1 ml. of concd. sulfuric acid was heated under reflux during 5 hr. Excess methanol was removed from the reaction mixture *in vacuo*, and the residue was taken up in 10 ml. of water. The methyl esters (254 mg.) obtained from ether extracts were treated with acetyl chloride in a sealed tube during 1 hr. at 60–65°, and at room temperature overnight. The mixture was worked up, and crude isomeric methyl acetoxyketostearates (252 mg.; VII and VIII, R = CH₃), were purified by means of molecular distillation, b.p. 133–143° (0.04 mm.) (air-bath).

Anal. Calcd. for $C_{21}H_{38}O_5$: C, 68.05; H, 10.34. Found: C, 67.98; H, 10.25.

A mixture of VII and VIII (R = H) was prepared by direct acetylation of synthetic XIII and XIV.

Anal. Calcd. for $C_{20}H_{36}O_5$: C, 67.38; H, 10.18. Found: C, 66.95; H, 10.08.

A 2,4-dinitrophenylosazone was also prepared from synthetic XIII and XIV in the usual way. The product, after recrystallization from ethanol, melted 148.5–149.5° (*cf.* above).

9,10-Diketostearic acid (XV)[28] was obtained by chromic acid oxidation of 9,10-dihydroxystearic acid,[33] according to the method of Nicolet and Jurist,[34] m.p. 83–84° (lit.[34] m.p. 86°).

Methyl 10-Acetoxy-9-ketodecanoate (VI, R = CH₃).—ω-Carbomethoxycaprylyl chloride [prepared from methyl hydrogen azelate (10.0 g., 0.049 mmol.) and thionyl chloride (11.9 g., 0.10 mmol.) at 60°], in 15 ml. of ether solution at −10°, was added slowly to diazomethane[35] (*ca.* 8.4 g., 0.20 mmol.) in 300 ml. of ether at −10°. A mild exothermic reaction was observed during addition. The reaction mixture was stirred and maintained between −10 and −5° during 2 hr., then stirred at room temperature overnight. Excess diazomethane was removed by careful distillation of ether until the yellow color of the reaction mixture disappeared. While heating was continued at 40–50°, dry glacial acetic acid[36] (1.25 g., 25 mmol.) was added, and reflux was continued during 1 hr. Ether and excess acetic acid were removed *in vacuo* to yield an amber-colored semi-solid. A portion of this residue (5.83 g.) was fractionally distilled. Fraction I (0.584 g., b.p. 83–102° (0.06 mm.)) was methyl azelate (identified by comparison of infrared spectrum to an authentic sample); fraction II (2.290 g., b.p. 108–119° (0.06 mm.)) crystallized upon cooling (m.p. 50.5–51.0°) and proved to be methyl 10-chloro-9-ketodecanoate.

Anal. Calcd. for $C_{11}H_{19}ClO_3$: C, 56.29; H, 8.16; Cl, 15.11. Found: C, 56.67; H, 8.06; Cl, 15.27.

The third fraction [b.p. 128–133° (0.04 mm.), 1.075 g.] was the desired methyl 10-acetoxy-9-ketodecanoate (VI, R = CH₃), m.p. 47.5–48.0° (ether–hexane).

(33) J. T. Scanlan and D. Swern, This Journal, **62**, 2305 (1940).

(34) B. H. Nicolet and A. E. Jurist, *ibid.*, **44**, 1136 (1922).

(35) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 165.

(36) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., 3rd ed., Boston, Mass., 1955, p. 281.

Anal. Calcd. for $C_{13}H_{22}O_5$: C, 60.44; H, 8.59. Found: C, 59.98; H, 8.67.

The compound was allowed to react with 2,4-dinitrophenylhydrazine in the usual way. The derivative, isolated and recrystallized from ethanol, m.p. 149.0–149.5°, was a 2,4-dinitrophenylhydrazone of the ketone portion of the parent molecule as well as a 2,4-dinitrophenylhydrazide of the carbomethoxy grouping; infrared absorption at 1736 and 1225 cm.⁻¹ showed the acetate function to be intact.

Anal. Calcd. for $C_{24}H_{28}N_8O_{11}$: C, 47.67; H, 4.67; N, 18.54. Found: C, 47.88; H, 4.73; N, 18.59.

1-Acetoxy-2-decanone (V).[37]—Pelargonyl chloride (10 g., 0.057 mol.) was allowed to react with excess diazomethane as described above. Acetolysis with dry acetic acid gave the crude crystalline acetoxy ketone, m.p. 45–53°. After repeated recrystallizations from cold ether, the pure compound amounted to 7.20 g., m.p. 55.0–55.8°.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 67.25; H, 10.35.

No indication of the presence of chloromethyl ketone was obtained as in the previous case.

