tion we obtain, as expressed by the LFE equations 10 and 11. The *trans* reaction series line still passes through zero, *i.e.*, encompasses the unsubstituted case, and the *cis* reaction series constitutes an entirely different line with a considerable positive intercept. Furthermore, the conclusions we have drawn above with regard to the manner of the 4-substituent effect transmission (field effect) and the factor of steric strain acceleration in the rate of tosylate solvolysis are almost unaltered by our choice of available σ_I-values for methyl and *t*-butyl.

However, our observations, here and previously,[10] that the purely electrostatic influence of the alkyl group, conveyed as a field effect is weakly electron attractive invites some speculation as to its origin. It seems clear enough that the $-CH_3$ group is a complex dipole where $\mu(C^--H^+) = 1.53$ D.[17] The effect of the negative carbon pole depends for its conveyance to the reaction center on the nature of the atom to which it is bonded. That is to say, the magnitude of electron release experienced depends upon the apparatus available for its transmission from this atom. If this atom is trigonal and a constituent of a π-electron connection to the seat of reaction, the electron-releasing influence can be transmitted either by inductive polarization or mesomerically. On the other hand, it has been shown[18] by means of nuclear quadrupole moment studies that when the negative end of the methyl dipole is attached to a tetrahedron carbon (*i.e.*, the 4-carbon of the cyclohexane ring), its electron release effect is completely damped out beyond two $-C-C-$ bond distances. Consequently, the positive pole of the methyl group, which is based on the hydrogen atoms on its periphery, and which must depend for its transmission on the total composition and nature of the transannular space, will manifest itself at the seat of reaction only if a sufficiently low dielectric medium is interposed. This is more likely to be the case where a cycloalkane ring, composed largely of hydrocarbon material, occupies the space between the positive periphery of the $-CH_3$ and the electric charge developing at the reaction center in the transition state.

(17) For a full discussion of this see C. A. Coulson, *Trans. Faraday Soc.*, **38**, 433 (1942).

(18) H. O. Hooper and P. J. Bray, *J. Chem. Phys.*, **33**, 334 (1960).

Experimental

Kinetic Measurements.—The general procedure recommended by Winstein and co-workers[19] was followed in measuring the acetolysis rates.

(19) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948).

(20) S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, *ibid.*, **70**, 817 (1948).

(21) E. L. Eliel and C. A. Lukach, *ibid.*, **79**, 5986 (1957).

(22) L. N. Owens and P. A. Robins, *J. Chem. Soc.*, 325 (1949).

(23) D. S. Noyce, G. L. Woo, and B. R. Thomas, *J. Org. Chem.*, **25**, 260 (1960).

(24) N. R. Campbell and J. H. Hunt, *J. Chem. Soc.*, 1379 (1950).

(25) E. L. Bennett and C. Niemann, *J. Am. Chem. Soc.*, **74**, 5076 (1952).

[CONTRIBUTION FROM THE CENTRAL BASIC RESEARCH LABORATORY, ESSO RESEARCH AND ENGINEERING CO., LINDEN, N. J.]

Nuclear Magnetic Resonance Spectra of Some Norbornadienes and Norbornenes

BY EUGENE I. SNYDER AND BORIS FRANZUS

A study of the n.m.r. spectra of several 7-substituted norbornadienes and norbornenes has established several criteria for configurational assignment of the 7-substituent with respect to the double bond(s). These criteria are: (1) a long-range coupling constant of 0.8 c.p.s. is present between the bridge hydrogen and the vinyl hydrogens *anti* to it; (b) the sum of the vicinal and allylic coupling constants of the bridgehead proton with the vinyl protons is greater when *syn* to the bridge hydrogen than when *anti*; (c) the bridge hydrogen is more shielded when *syn* than when *anti* to the double bond. The relation between the presence of the aforementioned long-range coupling and delocalization of the bridge carbon orbitals is discussed with reference to the abnormally fast solvolytic reactions of the systems above. A simple LCAO–MO calculation for 7-ketonorbornene is presented.

In the course of an investigation of some aspects of the chemistry of 7-substituted norbornadienes and norbornenes, we have observed a stereospecific, long-range coupling constant between the ring vinyl hydrogens and the *anti*-7-hydrogen. This paper presents the pertinent observations and a discussion of their significance, both as related to simply determining the stereochemistry of 7-substituted norbornenes and to the larger problem of orbital interaction between the π-electron

system of the ring carbons and the orbital system at the 7-carbon.

