); A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960); R. J. Abraham, *ibid.*, **34**, 1062 (1961); A. D. Buckingham, T. Schaefer, and W. G. Schneider, *ibid.*, **34**, 1064 (1961); J. I. Musher, *ibid.*, **37**, 34 (1962).

(41) P. Diehl and R. Freeman, *Mol. Phys.*, **4**, 39 (1961).

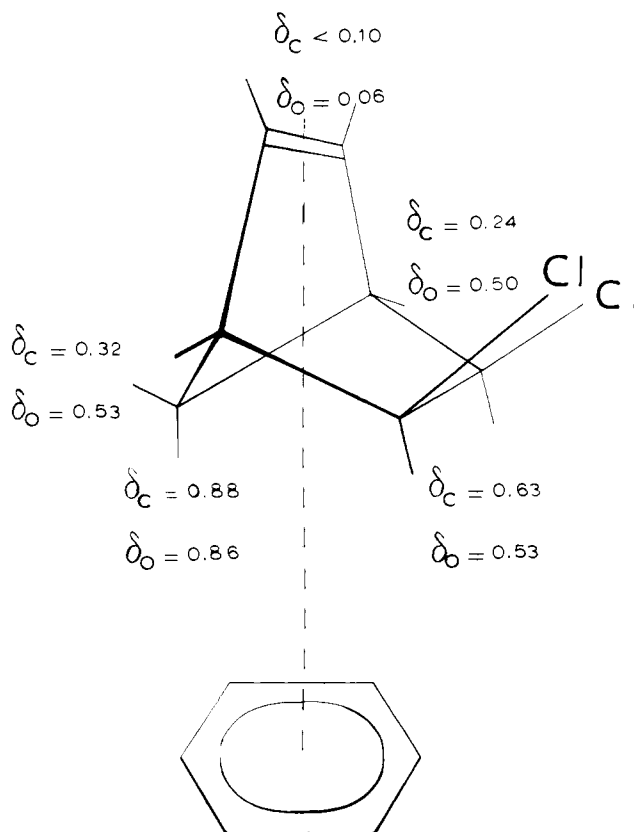


Fig. 2.—Suggested geometry for the association between compound I and benzene, as deduced from the solvent shifts: the observed ( $\delta_o$ ) and calculated ( $\delta_c$ ) chemical shifts are relative to CCl<sub>4</sub> solution.

the case for I; solvents of higher dielectric constant deshield the protons in an approximately regular manner.

Solvent shifts in benzene are quite different due to "ring current" anisotropy. Upfield shifts of relatively large magnitude are observed with a polar solute such as I. Dipole-induced dipole interactions between I and benzene result in a weak 1:1 molecular complex with the solute positioned above the plane of the benzene ring.<sup>42-45</sup> The well-known anisotropy of benzene results in increased shielding for all of the protons of I (Table II), since all are in the diamagnetic region above the ring.<sup>25, 46</sup>

A reasonable approximation of the possible geometry of the association of benzene with I is depicted in Fig. 2. It is observed experimentally that the olefinic hydrogen ( $H_d$  and  $H_e$ ) resonances are shifted least in benzene; these protons should be farthest away from the aromatic ring.<sup>43, 47</sup> Associations such as this are usually found to have the negative end of the solute dipole tending to lie off the ring and to be parallel to the plane of the ring.<sup>44, 45</sup> Hydrogens  $H_g$  and  $H_h$  may be sufficiently activated by the adjacent chlorine atoms<sup>48</sup> to act as weak proton donors in hydrogen bonding to the benzene ring. Solvent shifts of  $H_g$  and  $H_h$  in proton-accepting solvents (Table II), while small in absolute magnitude, are larger than those of other hydrogens in the molecule. On the other hand, a downfield shift of only 3 c.p.s. from CCl<sub>4</sub> was observed for  $H_g$  and  $H_h$  in ether solution.<sup>45</sup> Weak

(42) L. W. Reeves and W. G. Schneider, *Can. J. Chem.*, **35**, 251 (1957).

(43) J. V. Hatton and R. E. Richards, *Mol. Phys.*, **3**, 253 (1960); **5**, 139, 153 (1962).

(44) J. V. Hatton and W. G. Schneider, *Can. J. Chem.*, **40**, 1285 (1962).

(45) W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).

(46) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(47) H. M. McConnell, *ibid.*, **27**, 226 (1957).

(48) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1715 (1963).

TABLE III  
 DESCRIPTION OF SPECTRA AND CHEMICAL SHIFTS

Compd.	H <sub>a</sub>	H <sub>b</sub>	H <sub>c</sub>	H <sub>d</sub>	H <sub>e</sub>	H <sub>f</sub>	H <sub>g</sub>	H <sub>h</sub>	H <sub>i</sub>
I	101	85	192	376	376	192	264	264	...
	d.t	d	VII		III	VII		III	
II	107	120	179	376	376	186	255	...	216
	d.q.	d	V		III	VI	ABX		t
III	106	120	178.5	368.5	380	203	...	161.5	124
	d.d.t	d	br. <sup>a</sup>	ABXY		br. <sup>b</sup>		d.d	d.d
IV	92	80-90	173.5	363.5	376.5	185.5	268	135	67
	d.d.t	?	br. <sup>c</sup>	ABXY		br. <sup>a</sup>	d.t	d.d.d	d.d
V <sup>3,16</sup>	65 <sup>f</sup>	80 <sup>f</sup>	171	357.5	357.5	171	(96)	(96)	?
			br. <sup>d</sup>		III	br. <sup>d</sup>			
VI	?	?		H <sub>d</sub> - H <sub>c</sub> = H <sub>e</sub> - H <sub>f</sub> = 143 <sup>e</sup>					
			V		III	V			
VII <sup>3,3,21d</sup>	117	117	208	399	399	208	...	...	...
		III	VII		III	III			
VIII <sup>15</sup>	89	89	181	363	363	167	...	147	49
	br.	br.	br.		ABXY	br.		d.d	d.d

<sup>a</sup>  $w_h = 7.5$ . <sup>b</sup>  $w_h = 5.0$ . <sup>c</sup>  $w_h = 8.0$ . <sup>d</sup>  $w_h = 6.0$ . <sup>e</sup> Insoluble in carbon tetrachloride; this spectrum was examined in acetonitrile solution. <sup>f</sup> Ref. 21d.

C-H... $\pi$  hydrogen bonding, if present, would be facilitated by the geometry indicated in Fig. 2.