A sample of V (107 mg., 0.5 mmol.) was dissolved in 40 ml. of methanol to which was added 40 ml. of 0.1 *M* sodium metaperiodate solution. The mixture remained at room temperature, in darkness, and the progress of oxidation was followed by periodate analysis of aliquots.[38] One equivalent of periodate (0.497 mol.) was consumed during 24 hr., and the oxidation products were extracted into ether from the acidified mixture. The material obtained was heated in methanolic sulfuric acid for 18 hr. The presence of methyl pelargonate was indicated by gas chromatography (retention time identical to that of authentic methyl pelargonate).

Attempted Isomerization of Tiglyl Acetate.—Equal volumes (1 ml.) of glacial acetic acid and tiglyl acetate,[39] prepared by acetylation of tiglyl alcohol (the latter obtained *via* lithium aluminum hydride reduction of tiglic acid[40]), were mixed. A sample of the mixture was analyzed by gas chromatography immediately after mixing. The mixture was heated under reflux during 1 hr., and a sample again was analyzed by gas chromatography. The two samples gave superimposable chromatograms.

(37) Prepared by D. A. Teets.

(38) E. L. Jackson in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 361.

(39) W. Oroshnik and R. A. Mallory, This Journal, **72**, 4608 (1950).

(40) L. F. Hatch and P. R. Noyes, *ibid.*, **79**, 345 (1957).

The Proton Magnetic Resonance Spectra of Olefins. I. Propene, Butene-1 and Hexene-1

By Aksel A. Bothner-By and C. Naar-Colin

The high-resolution proton magnetic resonance spectra of propene, butene-1 and hexene-1 have been obtained on "neat" samples and on samples in dilute carbon tetrachloride solution. The spectra have been analyzed in terms of chemical shifts and spin–spin coupling constants. Some possible explanations of the chemical shifts are discussed. The spin–spin coupling constants observed in butene-1 may indicate that the three rotational conformers are equally abundant in the liquid.

In this paper are presented observations on the high resolution proton magnetic resonance spectra of propene, butene-1 and hexene-1, representing the first part of a general investigation into the spectra of olefins. Two facets of such an investigation which currently appear to us to be of interest include: (1) a determination of the effects of *gem, cis* and *trans* substitution on the chemical shift of ole-
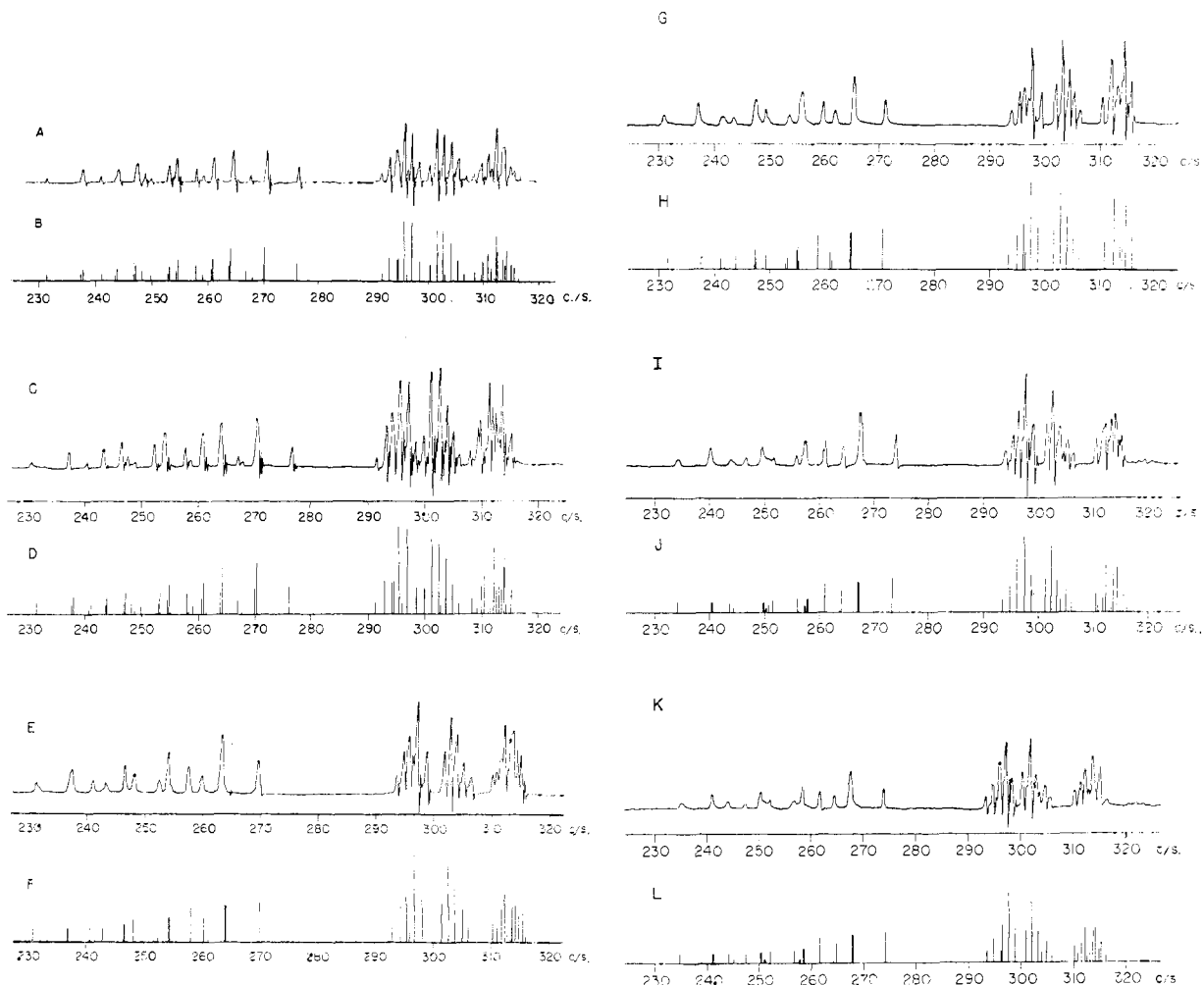
Fig. 1.—60-mc. olefinic proton magnetic resonance spectra of: propene neat, (A) observed, (B) calculated; propene standard, (C) observed, (D) calculated; butene neat, (E) observed, (F) calculated; butene standard, (G) observed, (H) calculated; hexene neat, (I) observed, (J) calculated; hexene standard. (K) observed, (L) calculated.