N.m.r. Spectra.—Inspection of the 60 Mc. n.m.r. spectrum of several 7-substituted norbornadienes reveals a differing multiplicity of the two ring vinyl hydrogen patterns (Fig. 1). The vinyl multiplet occurring at lower field appears as a triplet or, more precisely, as a quartet whose inner members are separated by an amount sometimes outside of instrumental
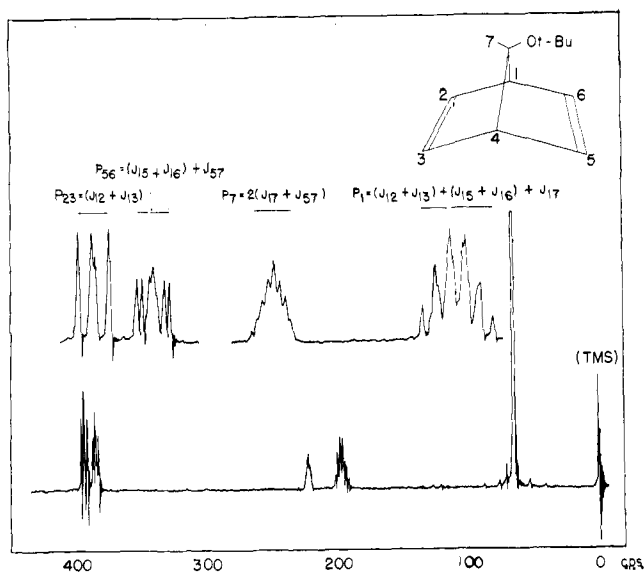
Fig. 1.—N.m.r. spectrum of 7-t-butoxynorbornadiene at 60 Mc.

resolution. The higher field multiplet appears to differ from the aforementioned multiplet by having its outer lines doubled (spacing ∼0.8 c.p.s.) and inner lines considerably broadened. This suggests that this one of the two vinylic proton pairs is coupled with one other proton in the molecule which, by symmetry, must be the bridge proton. Accordingly, the bridge proton appears not as a triplet, which might be expected if it were coupled only to the two bridgehead protons, but rather as a heptuplet. Using the numbering system
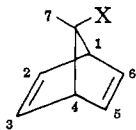
a 7-line pattern can be rationalized on the basis $J_{57} = J_{67} \backsim {}^1/_2 J_{17} = {}^1/_2 J_{47}$, $J_{27} = J_{37} = 0$, which agrees with the magnitudes of the coupling constants derived from the approximate treatment presented below. Irrespective of the magnitude of the couplings, the observation that only one of the vinyl proton pairs is spin coupled to the bridge proton demonstrates a highly stereospecific coupling mechanism. In analogy with other examples of long range spin coupling between protons separated by more than three single bonds[1] one might anticipate that the coupled hydrogens are transoid oriented, which implies that the bridge proton is *anti* to the vinyl protons with which it is coupled. That this is the correct stereochemical relation was simply established by investigation of the *syn–anti* pairs of 7-hydroxy- and 7-acetoxynorbornene. In both cases the vinyl proton resonance approximated a triplet in the *anti* isomer (*syn* bridge hydrogen) but approximated a doublet of triplets (doublet separation ∼0.8 c.p.s.) in the *syn* isomer (*anti* bridge hydrogen).

Spectral Analysis.—Although a complete spectral interpretation might be possible using double resonance experiments and/or computer solutions for a 7-spin system, the following "one-and-one-half order" analysis gives most of the desired parameters.

Referring to the notation above and considering the spectrum of the compounds under discussion to be the sum of several noninteracting spectral systems, we can describe the bridgehead-vinyl system, protons 1 and 4, 2 and 3, respectively, as an A_2X_2 system. Using the