The two 7-protons, H<sub>a</sub> and H<sub>b</sub>, are shielded by different amounts in benzene solution. Examination of Fig. 2 shows that H<sub>b</sub> (*syn* to H<sub>g</sub> and H<sub>h</sub>, strongly shifted) is closer to the benzene ring and should be more strongly shifted than H<sub>a</sub> (*syn* to H<sub>d</sub> and H<sub>e</sub>, weakly shifted). On this basis we assign resonance lines  $\alpha$  (benzene shift  $\cong 0.5$  p.p.m.) to H<sub>a</sub> and lines  $\beta$  (benzene

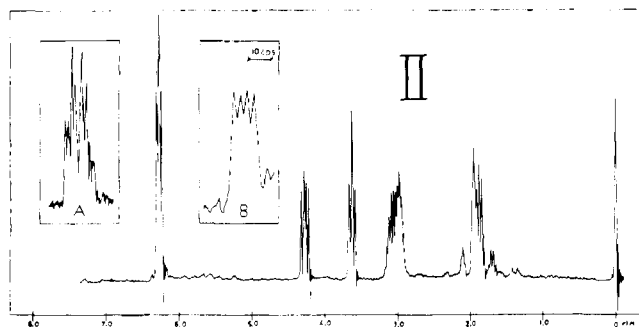


Fig. 3.—Spectrum of compound II in CCl<sub>4</sub> solution (bottom trace): box A, appearance of the olefinic multiplet in C<sub>6</sub>H<sub>6</sub> solution; box B, <sup>13</sup>C pattern relative to the olefinic protons.

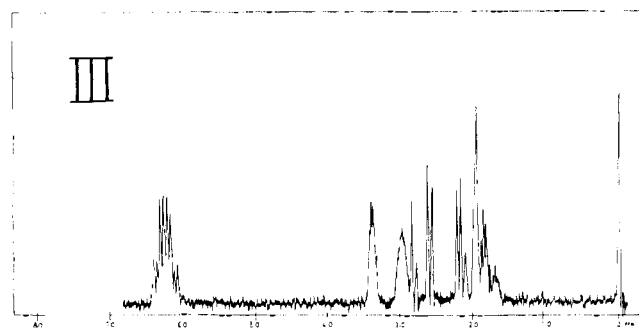


Fig. 4.—Spectrum of compound III in CCl<sub>4</sub> solution.

shift  $\cong 0.9$  p.p.m.) to H<sub>b</sub>. Using the Johnson-Bovey tables,<sup>46</sup> which are known to give an accurate estimate of the anisotropy effects in the neighborhood of the benzene ring, we have calculated the benzene shifts expected from the model (Fig. 2). Agreement with experimental shifts are reasonably good, especially since all other types of solvent effects and the possibility of hydrogen bonding were ignored in making the calculations. The

reference solvent, CCl<sub>4</sub>, is known, furthermore, to give rise to erratic shifts.<sup>41</sup>

A critical test for the coupling constants resulting from our analysis is the appearance of the bridgehead hydrogen (H<sub>c</sub>, H<sub>f</sub>) resonance, seen from Fig. 1 to be an "irregular" septet ( $S = 10.0$  c.p.s.). The multiplicity is accounted for by coupling or virtual coupling of each bridgehead proton to six other hydrogens—every other hydrogen in the molecule except its isochronous counterpart. The sum of the coupling constants already determined is:  $J_{af} + J_{df} + J_{ef} + J_{fg} + J_{fh} = 2.0 + 0.65 + 2.85 + 3.2 + 0.0 = 8.7$  c.p.s. In consequence, the upper limit of the one coupling constant remaining,  $J_{bf}$ , is  $10.0 - 8.7 = 1.3$  c.p.s., a value consistent with the observed width at half-height (3.0 c.p.s.) of the H<sub>b</sub> ( $\beta$ ) resonance. A splitting of this magnitude should be resolvable as a triplet, yet only a broad line is observed. A likely explanation is broadening due to additional coupling of H<sub>b</sub> to both olefinic protons H<sub>d</sub> and H<sub>e</sub>, perhaps *via* overlap of the  $\pi$ -orbitals of the double bond with the rearward lobe of the H<sub>b</sub> sp<sup>3</sup>-hybrid orbital. Well documented examples of such specific long-range coupling between olefinic hydrogens of 7-substituted norbornene and norbornadiene derivatives and the *anti*- but not the *syn*-C<sub>7</sub> proton have now been reported ( $J \cong 0.8$  c.p.s.).<sup>18,21a</sup> In the case of compound I, this coupling ( $J_{bd}$ ) must be less than 0.5 c.p.s. judging from the appearance of the olefinic <sup>13</sup>C side band pattern. The evidence of long-range H<sub>b</sub>-H<sub>d</sub>(H<sub>e</sub>) coupling reinforces the assignments,  $\alpha = H_a$ ,  $\beta = H_b$ .

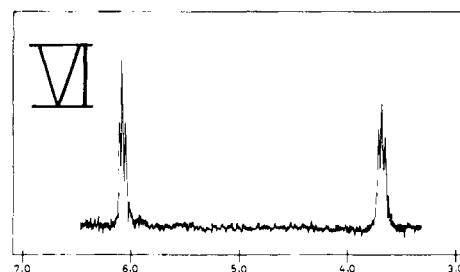


Fig. 5.—Spectrum of compound VI in CH<sub>3</sub>CN solution.

Analysis of the n.m.r. spectra of the remaining compounds studied, II-VIII, followed similar procedures. Data are summarized in Tables III-V and the spectra of compounds not available in the literature<sup>7,15,16,24</sup> are reproduced in Fig. 1, 3-5.

TABLE IV  
 COUPLING BETWEEN THE OLEFINIC AND ALLYLIC PROTONS

Compd.	$J_{ed}$	$J_{ce}$	$J_{ef}$	$J_{de}$	$J_{df}$	$J_{cf}$	$J_{bd} = J_{be}$	$J^{13C-H_d}$	Appearance of the olefinic multiplet
I	2.85	0.65 <sup>a</sup>	~0	5.55	0.65 <sup>a</sup>	2.85	<0.5	164 ± 1	III S = 3.5
II	2.90	0.70 <sup>a</sup>	~0	5.55	0.70 <sup>a</sup>	2.90	<.5	166 ± 1	III S = 3.8 <sup>b</sup>
III	3.0	..	~0	5.60	..	2.90	<.5	.....	ABXY $w_h = 2.0$
IV	2.80	..	~0	5.60	..	3.0	<.5	.....	ABXY $w_h = 2.0$
V <sup>21c</sup>	2.95	0.55 <sup>a</sup>	~0	5.80	0.55 <sup>a</sup>	2.95	<.5	166 ± 1	III S = 3.5
VI	$J_{ed} + J_{ce} = 4.0$		..	..	..	..	?	.....	III S = 4.0
VII <sup>7,21c</sup>	2.70	0.95	..	5.05	0.95	2.70	?	172 ± 1	III S = 3.6 $J_{ce} = J_{df} = 0.90^a$
VIII <sup>15</sup>	3.0	?	0	5.55	?	3.0	?	.....	ABXY $w_h = 2.0$

<sup>a</sup> Calculated as the difference  $S - J_{ed}$ . <sup>b</sup> Use of the selective benzene shift resulted in a striking modification in the appearance of this multiplet, which was thus transformed from an "irregular" triplet (III) to the regular 8-line pattern of an ABXY system, the accidental equivalence of H<sub>d</sub> and H<sub>e</sub> having been removed by their unequal shielding effects from the aromatic ring anisotropy (see Fig. 3). Examination of this pattern yielded:  $J_{de} = 5.2 \pm 0.2$ ;  $J_{ed} = J_{ef} = 3.0 \pm 0.2$ .