finic and allylic protons; (2) the effect of stereoiso-merism (particularly rotational isomerism about the bond between trigonal and tetrahedral carbon) on chemical shift and on short- and long-range proton–proton spin coupling constants.

The proton magnetic resonance spectrum of butene-1 has been recorded and analyzed previously by Alexander.[1] His spectrometer was operated at a frequency of 31.6 mc. We have repeated this work using the Varian 60 mc. spectrometer. The results of our analysis are in substantial agreement with those previously reported. This finding serves the double purpose of confirming both the previous assignments and our methods of calculation. Previously reported[2,3] spectra of propene and hexene-1 were not sufficiently resolved to permit a detailed analysis, and we have accordingly obtained new and more highly resolved recordings.

(1) S. Alexander, J. Chem. Phys., 28, 358 (1958).

(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. 244.

(3) N. F. Chamberlain, "Humble Catalog of NMR Spectra, April, 1959." Humble Oil and Refining Co., Baytown, Texas, Spectrum #44.

Experimental

Materials.—Ethylene was obtained from the Fisher Scientific Co.; propene, butene-1 and hexene-1 were Phillips 66 hydrocarbons. Carbon tetrachloride was reagent grade. Tetramethylsilane was obtained from Anderson Laboratories.

Preparation of Samples.—Spectra were obtained on both "neat" and standard samples. The hydrocarbon sample was introduced into the vacuum line and degassed by freezing and thawing under vacuum. For the "neat" samples, ca. 0.2 ml. of hydrocarbon was distilled into the samples tube, about 10% by volume[4] of tetramethylsilane was condensed in, and the tube was sealed off under vacuum.

Standard samples consisted of mixtures of carbon tetrachloride (mole fraction 0.9) and olefin (mole fraction 0.1). to which was added <1% of tetramethylsilane. The olefin and carbon tetrachloride were degassed and measured as vapors at low pressure in calibrated bulbs, then condensed into the sample tube. Tetramethylsilane was condensed in, and the tube was then sealed off under vacuum.

Recording of Spectra.—Spectra were obtained using the Varian 60 mc. Dual Purpose NMR Spectrometer at Mellon Institute. The magnet for this unit is fitted with sample-spinner, flux-stabilizer, thermal insulation, a controlled-temperature water supply, and mechanical and electrical field trimmers. Spectra were obtained at ambient temperature (27 ± 1°) under conditions of field stability and homogeneity such that the septet structure of the olefin proton