(1) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Am. Chem. Soc.*, **84**, 1594 (1962), and references cited therein; C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, **34**, 115 (1962).
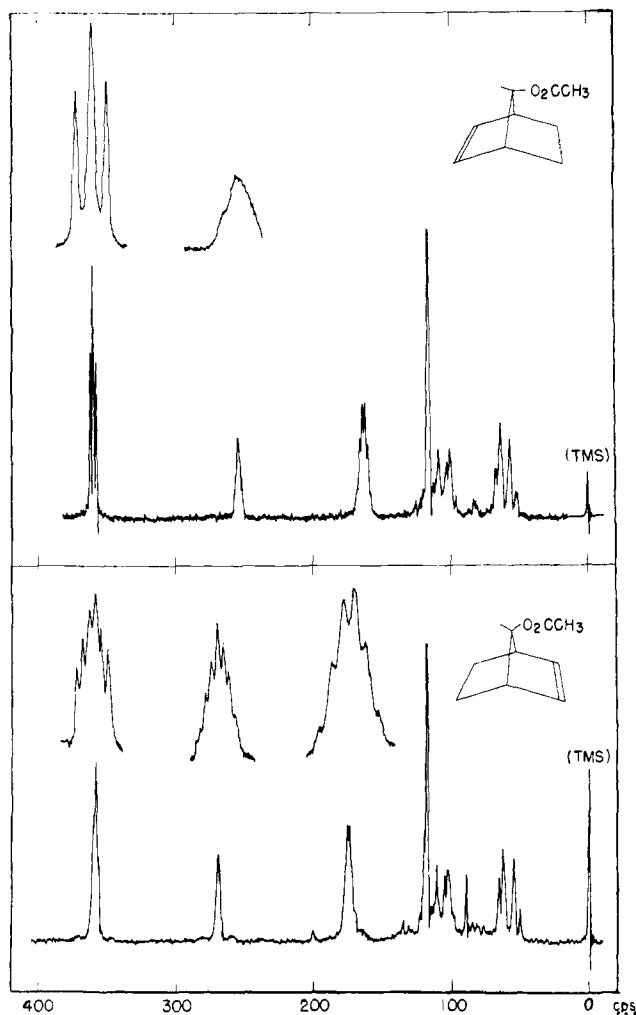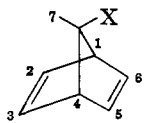

Fig. 2.—N.m.r. spectra of *syn*-7-acetoxynorbornene in CDCl₃ and *anti*-7-acetoxynorbornene in CCl₄ at 60 Mc.

terminology of Pople, Schneider, and Bernstein,[2] the separation between the most intense lines in both the A and X group of an A_2X_2 pattern is $N = J + J' = J_{12} + J_{13}$. For a degenerate A_2X_2 system where the signals approximate a triplet[3] the separation N is that between the outermost members of the group. Referring to observed separations as P_{ij}, $P_{23} = (J_{12} + J_{13})$ (*cf.* Fig. 1). Similarly, the bridgehead-vinyl protons, 1 and 4, 5 and 6, respectively, form a second A_2X_2 system, on the vinylic (X_2) half of which is superimposed a coupling between protons 5, 6, and bridge proton 7. The vinyl "triplet," of separation $J_{15} + J_{16}$, would then be transformed into a doublet of triplets whose inner members are not resolved in this case. The doublet separation of the outer members might be taken as $J_{57} = J_{67}$, but a better approximation would be to set the separation, P_{56}, between the *outermost* members of the vinyl multiplet as equal to the sum of coupling constants, $P_{56} = (J_{15} + J_{16}) + J_{57}$. The separation, P_1, of the outermost members of the bridgehead multiplet, which forms half of *two* independent A_2X_2 systems, would then be $(J_{12} + J_{13}) + (J_{15} + J_{16})$ *plus* the coupling constant, J_{17}, to the bridge proton, $P_1 = (J_{12} + J_{13}) + (J_{15} + J_{16}) + J_{17}$. Finally, the separation, P_7, between the outer members of the bridge multiplet is $P_7 = 2(J_{17} + J_{57})$; the factor of two is necessary because two equivalent vinyl protons and two equivalent bridgehead protons
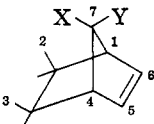
(2) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw–Hill Book Co., Inc., New York, N. Y., 1959, p. 138.

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

EUGENE I. SNYDER AND BORIS FRANZUS

TABLE I

N.M.R. SPECTRAL PARAMETERS FOR 7-SUBSTITUTED NORBORNENES AND NORBORNADIENES

X	Solvent	J_{17}	J_{57}	$(J_{12} + J_{13})$	$(J_{15} + J_{16})$	$\nu_1{}^a$	$\nu_2{}^a$	$\nu_5{}^a$	$\nu_7{}^a$
$-O_2CC_6H_5$	CHCl₃	1.74	0.76 (0.79)ᵇ	4.52	3.93	224	404	398	290
$-O_2CCH_3$	Neat	1.85	.83 (.82)	4.73	4.09	198	372	365	250
	CCl₄	1.78	.86 (.76)	4.82	4.02	213	402	392	269
	CDCl₃					216	404	396	276
$-OC(CH_3)_3$	Neat	1.75	0.78 (0.82)	4.81	4.29	184	367	359	207
	CCl₄	1.66	(0.76)ᶜ	4.92	4.24	197	394	385	223
	CDCl₃					204	399	395	228
$-OH$	Neat	(2.10)ᵉ	(0.70)ᵈ			201	395	393	229
	CDCl₃					206	399	396	230
$-Cl$	CDCl₃	1.66	0.69	4.40	3.87	217	407	398	253