 TABLE V  
 COUPLING BETWEEN THE REMAINING PROTONS

Compd.	$ J_{ab} $	$J_{ac} = J_{af}$	$ J_{aj} $	$J_{fg}$	$J_{bc} = J_{bf}$	$J_{gh}$	$J_{gj}$	$J_{ch}$	$J_{ej}$	$ J_{hj} $
I	9.1	2.0	..	3.2	<1.3-1.5	7.5	..	3.2	..	..
II	9.5	2.0	2.0	3.9	<1.3-1.5	..	2.1	..	0.0	..
III	9.4	1.8	3.0	..	<1.3-1.5	..	..	3.8	..0	13.2
IV	8.5	1.95	3.1	3.6	<1.3-1.5	8.2	3.4	3.75	..0	12.3
V <sup>21c</sup>	$J_{ac} + J_{bc} + J_{ch} \approx 2.0(?)$				?	?	?	?	?	?
VI	?	$J_{af} + J_{bf} = 3.0$		..	..	..	..	..	..	..
VII <sup>7,21c</sup>	?	1.5	..	..	1.5	..	..	..	..	..
VIII <sup>15</sup>	?	$J_{af} + J_{df} \approx 1.0$		..	?	..	..	3.9	0.0	12.0

### Experimental

<sup>13</sup>C patterns were used for the analysis of the spectra of compounds I, II, V (norbornene), and VII (bicycloheptadiene). Selective benzene shifts were used to break down the accidental equivalence of the olefinic hydrogens in compound II (Fig. 3).

We use the following typographical conventions

- d.t = a doublet of triplets
- d.d.t = a doublet of doublets of triplets, etc.
- br. = a broad line,  $w_h$  being its full width at half-height
- ABX = part X of an ABX system
- ABXY = part A and part B of an ABXY system

The remaining conventions are described in footnote c, Table I.

A Varian A-60 n.m.r. spectrometer was used to determine the spectra. Samples were run as 5% w./v. solutions in CCl<sub>4</sub> with tetramethylsilane internal reference at the operating temperature of the instrument (ca. 35°). The instrument sweep was calibrated with chloroform and the peak positions read from the spectra; the chemical shifts are generally accurate to ±1 c.p.s., the coupling constants to ±0.1 c.p.s.

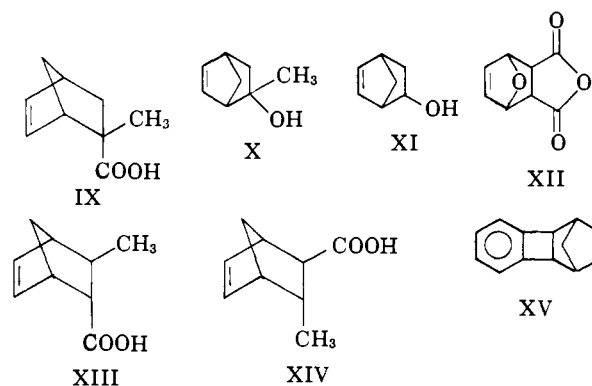
<sup>13</sup>C patterns were obtained, as already described,<sup>38</sup> through the use of a CAT digital computer. Its operation was triggered by a side band of the reference, produced by an audiooscillator, and the duration of an individual analysis was 32 sec., at a sweep rate of 2 c.p.s./sec. The total duration of the time integration procedure was ca. 45 min.

The samples, well-known Diels-Alder adducts of cyclopentadiene and various dienophiles, were prepared here or in the laboratories of the Union Carbide Chemicals Co., and kindly supplied. Purification was effected by distillation, by preparative gas chromatography, and by recrystallization.

### Discussion

**Chemical Shifts.**—Fraser<sup>15</sup> has established a method of configurational assignment in the 5- and 6-substituted 2-norbornene series. Upon hydrogenation of the double bond, 5- or 6-*exo*-hydrogen resonances move upfield while 5- or 6-*endo* peaks shift to lower fields, behavior attributed<sup>15</sup> to the magnetic anisotropy of the double bond.<sup>25,49</sup> The applicability of this method is limited by the frequently encountered difficulty in assignment of chemical shifts in norbornane derivatives, whose spectra are generally more compressed and individual features obscured. In norbornene derivatives *endo*-hydrogens H<sub>i</sub> and H<sub>j</sub> are generally found upfield from *exo*-proton resonances H<sub>g</sub> and H<sub>h</sub> (Table III and ref. 10, 15, 16, 26, and 27). The few exceptions to this

rule (e.g., chemical shifts for IX, are 6-*exo* = 77 c.p.s., 6-*endo* = 115 c.p.s.<sup>15</sup>) can plausibly be attributed to the inductive and/or anisotropy effects of the adjacent substituents; e.g., the 5-*endo*-carboxyl group of IX. When these inductive and anisotropy influences are canceled by appropriate intra- or intermolecular comparisons, H<sub>exo</sub> - H<sub>endo</sub> chemical shift differences, rather remarkably, vary but little (28-40 c.p.s.) from compound to compound (Table VI). When both *endo* and *exo* stereoisomers of a norbornene derivative are available, this difference would facilitate assignment of configuration and of chemical shifts.



Musher<sup>28</sup> has pointed out that *exo*-protons in norbornane derivatives are deshielded relative to *endo*-protons by 21 to 32 c.p.s., a range only slightly smaller in magnitude than that found for norbornene derivatives.<sup>50</sup> The H<sub>exo</sub> - H<sub>endo</sub> shift difference in these bicyclic compounds evidently are a feature of their molecular structure<sup>28</sup>; double bond anisotropy<sup>15</sup> can only be a contributing factor and apparently is not the chief cause of the *exo* - *endo* chemical shift difference in norbornene derivatives. The well-known upfield shift of *axial* protons relative to *equatorial* in cyclohexane systems<sup>25,51</sup> provides a close analogy for the present situation.<sup>11</sup>

(50) Deshieldings of *exo*-protons relative to *endo*- (5-30 c.p.s.) have been reported<sup>11</sup> for various norbornane derivatives more recently.