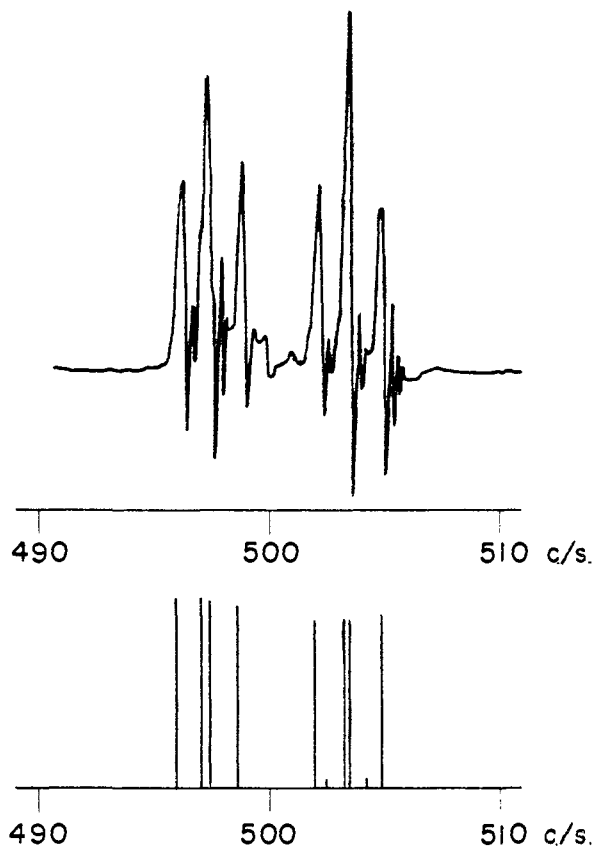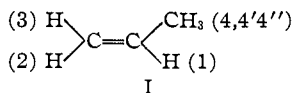(4) Except propene which was diluted 50-50 with tetramethylsilane.

Fig. 2.—60-mc. methyl proton magnetic resonance spectra of: propene neat, (A) observed, (B) calculated.

signal from isobutylene was well resolved (width of lines at half-height 0.2–0.4 c.p.s.). Spectra were calibrated using the side-band method[5] and graphical interpolation. The side-bands were produced by audiofrequency modulation of the magnetic field, using a modified Hewlett–Packard model 202A function generator, monitored by a Hewlett–Packard model 221C frequency counter. Numerous replicate spectra were obtained in each case, and examined for internal consistency. Separate determinations of line positions were made for each of five spectra; the values reported are the averages for the five values. Standard deviation of line position varied with conditions, but was usually ±0.3 c.p.s. and never exceeded ±0.5 c.p.s.

Experimental line positions are reported on a frequency scale. Increasing numbers correspond to increasing field and increasing shielding. The position of tetramethylsilane in each spectrum is defined as +600.00 c.p.s. Chemical shifts on this scale may be expressed in p.p.m. by dividing by 60, and the values thus obtained correspond to Tiers' "τ"-scale.

Interpretation of Spectra.—The procedure followed may be illustrated by the case of the propene (neat) spectrum (Fig. 1A; only the lines arising from the olefinic hydrogens are shown). A 40-mc. spectrum of intermediate resolution and preliminary values for some of the coupling constants are given by Pople, Schneider and Bernstein.[2]

$$\begin{array}{c} (3)\ H \\ (2)\ H \end{array} \!\! \diagdown \!\! C\!\!=\!\!C \!\! \diagup \!\! \begin{array}{c} CH_3\ (4,4'4'') \\ H\ (1) \end{array}$$

I

The sixteen lines arising from proton 1 (see numbering, formula I) occur at lowest field, and can be sorted by simple first-order considerations into a doublet ($J \sim 17$ c.p.s.) of doublets ($J \sim 10$ c.p.s.) of quartets ($J \sim 6$ c.p.s.); these give rough values for $J_{1,3}$ $J_{1,2}$ and $J_{1,4}$. The first closely-spaced group of lines at slightly higher field constitutes one member of the doublet with large spacing ($J_{1,3}$) and hence arises from proton 3, while the next complex arises similarly
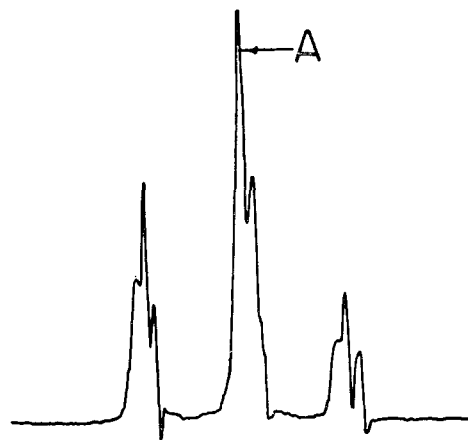

Fig. 3.—60-mc. methyl proton magnetic resonance spectrum of butene neat observed; A, line used in measuring chemical shift of the methyl group.

from proton 2. Closer scrutiny reveals that each of these bands consists of an overlapping doublet of quartets. The quartet splitting must arise from the methyl groups, and thus gives rough values for $J_{3,4}$ and $J_{2,4}$ while the doublet splitting corresponds to $J_{2,3}$. The band at highest field in the olefin region includes the high-field members of the doublets from protons 2 and 3; its appearance is complex. Certain of the coupling constants were given negative signs, in accordance with previous experimental findings[1,5 -7] and theoretical predictions.[8]