X	Y	Solvent	J_{17}	J_{57}			$\nu_1{}^a$	$\nu_2{}^a$	$\nu_5{}^a$	$\nu_7{}^a$
H	$-O_2CCH_3$	Neat	1.77	0.83	2.98	3.63	173	352	$\{$ ~55 (endo) $\}$ / $\{$ ~100 (exo) $\}$	265
		CDCl₃	1.66	0.96	3.46	3.50	175	358	$\{$ ~60 (endo) $\}$ / $\{$ ~110 (exo) $\}$	270
$-O_2CCH_3$	H	CCl₄	ᶠ	0	ᶠ	4.40	163	358	$\{$ ~60 (endo) $\}$ / $\{$ ~105 (exo) $\}$	254
H	$-OH$	CDCl₃	ᵍ	0.92	ᵍ	3.57	164	363	$\{$ ~55 (endo) $\}$ / $\{$ ~105 (exo) $\}$	225
$-OH$	H	CDCl₃	1.86ᶠ,ʰ	0	3.50ʰ	4.38	151	358	$\{$ ~58 (endo) $\}$ / $\{$ ~110 (exo) $\}$	212

ᵃ The chemical shifts, ν_i, are approximated by the distance in c.p.s. between the center of the multiplet of H₁ and internal TMS, at 60 Mc. ᵇ Numbers in parentheses refer to the doublet separation of the outer components of the H₅, H₆ vinyl resonance pattern. ᶜ Because the H₇ resonance was not well resolved, J_{57} was obtained from the H₅, H₆ vinyl resonance pattern. ᵈ From the spacing of the high-field side of the H₅, H₆ multiplet because the H₂, H₃ and H₅, H₆ multiplets overlap and P_{23}, P_{56} are not measurable. ᵉ From the relation $P_7 = 2(J_{17} + J_{57})$, using J_{57} from above. ᶠ The breadth of the H₇ resonance ($\nu_{1/2} \sim$ 4 c.p.s.) suggests unresolved couplings. ᵍ The

H₇ resonance was not resolved. ʰ Values for J_{17}, $(J_{15} + J_{16})$ were obtained from the spectrum of   D⟩⟨HO⟩ structure   in combination
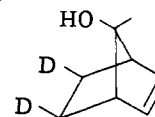
with the spectrum of undeuterated alcohol.

couple with the bridge hydrogen.[4] Setting $(J_{12} + J_{13}) = A$, $(J_{15} + J_{16}) = B$, we have four equations and four unknowns.

$$P_{23} = A$$
$$P_{56} = B + J_{57}$$
$$P_1 = A + B + J_{17}$$
$$P_7 = 2(J_{17} + J_{57})$$

Couplings in norbornadiene evaluated in this way are listed in Table I.[4a]

It is particularly significant that J_{57} evaluated from the four equations above is identical, to within the limits of experimental precision, with J_{57} measured by the doublet separation of the outer members of the vinyl (5, 6) resonance signal, because one of the four equations analogous to those above cannot, in general, be used for the norbornenes. With the numbering system

(4) It must be recognized that although the vinyl protons, e.g., 5 and 6, are not equivalent with regard to the bridgehead protons, they are equivalent with respect to the bridge proton. A similar statement holds for the bridgehead protons.

(4a) NOTE ADDED IN PROOF.—Recently Bly and Bly (*J. Org. Chem.*, **28**, 3165 (1963)) have observed similar multiplicity in vinyl proton signals of 7-substituted norbornenes, but have mistakenly referred to the separation between outer members of the multiplet as (in our notation) $P_{23} = (J_{12} + J_{23})$. The discrepancies, referred to by them, between their observed P_{23} values and those calculated from literature values of J_{12} and J_{23} arise from this incorrect assignment.
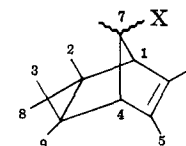


assuming[5] $J_{18} = J_{49} = 0$

$$P_{23} = (J_{12} + J_{13}) + J_{27} = A + J_{27}$$
$$P_{56} = (J_{15} + J_{16}) + J_{57} = B + J_{57}$$
$$P_1 = (J_{12} + J_{13}) + (J_{15} + J_{16}) + J_{17} = A + B + J_{17}$$
$$P_7 = 2(J_{17} + J_{57})$$