(51) See W. C. Neikam and B. P. Dailey, *J. Chem. Phys.*, **38**, 445 (1963); and references therein cited.

TABLE VI  
 CHEMICAL SHIFT DIFFERENCES, *endo*- vs. *exo*-PROTONS IN NORBORNENE DERIVATIVES

Cmpd.	Chemical shifts and chemical shift differences $ \Delta $ in c.p.s.						Ref.
	5- <i>H<sub>exo</sub></i>	5- <i>H<sub>endo</sub></i>	$ \Delta $ <sup>1</sup>	6- <i>H<sub>exo</sub></i>	6- <i>H<sub>endo</sub></i>	$ \Delta $	
Intramolecular comparisons							
II	255	...	...	...	216	39	Here
III	...	...	...	161.5	124	37.5	Here
V	96	60	36	96	60	36	Here, 16
Intermolecular comparisons							
VIII	...	...	...	147	49	28	Here, 15
IX	...	...	...	77	115	32	15
X, <i>endo</i> and <i>exo</i>	...	...	...	109	69	40	16
XI, <i>exo</i>	...	222	...	...	...	...	16
<i>endo</i>	258	...	36	...	...	...	16
XII, <i>exo</i>	...	195	...	...	195	...	27
<i>endo</i>	233	...	38	233	...	38	27
XIII	...	...	...	...	106	...	15
XIV	...	...	...	143	...	37	15
XV, <i>exo</i>	...	184	...	...	184	...	10
<i>endo</i>	212	...	28	212	...	28	10

Further evidence against double bond anisotropy acting as a major influence in these molecules is found in the lack of large and consistent differences in chemical shifts of the *syn* and *anti* protons ( $H_a$  and  $H_b$ ) at the 7-position (Table III).<sup>15,16</sup> Epimeric 7-substituted norbornenes have been examined in only two instances; in one study<sup>21</sup> *syn* - *anti* chemical shift differences of 13 c.p.s. were noted; in the other investigation<sup>52</sup> both isomers absorbed at the same field. Unfortunately, a full analysis of norbornene itself, which would help to establish this point, is not yet available.<sup>52</sup>

In the compounds for which assignments of  $H_a$  and  $H_b$  are known (Table III), chemical shifts are influenced by neighboring substituents.  $H_b$ , closer in space to the substituent chlorine atoms, is much more sensitive than  $H_a$  to structural modifications, thus confirming our assignments.  $H_b$  moves from an upfield position when the chlorines are *endo* (I and IV) to a downfield position when at least one chlorine is *exo* (II and III) due to the expected proximity effect.<sup>34</sup>

The chlorine substituents influence chemical shifts of other protons in the molecule to differing extents. As expected, the more distant the protons from the chlorine substituents, the smaller is the effect. Paasivirta,<sup>16</sup> after an examination of three stereoisomeric pairs of norbornene derivatives, concluded that 5-*endo* substituents caused a greater downfield shift in position of the olefinic proton resonances than did corresponding 5-*exo* substituents. This behavior is not verified here nor in other examples from the literature.<sup>15,27</sup> The chemical shifts of  $H_d$  and  $H_e$  in compounds V (no substituents), I (two *endo*-chlorines), and II (one *endo*- and one *exo*-chlorine) are all the same. One *endo*-chlorine (IV) or two *geminal* chlorines (III) shift the nearer olefinic hydrogen resonance ( $H_e$ ) to *higher* fields while leaving the other ( $H_d$ ) essentially unchanged. Erratic behavior is also noted in other stereoisomeric pairs.<sup>15,27</sup>

As we have noted earlier<sup>24</sup> the influence of a 5-substituent on  $\gamma$ -bridgehead proton  $H_c$  is less than on the  $\beta$ -bridgehead  $H_f$ .  $H_f$  is deshielded by an adjacent chlorine by about -15 c.p.s., but  $H_c$  is affected to a much smaller extent (*ca.* -3 c.p.s.). The inductive effect of chlorine decreases from the  $\beta$ - to the  $\gamma$ -position and anisotropic influences are known to fall off with the third power of the distance. Careful analysis of the  $H_c$  and  $H_f$  values for I-V fails to reveal an additivity relationship; evidently, the chlorine groups interact with each other to produce erratic total effects on proton chemical shifts.

(52) L. M. Jackman, private communication; however, see ref. 21d.

Regular influence of chlorine substituents on chemical shifts has been noted in ethylene derivatives.<sup>53</sup> Substitution of a chlorine in ethylene causes a marked deshielding of the  $\alpha$ -proton (-53 c.p.s. at 60 Mc.), and influences both *cis* (-6 c.p.s.) and *trans* (+1 c.p.s.)  $\beta$ -proton chemical shifts but little. Also, introduction of additional chlorines on the  $\beta$ -position affects  $H_a$  hardly at all, these attenuations attributed<sup>53</sup> to conjugation with the double bond. In a formal sense, positions 5 and 6 of compounds I-V are analogous, since the conformations are fixed by the rigid ring system. Here again the  $\alpha$ -proton is deshielded (*ca.* -172 c.p.s.) by a chlorine substituent and further  $\beta$ -chlorine substitution has little additional influence on the  $\alpha$ -proton (I and II, -156 to -168 c.p.s.). A chlorine substituent in IV, with no double bond to attenuate its influence, deshields both  $\beta$ -protons to different extents (*cis*, -7 c.p.s.; *trans*, -39 c.p.s.). The dependence of the electronegativity effect of substituents on chemical shifts upon dihedral angle has been noted before.<sup>23,24</sup> The *gem*-dichloro group in III produces identical chemical shift variations in both adjacent  $C_6$ -protons (*endo*, -64 c.p.s.; *exo*, -66 c.p.s.), but no simple additivity relationship is apparent.

 TABLE VII  
 SUMMARY COMPARISON OF NORBORNENE AND NORBORNANE  
 COUPLING CONSTANTS<sup>a</sup>

	$J_{gh}$	$J_{ij}$	$J_{gl}$	$J_{cj}$	$J_{cb}$	$J_{ac}$
Norbornenes	7.5-9.2	Not avail. <sup>b</sup>	2.1-4.6	<i>ca.</i> 0	3.2-4	1.5-2.0
Norbornanes	8.9-11.4	5.8-7.7	2.2-5.8	<i>ca.</i> 0	3.0-6.0	$\leq 0.5$

<sup>a</sup> See text for references and discussion. <sup>b</sup> A value of 7.1 c.p.s. has been found (N. A. LeBel, private communication).