A predicted spectrum was calculated based on the rough parameters obtained above. The method of calculation was that described by Pople, Schneider and Bernstein.[9] The calculation was performed on an IBM 704 high speed computer. The program, written for this purpose, accepts as input data the number of proton spins (up to 7), the chemical shifts (expressed in c.p.s.) for each, and the spin-coupling constants (also in c.p.s.). It computes the appropriate matrix elements, and obtains the corresponding eigenvalues and eigenvectors. It then computes all line positions and intensities, and presents these in tabular form, together with the input data, and some matrix sums which permit a rapid estimation of the accuracy of the calculation.[10]

The predicted spectrum, obtained using the rough parameters, was compared with the experimental spectrum. Corresponding lines could be identified without difficulty. The rough parameters were corrected according to first order, and a new predicted spectrum was calculated from the revised parameters. Two or three repetitions of the correction–calculation cycle ordinarily sufficed to obtain satisfactory agreement between the observed (Fig 1A) and predicted (Fig. 1B) spectra. In the cases of propene, butene-1 and hexene-1, the appearance of the complex band at highest field in the olefinic part of the spectrum was very much affected by small changes in the parameters, and served as a sensitive indicator of the correctness of the fit. Attempted calculations using positive values for the long-range couplings $J_{2,4}$ or $J_{3,4}$ or a negative sign for $J_{2,3}$ could not be made to converge on the observed spectra. In Fig. 1(A-L) are given the observed and calculated olefinic proton spectra for propene, butene-1 and hexene-1, both "neat" and in "standard" solution.[11] The signal from the methyl group of propene is shown in Fig. 2, along with the predicted spectrum. In the case of butene-1 and hexene-1, the machine calculations were performed neglecting coupling of the methylene adjacent to the double bond with the other pro-

(5) A. D. Cohen and N. Sheppard, *Proc. Roy. Soc. (London)*, **A252**, 488 (1959); C. N. Banwell, A. D. Cohen, N. Sheppard and J. J. Turner, *Proc. Chem. Soc.*, 266 (1959).

(6) J. A. Elvidge and L. M. Jackman, *ibid.*, 89 (1959).

(7) F. S. Mortimer, *J. Mol. Spec.*, **3**, 335 (1959).

(8) M. Karplus, private communication.

(9) Reference 2, p. 103 ff.

(10) Copies of this program are available upon request from Mellon Institute, 4400 Fifth Ave., Pittsburgh 13, Penna.

(11) Tables giving the concordance of observed and calculated lines are available upon request.

tons in the side chain, so that the patterns could not be compared with the experimental spectra. The chemical shifts of the terminal methyl groups were taken as the position of the strong sharp component of the central group of the triplet (Fig. 3). This line arises from transitions of methyl protons in molecules in which the adjacent methylene protons are in essentially pure singlet states.

In making the calculations it was assumed that the coupling constants were not affected by the change from a "neat" sample to a "standard" solution. This assumption is probably not strictly valid, since some of the coupling constants will probably depend on the rotational conformation about the bond between trigonal and tetrahedral carbon, and the populations of the rotameric states would be expected to be influenced by solvent composition. However, the spectra are fitted within experimental error under this assumption, so that if deviations do occur, they are too small to be detected with the present data.

Finally, the refined parameters obtained from the best fit of calculated and observed 60 mc. spectra of butene-1 (neat) were converted to the values expected at 31.6 mc., and a spectrum was calculated and compared with that published by Alexander.[1] The fit obtained appeared completely satisfactory.

Results and Discussion

The values obtained for the coupling constants and shifts are given in Table I.

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR
1-ALKENES,[a] H_2C=$CHCH_2R$

Chemical shift	R = H		R = CH₃		R = C₃H₇	
	Neat	Standard	Neat	Standard	Neat	Standard
$W(1)$	255.97	255.97	252.36	253.18	255.89	256.55
$W(2)$	307.46	307.00	307.98	308.08	307.61	307.30
$W(3)$	302.20	302.00	302.99	303.64	303.55	303.55
$W(4)$	500.3	497.2	481.2	480.0	478.3	477.9
Terminal methyl	....	....	541.2	540.3	548.3	545.7
Coupling constant						
$J_{1,2}$		10.02		10.32		10.23
$J_{1,3}$		16.81		17.23		17.03
$J_{1,4}$		6.40		6.22		6.55
$J_{2,3}$		2.08		1.96		2.23
$J_{2,4}$		−1.33		−1.26		−1.18
$J_{3,4}$		−1.75		−1.66		−1.51

[a] On a frequency scale with $W(SiMe_4)$ = +600.00.

Some features of the data are immediately evident: (1) The chemical shifts of the olefinic protons in the series propene, butene-1, hexene-1, are remarkably constant: in standard solution, $W(1)$ = 254.87 ± 1.70 c.p.s. ($\tau(1)$ = 4.248); $W(2)$ = 307.54 ± 0.54 c.p.s. ($\tau(2)$ = 5.126) and $W(3)$ = 302.92 ± 0.72 c.p.s. ($\tau(3)$ = 5.049). (2) The values of the coupling constants are also quite similar in the series. (3) The effect of change of solvent from hydrocarbon to carbon tetrachloride is to lower the position of the resonance of proton two relative to that from protons one and three.