In the *syn* isomers (H₇ *anti* to the double bond) $J_{27} = 0$. But the *exo* protons (2, 3) are part of an extensively coupled system including the bridgehead-*endo* pairs and P_{23} is usually not available. One must then turn to the equally good approximation for J_{57} described above and evaluate the other three unknowns from P_{56}, P_1, and P_7. A check on the validity of this treatment is available by comparing $(J_{12} + J_{13})$ obtained therefrom with the values reported in other systems.

For the *anti* isomers, the bridge proton is a broad, unresolved band, probably because $J_{78} \neq 0$,[6,7] and only

(5) R. W. King and P. Butler, 144th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962. We wish to acknowledge our appreciation to Dr. Butler for providing us with a summary of their data.

$(J_{15} + J_{16})$ can be measured with certainty (together with $J_{57} \sim 0$). In the case of *exo,exo*-5,6-dideuterio-*anti*-7-hydroxynorbornene
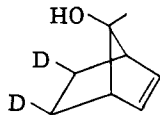
a more complete analysis is possible, for

$$P_{56} = B$$

$$P_1 = \frac{1}{6.5} A + B + J_{17} \sim B + J_{17}$$

(The factor $1/6.5$ is the ratio J_{H-X}/J_{D-X} arising from the difference in magnetogyric ratios between hydrogen and deuterium.) The value A is then merely the difference between the values of P_1 measured in the normal and dideuterated species. Spectral parameters for norbornenes are also listed in Table I.

Discussion of Spectral Parameters. A.—Several facets of the data of Table I can be applied to the determination of the stereochemistry of 7-substituted unsaturated bicyclo[2.2.1]heptyl systems. Foremost is the stereospecific coupling of 0.7–0.9 c.p.s. between the bridge proton and ring vinyl protons *anti* to it. Certainly the presence of such a coupling in the ring systems under discussion could be taken as evidence for an *anti*-bridge proton–ring vinyl configuration. In addition, the data clearly show that the sum of the couplings between the bridgehead and vinyl protons is invariably greater (by 0.5–0.9 c.p.s.) when the vinyl group is *syn* to the bridge hydrogen than when *anti* to it. Unfortunately, the largest of the latter (4.29 c.p.s. for 7-*t*-butoxynorbornadiene) is not significantly different from the smallest of the former (4.38 c.p.s. for *anti*-7-hydroxynorbornadiene) so that both members of the isomeric pair of 7-substituted norbornenes or norbornadienes should be compared for a confident configurational assignment. The origin of the difference between $(J_{12} + J_{13})$ and $(J_{15} + J_{16})$ in the norbornadienes can probably be ascribed to a loss of geometric symmetry about the C_1–C_4–C_7 plane which results from establishment of inequality between the C_7–C_1–C_2 and C_7–C_1–C_6 angles. A third criterion of configurational assignment may reside in the observation that the bridge proton resonance seems to lie toward higher fields when *syn* to the double bond than when *anti* to it. This is in agreement with the expectation that the bridge proton resides in the diamagnetic cone of the double bond when *syn* to it.

The ease of stereochemical assignment suggested by the present work is to be compared with the tedium of the multi-step methods, based ultimately on dipole moment measurements, previously utilized.[8]

B.—The coupling constant between the bridge and bridgehead protons varies but little about 1.8 c.p.s., similar to other reported values.[6,9,10] The sum of coupling constants, $J_{12} + J_{13}$, between the *exo* and bridgehead protons in norbornenes is, according to our method of analysis, 3.0–3.5 c.p.s. Since $J_{13} \sim 0$, $J_{12} \sim 3.0$–3.5 c.p.s., somewhat lower than values obtained by other groups.[5–7,11] The slight decrease in half-width of the vinyl resonance observed in going from *anti*-7-hydroxynorbornene to its *exo,exo*-2,3-dideuterio derivative is consistent with a small cross-ring coupling of the type described by King and Butler.[5]

(6) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).

(7) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963).

(8) For example, see S. Winstein and M. Shatavsky, *J. Am. Chem. Soc.*, **78**, 592 (1956).

(9) F. S. Mortimer, *J. Mol. Spectry.*, **3**, 528 (1959).

(10) A value of 0.5 c.p.s. was favored in ref. 7.