**Geminal Coupling Constants.**—The coupling constants for I-VIII are presented in Tables IV and V and certain of these are compared in Table VII with known values for norbornane derivatives.

Two types of methylene groups are present in 5-substituted norbornenes, at  $C_7$  and at  $C_6$ , which differ in the magnitude of their internal angles,  $C_1-C_7-C_4 \cong 96.5^\circ$  and  $C_2-C_3-C_4 \cong 104^\circ$ .<sup>54-56</sup> and of the coupling constants

(53) E. B. Whipple, W. E. Stewart, G. S. Reddy, and J. H. Goldstein, *J. Chem. Phys.*, **34**, 2136 (1961); J. H. Goldstein and G. S. Reddy, *ibid.*, **36**, 2644 (1962).

(54) V. Schomaker and W. Hamilton, unpublished; W. Hamilton, Ph. D. Thesis, California Institute of Technology, 1954. Cf. W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5653 (1956).

(55) G. Ferguson, C. J. Fritchie, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.*, 1976 (1961); D. A. Brueckner, T. A. Hamor, J. M. Robertson, and G. A. Sim, *ibid.*, 799 (1962).

(56) C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **82**, 414 (1960).

$|J_{ab}| = 8.5\text{--}9.5$  c.p.s. (Table V) (lit.<sup>10</sup> 8 c.p.s.) and  $|J_{hj}| = 12.3\text{--}13.2$  c.p.s. (Table V) (lit. 12.0,<sup>15</sup> 10.4–12.5,<sup>24</sup> 12.6–13.3,<sup>23</sup> 9–12 c.p.s.<sup>16</sup>). Geminal coupling constants should vary with the size of the H–C–H angle,<sup>37</sup> but substituent effects often are so large as to obscure any direct relationship.<sup>58</sup> For methylene groups in alicyclic molecules, the size of the H–C–H angle is related to the value of the corresponding C–C–C angle at the same position.<sup>59</sup> Therefore, for compounds with minimal substituent effects,  $J_{gem}^{HH}$  should be related to the C–C–C angle. Besides  $J_{ab}$  and  $J_{hj}$  cited above, the following serve as illustrations: cyclopropane derivatives ( $\angle C\text{--}C\text{--}C \cong 60^\circ$ ),  $|J_{gem}| = 4.3$  to 9.1 c.p.s.<sup>60</sup> (best values, for the least heavily substituted examples, are the smaller of these; the cyclobutanoid methylene in bicyclo[2.1.1]hexane derivatives ( $\angle C\text{--}C\text{--}C \cong 85^\circ$ ),<sup>56</sup>  $|J_{gem}| = 6.3\text{--}8.4$  c.p.s.<sup>61</sup>; and cyclohexane derivatives ( $\angle C\text{--}C\text{--}C \cong 111.5^\circ$ ),<sup>62</sup>  $|J_{gem}| = 12.4\text{--}13.1$  c.p.s.<sup>63</sup> Most of these geminal coupling constants are now known to be opposite in sign to the vicinal couplings; this point was not investigated in the present work, but has been established for related compounds by Musher.<sup>28</sup>

**Vicinal Coupling Constants.**—The range for coupling between the olefinic protons in norbornene derivatives,  $J_{de}$ , is 5.0–6.0 c.p.s. for a large number of examples (Table IV and ref. 16, 19, 24, 31, and 33). Obviously, substituents two bonds away have little effect on the magnitude of this value.<sup>24</sup> The dependence of  $J_{cis}$  for olefins upon ring size has been discussed at length.<sup>31–33,64</sup> Also little affected by substituents are the vicinal couplings between olefinic and bridgehead hydrogens,  $J_{cd}$  and  $J_{ef} = 2.4\text{--}3.0$  c.p.s. (Table IV and ref. 11, 16, 19, 21, and 31). Even though the dihedral angle here is near  $0^\circ$ , the coupling constant is quite different in magnitude from  $J_{de}$  and from  $J_{gh}$ , both of which also have  $0^\circ$  dihedral angles. This emphasizes again the dependence of the coupling constant on the hybridization of carbon,<sup>24,64</sup> as well as on the dihedral angle, and on ring size.<sup>32</sup>

The *exo-exo* coupling constants,  $J_{gh}$ , studied here and previously<sup>15,19,23,24</sup> depend on substituent electronegativities<sup>23,24</sup> and range from 7.5 to 9.2 c.p.s. The similar coupling in norbornane derivatives, 8.9–11.4,<sup>5,11,21a,28</sup> c.p.s., is larger in magnitude by 1–2 c.p.s., while  $J_{endo-endo}$  (5.8–7.7 c.p.s. for saturated systems<sup>9,17,21a,28</sup>; data for norbornenes are not yet available) is smaller. These differences are not understood.<sup>23</sup> *trans* (*endo-exo*) coupling,  $J_{gj}$ , was of comparable range in norbornene (Table V),<sup>15</sup> norbornane,<sup>8,11,12,19,21a,28</sup> and polychloronorbornene<sup>23</sup> derivatives (2.1–5.8 c.p.s.); variation of  $J_{gj}$  with substituent electronegativities has also been established.<sup>23</sup>

The difference between coupling of *endo* ( $J \cong 0$ )

(57) H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959); H. S. Gutowsky, V. D. Mochel, and B. G. Somers, *ibid.*, **36**, 1153 (1962); C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

(58) H. J. Bernstein and N. Sheppard, *J. Chem. Phys.*, **37**, 3012 (1962); M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963).

(59) See, for example, C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.*, 3161 (1963).

(60) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **41**, 684, 1623, 2774 (1963); K. L. Williamson, C. A. Lanford, and C. R. Nicholson, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, p. 3T; K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **85**, 2788 (1963); D. J. Patel, M. E. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963).

(61) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Am. Chem. Soc.*, **84**, 1594 (1962).

(62) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963).

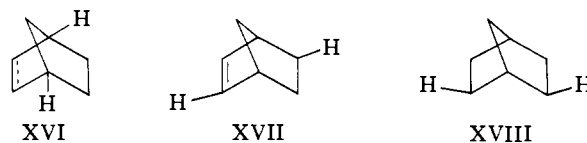
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c.p.s.)<sup>4,8,21a,28,65</sup> and of *exo* ( $J = 3.0\text{--}5.0$ )<sup>4,8,11–13,15,16,19–21,21a,24,28,66</sup> protons with the adjacent bridgehead hydrogen, so useful<sup>20</sup> for configurational assignment in the norbornene and norbornane series, is confirmed here, although the range for  $J_{ch}$  and  $J_{fg}$ , 3.2 to 3.9 c.p.s. (Table V),<sup>16</sup> is somewhat smaller than for analogous couplings in norbornane compounds.