Solvent Effects.—The solvent effects on the chemical shifts are small enough so that they do not complicate the considerations of the intramolecular sources of shielding, but large enough to be undeniably real. The downfield shift of the resonance signal arising from proton two relative to that from protons one and three which results from the change of solvent to carbon tetrachloride probably reflects the slightly greater accessibility of H(2) to solvent.[12]

Olefinic Proton Shielding.—The chemical shift of ethylene protons in standard solution is W =

(12) A. A. Bothner-By, J. Mol. Spec., **5**, 52 (1960).

279.03 c.p.s. or τ = 4.650 p.p.m. The substitution of an alkyl group into ethylene thus results in these changes: $\tau(1)$ - τ(ethylene) = −0.402 p.p.m., $\tau(2)$ − τ(ethylene) = +0.476 p.p.m., and $\tau(3)$ − τ(ethylene) = +0.399 p.p.m. It is interesting to attempt to rationalize these shifts.

Some of the factors which have been suggested as affecting proton shielding in organic compounds are: (1) Proximity of groups which donate or withdraw electrons either inductively or by a resonance mechanism.[13] (2) Proximity of groups of anisotropic diamagnetic susceptibility.[14] (3) Presence of indigenous permanent electric fields which might distort the electronic orbitals about the protons.[15] (4) Near approach of polarizable groups which lead to a non-vanishing mean square electric field at the proton, reducing its shielding.[12]

The paramagnetic contribution from within the C–H bond is generally considered[16] to be unimportant or to constitute a reasonably constant fraction of the diamagnetic contribution.

In 1-alkenes, the alkyl group is thought to donate electrons to the double bond both by an inductive and by a resonance (hyperconjugative) process. The effect due to the inductive process should fall off monotonically with distance and should yield the greatest electron density on the nearest carbon. This leads to the prediction of greater shielding for proton one than for protons two and three, in contradiction to the experimental findings. Consequently, inductive donation of electrons is not the controlling factor in this case. Invoking the hyperconjugative process (symbolized by II ↔ III)
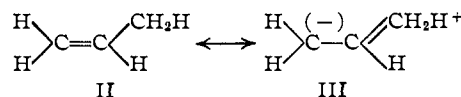
leads to the correct prediction that the β-protons will be more shielded, but it is not clear that there should be a difference between them, or in which direction such a difference should occur.

In a number of cases, it appears possible to rationalize proton shifts by assigning a diamagnetic anisotropy to the C–C single bond[14c,d]: such a diamagnetic anisotropy must be in the sense that the largest diamagnetism is observed transverse to the bond. In the case of propene, calculations indicate that this postulate would lead to a downfield shift of the resonance from H(1) and an upfield shift of that from H(3), as observed. However, it would predict a downfield shift for the resonance from H(2), in contradiction to the observation, and the effects of such a diamagnetic anisotropy cannot, therefore, be important, in these cases.

The dipole moment of 1-alkenes[17] probably lies along the general line indicated in IV.

(13) (a) J. N. Shoolery and B. P. Dailey, THIS JOURNAL, **77**, 3977 (1955); (b) A. A. Bothner-By and R. E. Glick, ibid., **78**, 1071 (1956); (c) P. L. Corio and B. P. Dailey, ibid., **78**, 3043 (1956).

(14) (a) J. A. Pople, J. Chem. Phys., **24**, 1111 (1956); Proc. Roy. Soc. (London), **A239**, 550 (1957); (b) H. McConnell, J. Chem. Phys., **27**, 226 (1957); (c) A. A. Bothner-By and C. Naar-Colin, Ann. N. Y. Acad. Sci., **70**, 833 (1958); (d) P. T. Narasimhan and M. T. Rogers, J. Phys. Chem., **63**, 1388 (1959).

(15) (a) W. G. Schneider, H. J. Bernstein and J. A. Pople, J. Chem. Phys., **28**, 601 (1958); (b) A. A. Bothner-By and C. Naar-Colin, THIS JOURNAL, **80**, 1728 (1958).

(16) Reference 2, p. 176.