(11) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

The magnitude of $(J_{12} + J_{13})$ and $(J_{15} + J_{16})$ in the norbornadienes imply that the *vicinal and allylic coupling constants are of the same sign contrary to the sign behavior in the fragment* $>CH—CH=CH$ *in acyclic systems.*[12] If J_{12}, J_{13} were of opposite sign, then $|J_{12}| \gtrsim (J_{12} + J_{13}) \gtrsim 4.5$ c.p.s., significantly greater than the range 2.4–3.1 found by other workers[5,6] for some norbornenes. If, however, we assume J_{12}, J_{13} are of the same sign and use $J_{13} \sim 1.0$–1.5 c.p.s., the value observed in acyclic systems, $|J_{12} + J_{13}| \sim 3 + 1.3 \sim 4.3$, in agreement with observations.

The conclusion that J_{12}, J_{13} have opposite signs may be reached by considering the conditions which must be met so that an A_2X_2 system affords a simple triplet pattern. Previous workers have shown that the minimum condition is that $L^2/2M < \nu_{1/2}$, where for the systems at hand $|L| = |J_{12} - J_{13}|$, $|M| = |J_{23} - J_{14}|$, and $\nu_{1/2}$ is the half-width of the vinyl resonance lines.[3] The quantity $L^2/2M$ actually represents the separation between the inner components of the A_2X_2 multiplet. From previously reported ranges for J_{23}, J_{14} of 3.5–6.0 and 0–1.3 c.p.s.,[5,6] coupled with the assumption that both are of the same sign,[13] $|M| \leq 6.0$.

(I) $J_{13} = 0$, $|L| = |J_{12} - J_{13}| = 4.5$ c.p.s.

      $L^2/2M > (4.5)^2/12 = 1.7$ c.p.s.

(II) $J_{13} < 0$, $|L| = |J_{12} - J_{13}| > |J_{12} + J_{13}| = 4.5$

      $L^2/2M \gg 1.7$ c.p.s.

Considering cases I and II where $J_{13} \leq 0$ with $J_{12} > 0$, a *minimum* separation of 1.7 c.p.s. between the inner components is predicted. Since (a) a splitting of 0.5 c.p.s. between inner components was *fully resolved* in neat 7-*t*-butoxynorbornadiene (Fig. 1) and since (b) in no case was the half-width of an unresolved center component of a vinyl triplet greater than 1.3 c.p.s.,[14] we conclude that only $J_{13} > 0$ is consistent with our data. It is significant that whereas Mortimer in his analysis of norbornadiene also concluded the vicinyl and allylic coupling constants were of the same sign[9] no one to our knowledge has commented on the divergence of these results with those found for acyclics.[15,15a]

(12) R. Freeman, *Mol. Phys.*, **4**, 385 (1961).

(13) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960); a positive sign has been experimentally determined in the related system 2-pentyne (B. Braillon, *J. chim. phys.*, **58**, 495 (1961)).

(14) That this is true only when the vinyl group is not involved in coupling with the bridge hydrogen does not in any way affect the arguments presented above.

(15) Dr. Paul Schleyer has arrived at the same sign relations for the vicinal and allylic couplings of the vinyl group in several norbornenes.

(15a) NOTE ADDED IN PROOF.—That the vicinal and allylic couplings are of the same sign may be particularly relevant to the mechanism(s) of allylic coupling. The geometry of the norbornadiene and norbornene system is such that the bridgehead C–H bond lies almost exactly in the nodal plane of the vinyl π-orbital system. This effectively reduces to zero the π-contribution to allylic coupling. Since calculations for allylic couplings, which predicted[12] a negative allylic coupling constant, subsequently experimentally verified,[12] were based on a π-mechanism only, *our observations are not necessarily in conflict with either theory or previous experimental determinations.* Instead our results suggest that, at the very least, there may be some situations which permit allylic coupling by one or more alternate mechanisms. One possibility might be coupling transmitted through the σ-orbital framework of the three-carbon system $C=C—C$; this mechanism would be of a type similar to that proposed for vicinal coupling in the fragment H–C–C–H. A second possibility is that nuclear spin polarization is transmitted *via* interaction between the rear lobes of the sp³ (bridgehead) C–H and the sp² (vinyl) C–H bonds; the geometry of the norbornadiene and norbornene systems is quite favorable for such interactions. Our observations do not permit distinction between these two mechanisms, although the two mechanisms might give rise to 1,3-couplings of different signs. [Negative 1,3-coupling constants have been reported for systems where H, CH₃ are *gauche*, e.g., CH₃CHXCHXCH₃ (A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **84**, 743 (1962); F. A. L. Anet, *ibid.*, **84**, 747 (1962)) and CH₃CHBrCHBrCO₂H (R. Freeman and K. Pachler, *Mol. Phys.*, **5**, 85 (1962)), but a positive 1,3-coupling is observed when the coupled H, CH₃ are *trans*, as in CH₃CHBrCH₂Br (R. Freeman and N. S. Bhacca, *J. Chem. Phys.*, **38**, 1088 (1963))]. The second mechanism, which the authors prefer, might predict the presence of (positive?) 1,4-couplings in the fragment HC—C=C—CH when the usual π-contribution is zero pro-