The couplings  $J_{ac}$ ,  $J_{af}$  are typical of norbornene and norbornadiene derivatives, ranging between 1.5 and 2.0 c.p.s. (Table V and ref. 21). In norbornane derivatives, such couplings between the bridge and bridgehead hydrogens are likely to be much smaller, perhaps of the order of 0.5 c.p.s., as suggested by Musher.<sup>28</sup> We find that  $J_{ac}$  is different from  $J_{bc}$ , but it is not clear why this should be. Although  $H_a$  and  $H_b$  are not equivalent, inspection of molecular models shows both dihedral angles involving these hydrogens and the bridgehead protons to be the same. The nonequality of  $J_{ac}$  and  $J_{bc}$  is another peculiarity exhibited by the coupling phenomenon in bicyclo[2.2.1]heptene derivatives.<sup>21</sup>

**Long Range Coupling.**—The compactness of these molecules results in all protons being within five bonds of one another and in definite and fixed geometrical relationships. It is not surprising that numerous examples of specific long range couplings have been described in norbornane, norbornene, and norbornadiene derivatives and their oxo counterparts. The magnitude of these long range couplings varies from one compound type to another and are not observed in every instance. Although definite geometrical arrangements appear to be required for such coupling to take place, little more is known about this phenomenon and precise prediction is not possible.



An example is long range coupling between bridgehead protons XVI ( $J_{cf} \cong 1.5$  c.p.s.), reported first by King and Butler<sup>14</sup> for 7-isopropylidenenorbornene derivatives. Couplings of similar magnitude ( $J = 1.1\text{--}1.4$  c.p.s.) have now been observed in certain oxanorbornanes.<sup>21b</sup> In the present work, when bridgehead protons  $H_c$  and  $H_f$  are not isochronous (compounds II–IV, VIII), they would display either some broadening or some extra lines, were they substantially coupled. This is clearly not so; hence,  $J_{cf}$  must be less than 0.5 c.p.s. in these compounds. King and Butler<sup>14</sup> also found a  $J$  of small magnitude, XVII,  $J_{dg} \cong 0.5$  c.p.s. (cf. ref. 18). This coupling, if present in the compounds we examined, must be very small because of the narrowness of the observed multiplet lines. Similarly,  $J_{ah}$  is probably nonexistent, although analogous couplings XVIII  $J_{2-exo-6-exo} = 1\text{--}2$  c.p.s. have been reported for norbornane systems.<sup>8,11,21b,23,66</sup>

By examining isomeric 7-substituted norbornene derivatives, Snyder and Franzus<sup>21a</sup> have established the stereospecific nature of the coupling between the olefinic and *anti*-7-protons XIX. The magnitude of  $J_{bd}$ , also found in 7-substituted norbornadienes, was 0.69–0.96 c.p.s.<sup>21a</sup> Our compounds do not possess 7-substituents

(65) Nonzero coupling constants ranging up to 2.1 c.p.s.<sup>9–13,17</sup> have been reported for the *endo*-protons, but these may involve long range coupling to the *anti*-7-proton; see ref. 20.

(66) The highest reported *exo* bridgehead coupling constant, 6 c.p.s., was the result of an early study on  $\alpha$ -bromocamphor.<sup>4</sup> We have repeated this measurement and find  $J_{3-endo-4} = 5.0$ . The individual lines of this doublet are broadened ( $w_h = 2.7$  c.p.s.) suggesting<sup>28</sup> long range coupling with the 5-*exo*-proton.<sup>8–11,21a,28</sup> This long range coupling ( $J = 1.0$  c.p.s. in  $C_1D_2$ ) has recently been confirmed (A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, No. 5, 233 (1964)).

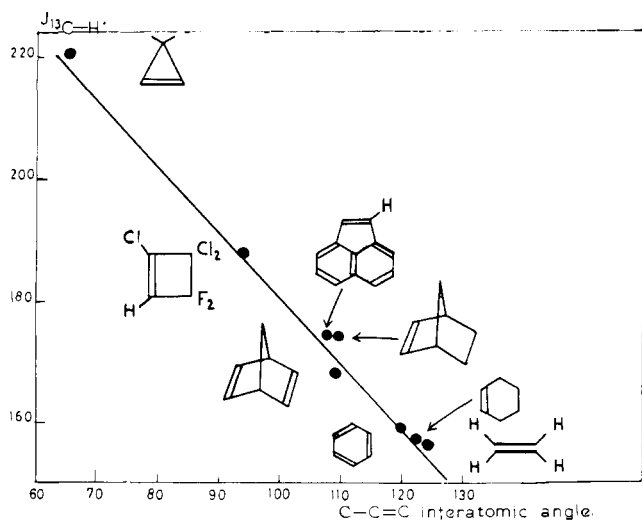
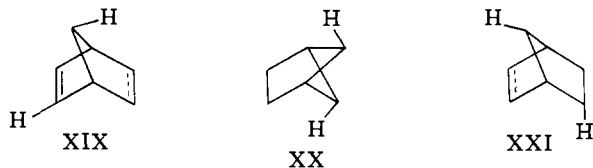


Fig. 6.—Plot of  $J^{13\text{C-H}}$  against the  $\text{C}=\text{C}=\text{C}$  interatomic angle for cyclic alkenes.

and such coupling definitely must be present but must be less than 0.5 c.p.s. If  $\text{H}_b$  were substantially coupled to the olefinic protons  $\text{H}_d$  and  $\text{H}_e$ , the  $^{13}\text{C}$  patterns should reveal this fact, contrary to observation. Again, it is not clear how 7-substitution effects alteration of the magnitude of  $J_{bd}$ .