TABLE II

SPIN-SPIN COUPLING CONSTANTS REPORTED FOR SEVERAL OLEFINIC COMPOUNDS

$$\begin{array}{c} (3)\ H \\ \diagdown \\ (2)\ H \end{array} C=C \begin{array}{c} CH_2R\ (4) \\ \diagup \\ \diagdown \\ H\ (1) \end{array}$$

Compound	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	Source
H/Cl C=C CH₂Cl/H	..	13.1	7.1	..	..	0.5	a
	..	13.1	7.3	..	..	−1.2	b
Cl/H C=C CH₂Cl/H	7.2	..	7.2	..	0.9	...	a
	7.0	..	7.4	..	−1.2	...	b
H/H C=C CH₂Cl/Cl	..	..	..	1.9	(0.3, 0.9)		a
	..	..	..	1.9	(0.3, 1.0)		b
H/H C=C CH₂Br/Br	..	..	..	2.2	( ) (0.3, 1.0)		c
H/H C=C C₆H₅/H	10.6	17.2	..	1.6	..	...	d
	11.3	17.8	..	1.2	..	...	e
H/H C=C CN/H	11.28	18.19		1.27	..		f

^{a} Ref. 7. ^{b} Ref. 5. ^{c} W. A. Anderson, *Phys. Rev.*, **102**, 151 (1956). ^{d} T. Shimizu, S. Matsuoka, S. Hattoci and K. Senda, *J. Phys. Soc. Japan*, **14**, 683 (1959). ^{e} R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **31**, 996 (1959). ^{f} J. S. Waugh, private communication.

IV
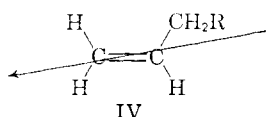
If the very rough approximation is made that the dipole may be replaced by a uniform electric field in the same direction, both the signs and relative magnitudes of the shifts are predicted correctly. (It is supposed that a field tending to push electrons out along the bond on to the proton increases the shielding.) It would be expected that the dipole moments of the 1-alkenes would be about the same, and the constancy of the shifts is not unexpected on this basis.

The decrease in proton shielding caused by the approach of a polarizable group may be roughly computed using the expression[12]

$$\Delta\sigma = -1.5 \times 10^{-18}\ \alpha\epsilon/r^6$$

where $\Delta\sigma$ is the change in shielding, expressed as a dimensionless fraction, α is the polarizability of the group in cc., ϵ the ionization energy in ergs, and r the distance of approach in cm. Because of the r^{-6} dependence, approach must be essentially to contact distance (~ 2 Å.) before an appreciable effect on the shielding is exerted. Thus although the effect of the dispersion force attraction between the alkyl group and the three olefinic protons leads to the correct prediction $W(1) << W(3) < W(2)$, any realistic choice of values for α and ϵ give shifts which are much too small.

The most satisfactory explanation appears then to be that based on the presence of a permanent dipole in the molecule. The chemical shifts observed for the protons in the alkyl side chains are unexceptional. The β- and γ-methylenes of the butyl group in hexene-1 give rise to a complex of lines with a center at *ca.* 524 c.p.s. (neat) or 521 c.p.s. (standard). The chemical shift of the signal

(17) (a) J. W. Smith, "Electric Dipole Moments," Butterworth, London, 1955, p. 198; (b) Lide and Mann, *J. Chem. Phys.*, **27**, 868 (1957).

from these methylenes and from the terminal methyls is within experimental error of that observed for long-chain saturated hydrocarbons.[15b]

Spin–Spin Coupling Constants.—Previously reported spin–spin coupling constants for several olefinic substances are summarized in Table II. The magnitude of the spin–spin coupling constants in the 1-alkenes is in harmony with those previously reported.

In the case of 1-butene, rotational isomerism about the bond joining tetrahedral carbon and trigonal carbon (to be symbolized C_{III}–C_{IV}) is possible. Previous suggestions[18,19] that the energy minima are probably such that ϕ, the H–C_{III}–C_{IV}–H dihedral angle, has the values 60°, 180° and 300°, have received support from microwave studies on propylene.[20] It might be expected that the coupling constants $J_{1,4}$, $J_{2,4}$ and $J_{3,4}$ would all be functions of ϕ, and might thus give information about the preferred conformation of the molecule.

The form of the functional dependence of $J_{IV,IV}$, the coupling constants between protons on adjacent tetrahedral carbons, on ϕ, the dihedral angle H–C_{IV}–C_{IV}–H, has been calculated[21,22] and deduced experimentally.[22,23] It is positive when ϕ is 0°, drops to near zero when $\phi = 90°$ and rises again to a positive value again at $\phi = 180°$. While the calculated curve indicates not much difference between the constant when $\phi = 0°$ and when $\phi = 180°$, experimental evidence, particularly the coupling in ethyl and isopropyl derivatives,[24] suggests that the coupling when $\phi = 180°$ must be near 16–18 c.p.s.,

(18) (a) N. Sheppard, *J. Chem. Phys.*, **17**, 74 (1949); (b) J. G. Aston, G. J. Szasz, H. W. Woolley and F. G. Brickwedde, *ibid.*, **14**, 67 (1946).

(19) J. E. Kilpatrick and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **38**, 191 (1947).