It is generally felt that for proton–proton coupling nuclear spin–spin interaction is transmitted *via* the bonding electrons.[16] The presence of spin coupling between the bridge proton and the vinyl protons *anti* to it imples that resonance structures such as i and ii

i   ii
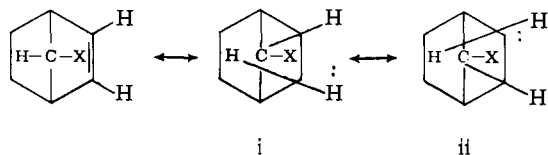
are important, at least in the spin coupling sense. In molecular orbital language, the observed spin coupling arises from interaction of the backside of the C_7 sp^3-orbital used in bonding with the hydrogen with the π orbital system of the ethylenic double bond, together with configuration interaction between the sp^2-orbital used for vinyl hydrogen bonding and the p-orbital on that carbon. This sort of delocalization is analogous to that postulated to occur in 7-norbornenyl and 7-norbornadienyl carbonium ions.
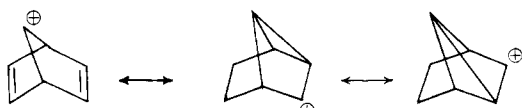
The presence in the n.m.r. spectrum of 7-norbornadienyl cation of a coupling constant of 5 c.p.s. between the bridge and vinyl protons had, in fact, already been cited as furnishing physical evidence of such delocalization.[17]

Facile solvolyses in the 7-norbornadienyl and *anti*-7-norbornenyl series has usually been ascribed to delocalization of the resulting carbonium ion. The reasoning involved is that inasmuch as the activated complex partakes of carbonium ion character its energy will be lowered, relative to a classical structure, by extensive delocalization of charge into the ring. Accordingly, the energy difference between the delocalized activated complex and the *assumed localized* ground state will decrease and solvolytic rates will increase relative to a localized activated complex such as those from the solvolyses of 7-substituted norbornanes. Our results do not negate this hypothesis; they do, however, demonstrate that delocalization occurs even in the ground state. Insofar as the magnitude of the spin coupling constants reflects a hyperconjugative delocalization energy, then the 0.8 c.p.s. coupling in the diene *vs.* the 5 c.p.s. coupling in the 7-dienyl cation suggests significant ground state hyperconjugative stabilization.

Carbonyl compounds have frequently been taken as models for carbonium ion systems.[18] We were therefore somewhat surprised to note that the n → π^* transition energy for 7-ketonorbornene (1) was higher than that for 7-ketonorbornane (2) (λ_{max}^{EtOH} = 274, 290 mμ, respectively[19]). At first glance this seemed to deny interaction of the π-carbonyl system with the π-ethylenic system (and by analogy interaction between the empty

bridge orbital and ethylenic systems in 7-norbornadienyl and 7-norbornenyl systems). Interestingly, and perhaps surprisingly, simple MO calculations, a summary of which appears in Table II (see Experimental for details), predicts the observed sequence, so that the ultraviolet data are fully consistent with a delocalized system. Although the LCAO–MO method predicts
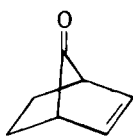
$$E_{(1)}{}^{n \to \pi^*} > E_{(2)}{}^{n \to \pi^*}$$

it predicts

$$E_{(2)}{}^{\pi \to \pi^*} >> E_{(1)}{}^{\pi \to \pi^*}$$

with the latter approaching the $\pi \to \pi^*$ transition energy found for simple conjugated carbonyl compounds.[20]