Analyses of the spectra of compounds II, III, and IV demonstrate the intervention of a long range coupling over four bonds involving  $\text{H}_a$  and  $\text{H}_j$  (XXI), groups bearing a "transoid" relationship to one another.<sup>67</sup>  $J_{aj}$ 's found here are intermediate in magnitude (2.0–3.1 c.p.s.) between analogous couplings found<sup>61,67</sup> for bicyclo[2.1.1]hexane derivatives XX (6.7–8.1 c.p.s.) and for ordinary norbornane derivatives XXI (1.4–1.85 c.p.s.).<sup>28</sup> Very recently, Meinwald<sup>20</sup> has reported a much larger coupling of type XXI (3–4 c.p.s.) in 3-*exo*-halo-2-norbornanes. On the other hand, a long range coupling observed by Fraser<sup>15</sup> in compound VIII and now clearly identified as  $J_{aj}$  (XXI) was 2.0 c.p.s. or less. The rationalization offered by Meinwald and Lewis<sup>67</sup> for these couplings, involving "fairly extensive overlap between the small lobes of the orbitals directed  $180^\circ$  away from the directions of the C–H bonds (and consequently pointed toward each other)," continues to account for the stereospecificity observed (XVI–XXI).<sup>68</sup> Coupling of type XIX may similarly involve overlap of the rear orbital of  $\text{H}_b$  with the  $\pi$ -electrons of the double bond. The shorter distance between coupled protons in XX than in XXI accounts for the increased coupling in the former, but it is difficult to explain convincingly the variations in magnitude of  $J$ 's within XXI on this basis. Furthermore, the  $\text{C}_1\text{--C}_4$  distance in norbornane is quite short,<sup>54–56</sup> but the observed coupling,  $J_{ef}$  (XVI), is quite small. Clearly, current theories of long range coupling are not very good for quantitative predictive purposes.

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

(68) A comprehensive review and discussion of long range proton coupling constants is now available: C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, **34**, 115 (1963); also see A. Rassat, *et al.*, ref. 66, and E. W. Garbisch, Jr., in press.



A small, positive allylic coupling XXII ( $J_{ce} = +0.5$  to  $+1.0$  c.p.s.) is observed in norbornene derivatives. A positive allylic coupling of 0.95 c.p.s. was also observed by Mortimer<sup>7</sup> for norbornadiene (VII). From an analysis of the sum of vicinal ( $J_{de}$ ) and allylic ( $J_{ce}$ ) coupling constants in norbornene and norbornadiene derivatives, Snyder and Frauzis<sup>18, 21a</sup> have also concluded that the signs of both are the same. The question of the relative signs of vicinal and allylic coupling constants is of considerable current interest. Karplus<sup>69</sup> predicted theoretically that these signs should be opposite and this suggestion has received experimental support in acyclic<sup>70</sup> and cyclic<sup>32</sup> systems.<sup>29, 30, 65</sup> The above results with norbornene furnish an important calibration point because of the known and fixed geometry and should not be overlooked in analysis of these couplings. Several reports on vicinal ( $J_{12}$ ) and allylic ( $J_{13}$ ) couplings in bicyclo[2.2.2]octene derivatives (XXIII) are also available.<sup>71–74</sup> In one case,<sup>71</sup> the allylic and vinylic coupling constants were also found

TABLE VIII  
VARIATION OF OLEFINIC  $J^{13\text{C-H}}$  WITH  $\text{C}=\text{C}-\text{C}$  ANGLE

Compound	$\text{C}=\text{C}-\text{C}, ^\circ$	$J^{13\text{C-H}}, \text{c.p.s.}$
Cyclooctatetraene	126.8 <sup>i</sup>	155 <sup>k</sup>
Ethylene	122.3 <sup>a</sup>	156.4, <sup>b</sup> 157.0 <sup>b1</sup>
Cyclohexene	122.5 <sup>c</sup>	157 $\pm$ 2 <sup>31,d</sup>
Benzene	120	159.0 <sup>31</sup>
Cyclopentene		160 $\pm$ 1 <sup>31</sup>
I	(109.1) <sup>54</sup>	164 $\pm$ 1
II	(109.1) <sup>54</sup>	166 $\pm$ 1
VII	(109.1) <sup>54</sup>	168 $\pm$ 1
V	109.1 <sup>54</sup>	174 $\pm$ 1
Ferrocene	108 <sup>e</sup>	172 <sup>75</sup>
2-Chloronorbornene		176 $\pm$ 1
2-Bromonorbornene		178 $\pm$ 1
Acenaphthylene (five ring)	108 <sup>e</sup>	178 $\pm$ 1 <sup>31</sup>
1,4,4-Trichloro-3,3-difluorocyclobutene	94.0 <sup>g</sup>	188 $\pm$ 1 <sup>f</sup>
3,3-Dimethylcyclopropene <sup>h</sup>	64.6 <sup>i</sup>	220 <sup>h</sup>

<sup>a</sup> L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **31**, 400 (1959). <sup>b</sup> R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc. (London)*, **A269**, 385 (1962). <sup>c</sup> E. J. Corey and R. A. Sneed, *J. Am. Chem. Soc.*, **77**, 2505 (1955). <sup>d</sup> The older value, 170 c.p.s. (P. C. Lauterbur, *J. Chem. Phys.*, **26**, 217 (1957)), appears to be incorrect. <sup>e</sup> Regular pentagon assumed. <sup>f</sup> J. D. Park, L. H. Wilson, and J. R. Lacher, *J. Org. Chem.*, **28**, 1008 (1963). <sup>g</sup> Datum for cyclobutene, E. Goldish, K. Hedberg, and V. Schomaker, *J. Am. Chem. Soc.*, **78**, 2714 (1956). <sup>h</sup> G. L. Closs, *Proc. Chem. Soc.*, 152 (1962). <sup>i</sup> Datum for cyclopropene, R. H. Kasai, R. J. Meyers, D. F. Eggers, Jr., and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959). <sup>j</sup> D. Bastiansen, K. Hedberg, and L. Hedberg, *ibid.*, **27**, 1311 (1957). <sup>k</sup> H. Spiessack and W. G. Schneider, *Tetrahedron Letters*, No. 14, 468 (1961).

(69) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

(70) R. Freeman, *Mol. Phys.*, **4**, 385 (1961); A. A. Bothner-By, C. Naar-Colin, and H. Günther, *J. Am. Chem. Soc.*, **84**, 2748 (1962).

(71) Bicyclo[2.2.2]octatriene: R. G. Miller and M. Stiles, *J. Am. Chem. Soc.*, **85**, 1798 (1963), and personal communication;  $J_{12} = +6.13$ ,  $J_{13} = +1.27$ ,  $J_{23} = +10.0$  c.p.s.

(72) Bicyclo[2.2.2]octatriene (barrelene): H. Zimmerman, personal communication;  $|J_{13}| = 1.50$  c.p.s.

(73) A bicyclo[2.2.2]octenone derivative: W. A. Ayer, C. E. McDonald, and G. C. Iverach, *Tetrahedron Letters*, No. 17, 1095 (1963);  $|J_{13}| \cong 2$ ,  $J_{12} \cong 6$ ,  $J_{23} \cong 8$  c.p.s.; also for various pyridine-derived photodimers: E. C. Taylor and R. O. Kan, *J. Am. Chem. Soc.*, **85**, 776 (1963);  $|J_{12}| \cong 6.5$ ,  $|J_{13}| \cong 1.5$ ,  $|J_{23}| \cong 7.5$  c.p.s.

(74) A bicyclo[2.2.2]octadiene derivative: J. G. Atkinson, D. E. Ayer, G. Büchi, and E. W. Robb, *J. Am. Chem. Soc.*, **85**, 2257 (1963);  $J_{12} + J_{13} = 8$  c.p.s. The analysis reported for  $J_{12}$  and  $J_{13}$  in this paper is clearly incorrect; virtual coupling is operating throughout this system resulting in averaging.



to have the same sign, paralleling the observations for norbornenes (XXII). All three coupling constants,  $J_{12}$ ,  $J_{13}$ , and  $J_{23}$ , are all significantly larger in bicyclo-[2.2.2]octene derivatives (XXIII)<sup>71-74</sup> than in corresponding norbornane compounds, despite the similarity of the dihedral angles. This suggests the operation of "ring size effect" similar to that already observed for vicinal olefinic coupling constants.<sup>31-33,64</sup>

**<sup>13</sup>C-H Coupling Constants. Variation with Ring Size.**—Foote<sup>75</sup> has demonstrated that a linear correlation exists between the  $J_{13CH}$  coupling constant of methylene groups and the C-C-C interatomic angle, interpreted as indicating a relationship between hybridization and bond angle.<sup>59,76</sup> The C<sub>1</sub>-C<sub>5</sub>-C<sub>6</sub> angle of norbornene is strained (*ca.* 104.5°).<sup>54-56</sup> The Cl-<sup>13</sup>C-H coupling constants observed here for 5-chloronorbornene derivatives I and IV were 155 c.p.s., significantly higher than expected for unstrained chlorides (150-151 c.p.s.).<sup>77</sup> By way of confirmation, we have measured the Cl-<sup>13</sup>C-H coupling constant of the more highly strained cyclo-

butane and cyclopropane derivatives 1,1,2,2,3-pentachloro-4,4-difluorocyclobutane ( $J_{13C-H} = 165.5$  c.p.s.) and pentachlorocyclopropane ( $J_{13C-H} = 193$  c.p.s.). (The extra halogen substituents in these molecules probably have a small but relatively insignificant effect.<sup>51,77</sup>) The variation of  $J_{13C-H}$  with ring size (internal angle) is demonstrated again in these examples.<sup>75,76</sup>

A direct extension of the Foote  $J_{13C-H}$  bond angle relationship<sup>75</sup> to the olefinic proton of C=C-C systems is possible. Pertinent data are collected in Table VIII and plotted in Fig. 6. The sensitivity of  $J_{13C-H}$  to bond angle changes of olefinic C-H is comparable to that found for saturated C-H.<sup>75</sup>

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(75) C. S. Foote, *Tetrahedron Letters*, **No. 9**, 579 (1963). Foote (personal communication) has also found the  $J_{13CH}$  bond angle relations of olefinic hydrogens (Table VIII and Fig. 6).

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(77) E. R. Malinowski, *J. Am. Chem. Soc.*, **83**, 4479 (1961); G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **38**, 2736 (1963).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

## Reactions between Secondary Alcohols, Ketones, and Hydrogen on Metallic Catalysts<sup>1</sup>

BY JOHN NEWHAM AND ROBERT L. BURWELL, JR.<sup>2</sup>

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In the presence of large amounts of hydrogen and at temperatures of 115-150°, the reaction 2-propanol + 2-butanone = acetone + 2-butanol occurs as a coupled surface reaction on metallic copper at about 2.5 times the rate of net hydrogenation. The same reaction occurs on palladium-on-alumina at 96-130° but accompanied by some hydrogenolysis, and it occurs on nickel-silica at 77° in the liquid phase in the absence of added hydrogen. In experiments on copper in which deuterium was substituted for hydrogen, the 2-butanol which was formed was nearly completely 2-butanol-2-*d*. In the presence of deuterium, optically active 2-butanol reacts on copper at 135-155° to form racemic 2-butanol-2-*d* and butanone. Only small amounts of exchange occur in the side chains. At low degrees of dehydrogenation,  $\alpha$ , the fractional loss in rotation, is nearly proportional to  $\alpha$ . Values of  $\alpha$  considerably in excess of that which would correspond to equilibrium in the presence of hydrogen can be attained because of a kinetic isotope effect: the reaction of butanone is slower with deuterium than with

hydrogen. A mechanism is proposed in which adsorbed alcohol is RO—\* and adsorbed ketone is R'<sub>2</sub>C=O—\*<sup>⊕</sup><sub>⊖</sub>. Indirect reaction between these two species somewhat analogous to that in the Meerwein-Ponndorf reaction is suggested as interconverting adsorbed alcohol and adsorbed ketone.

Hydrogenations of the carbon-oxygen double bond in ketones and of the carbon-carbon double bond in olefins are catalyzed by the same metallic catalysts. Both types of hydrogenation have been studied from a mechanistic point of view, but ketone hydrogenation has received much less attention. The present study is an attempt to specify more closely the nature of the adsorbed intermediates in the reaction, ketone + hydrogen  $\rightleftharpoons$  secondary alcohol.

The heat of hydrogenation of a ketone is much less than that of an olefin (acetone, 14 kcal.; isobutylene, 28 kcal.). Largely owing to this,  $K_p$  sinks to unity at a much lower temperature in ketone than in olefin hydrogenation (acetone, 200°; isobutylene, over 600°). Thus, ketone hydrogenation and its reverse, dehydrogenation of secondary alcohols, can be studied in conjunction at relatively modest temperatures, a situation which facilitates mechanistic studies.

The addition of deuterium to olefins on metallic catalysts usually gives an alkane product with a rather complicated distribution of deuterium atoms.<sup>3</sup> The addition of deuterium to acetone is simpler. The principal product is CH<sub>3</sub>-CDOD-CH<sub>3</sub><sup>4-6</sup> although there is some introduction of deuterium into the methyl groups.<sup>6</sup> It is clear, then, that no large fraction of acetone is hydrogenated *via* an enolic intermediate which would of necessity lead to the introduction of one deuterium atom on a methyl group.

The mechanism shown in eq. 1 has been proposed to account for these data. The last step is assumed to be rate determining.<sup>6</sup> In addition, it is known that the interaction of deuterium and isopropylalcohol on metallic catalysts to form CH<sub>3</sub>CHODCH<sub>3</sub> is rapid compared to

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(2) To whom queries concerning this paper should be addressed.