TABLE II

ENERGY LEVELS AND TRANSITION ENERGIES FOR VARIOUS CARBONYL SYSTEMS

System	Energy levels	Transition energies $E^{n \to \pi^*} + E^{n}$	$E^{\pi \to \pi^*}$
$>C=O$	$\alpha + 2.414\beta$	-0.414β	-2.828β
	$\alpha - 0.414\beta$		
$-C=C-C=O$	$\alpha + 2.495\beta$	-0.220β	-1.440β
	$\alpha + 1.220\beta$		
	$\alpha - 0.220\beta$		
	$\alpha - 1.496\beta$		
	$\alpha + 2.439\beta$	-0.543β	-1.646β
	$\alpha + 1.104\beta$ $\beta_{27} = 0.3394\beta$		
	$\alpha - 0.543\beta$		
	$\alpha - \beta$		
	$\alpha + 2.425\beta$	-0.475β	-1.525β
	$\alpha + 1.050\beta$ $\beta_{27} = 0.2289\beta$		
	$\alpha - 0.475\beta$		
	$\alpha - \beta$		

Experimental

vided that the C–H bonds approach collinearity and are spatially near one another. Because the latter two conditions are met in the norbornadienes and norbornenes, the discrepancy between Laszlo and Schleyer's[6] values for bridgehead–bridgehead couplings ($J \sim 0$) and those of King and Butler[5] ($J \sim 1.2$) assumes added importance. (Prof. Garbisch has communicated privately that bridgehead–bridgehead couplings in bicyclo[2.2.2]octenes and -octadienes are ~ 0.4 c.p.s.) We wish to acknowledge a stimulating exchange of letters with Prof. E. W. Garbisch which helped focus many of the points considered above.

(16) See ref. 13 and earlier works cited therein.

(17) P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **84**, 4876 (1962); *cf.* P. R. Story, *et al.*, *ibid.*, **85**, 3630 (1963).

(18) H. C. Brown and K. Ichikawa, *Tetrahedron*, **1**, 221 (1957).

(19) B. Franzus and E. I. Snyder, unpublished results. A value of $\lambda_{max}^{EtOH} = 274$ mμ has recently been reported (P. G. Gassman and P. G. Pape, *Tetrahedron Letters*, 9 (1963)).

(20) Examination of the low wave length portion of the ultraviolet spectrum of **2** indicated an extinction coefficient of *ca.* 500 at 215 mμ in the end absorption.

(21) We wish to acknowledge the gift of a generous sample of 7-chloronorbornadiene from Dr. P. R. Story of the Bell Telephone Laboratories.

(22) We wish to express our appreciation to Dr. W. C. Baird, Jr., for a gift of this compound.
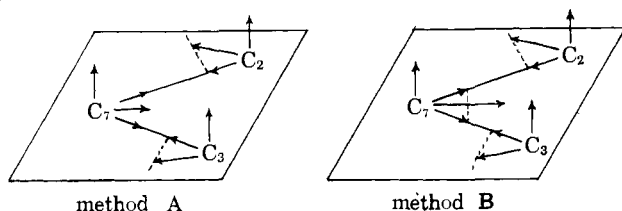
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The in-plane components of the C_2, C_3 p-orbitals are then resolved along their respective internuclear lines with C_7. The question now remains regarding the proper vectorial decomposition of the C_7 in-plane component with regard to the two internuclear 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.

method A   method B

Method A gives results virtually identical with the procedure described by Roberts,[24] but method B gives different values. Using Kopineck's tables,[26] 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 β_{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 (β) were those listed by Streitwieser.[27]

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 → π^* transition is $E^{n \to \pi^*} = E^{\pi^*} - E^n$, the difference in n → π^* transition energies is then dependent upon only the relative energy levels of the first antibonding orbital, $E_{(1)}^{n \to \pi^*} E_{(2)}^{\to \pi^*} = E_{(1)}^{\pi^*} - E_{(2)}^{\pi^*}$. Transition energies for the $\pi \to \pi$ transition are the difference between the lowest antibonding and the highest bonding orbital.

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Analysis of the Nuclear Magnetic Resonance Spectra of Norbornene Derivatives[1]

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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}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_{ee}) and the olefinic 1,2(J_{ed}) coupling constants were found to have the same sign. The magnitudes of ^{13}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[3–21] assigned certain chemical shifts and established the applicability of the well

known Karplus relationships between vicinal coupling constants and dihedral angles (ϕ)[22] 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.[23,24] 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[15,16] 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.[25] Similar considerations apply also to 7-oxabicyclo[2.2.1]heptene derivatives.[26,27] Musher[28] 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 ϕ's $(0°)$; and (c) unusual magnetic shieldings. We wished to see whether these anomalies occurred in the spectra of norbornene

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