(20) D. R. Hershbach and L. C. Krisher, *J. Chem. Phys.*, **28**, 728 (1958).

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or about twice that when $\phi = 0°$. In the H–C$_{III}$–C$_{III}$–H case, two situations may be distinguished: when a formal double bond joins the carbons, ϕ can assume only the values $0°$ and $180°$, and $J_{III,III}$ then possesses values of about 10 and 17 c.p.s., respectively; alternatively, the trigonal carbons may be joined by a single bond, and in this case.[6] $J_{III,III} \cong 16$ c.p.s. when $\phi = 180°$.

The $J_{III,IV}$ coupling observed in propene (6.40 c.p.s.) is the average of that for the three protons, two of which are found[20] at $\phi = \pm60°$ and one at $\phi = 180°$. The spectra of cyclohexene and cyclopentene[25] indicate that $J_{III,IV}$ ($\phi = \pm60°$) is of the order of one–three cycles, which requires $J_{III,IV}$ ($\phi = 180°$) to be of the order of 16 c.p.s. All of these observations are consistent with the postulate that the coupling constant for the H–C–C–H system depends primarily on the dihedral angle, and that the change in hybridization of the carbons from sp^3 to sp^2 introduces only a small perturbation on the form of the functional dependence.

It was noted above that $J_{1,4}$ in propene, butene-1 and hexene-1 are roughly equal. If the functional dependence postulated above is accepted, then the

(25) To be published.

observed $J_{1,4}$ would depend steeply on the relative populations of the conformers V–VII.
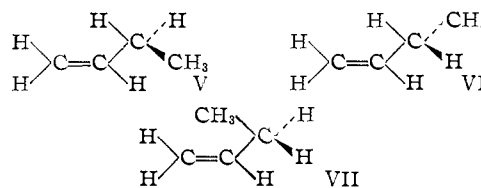
For example, if the butene were entirely V and VI, one would predict the value $(2 + 16)/2 = 9$ c.p.s. for $J_{1,4}$. On the other hand, equal population of all states V–VII, would lead to equality with that observed for propene. Such an equality is at variance with previous suggestions[18,19] based on Raman spectroscopy and heat capacity measurements.

Attempts to obtain definite evidence on the form of the functional dependence of $J_{III,IV}$ on ϕ will continue.

The Behavior of Ketene toward Acetals, Hemiacetal Chlorides, Acylals, Mixed Acetal-Acylals and Hemiacylal Halides

BY CHARLES D. HURD AND RAYMOND D. KIMBROUGH, JR.[1]

Ketene reacts not only with acetals and hemiacetal chlorides if catalyzed by Lewis acids but also with mixed acetal-acylals thereby increasing the length of the chain by two carbons. Ketene fails to add to full acylals or to hemiacylal halides under comparable conditions. Study of the reaction of ketene with acetals and hemiacetal chlorides has been extended to determine its limitations and to include heterocyclic members. Mixed acetals react according to both of the possible paths. Electron-withdrawing groups exert an inductive effect in lessening or even inhibiting this reaction. Hemiacetal chlorides in the carbohydrate series such as triacetylarabinosyl chloride or triacetylxylosyl chloride failed to react. A mechanism covering these findings is included.
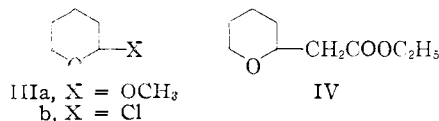
Certain aldehyde derivatives, namely, hemiacetal chlorides[2] (I) and acetals[3] (II), have been shown to react with ketene when catalyzed by zinc chloride,

$$\begin{array}{cc} R\text{—}CH\text{—}Cl & R\text{—}CH\text{—}OR' \\ | & | \\ OR' \quad I & OR' \quad II \end{array}$$

and these reactions were reported to be general, at least for simple members of the series. When ethyl alcohol was used in the step of purification the products were β-alkoxy esters, $RCH(OR')$-$CH_2COOC_2H_5$.

In the present study this reaction was extended to include cyclic acetals, cyclic hemiacetal chlorides and acylals. Limitations of the reaction were investigated also.

Ketene ($ZnCl_2$, then C_2H_5OH) reacted with both 2-methoxytetrahydropyran (IIIa) and tetrahydropyran-2-yl chloride (IIIb) to form ethyl 2-tetra-

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IIIa, X = OCH$_3$ IV
  b, X = Cl

hydropyranacetate (IV). The yield of IV from IIIb was 60%, whereas that from IIIa was only 11%; but it will be noticed that IIIa is a mixed acetal, hence IV is but one of the predicted products. The other anticipated product would be ethyl 3-methoxy-7-hydroxyheptanoate (V) and it was formed in 24% yield.

$$\underset{\underset{OCH_3}{|}}{HOCH_2CH_2CH_2CH_2CHCH_2COOC_2H_5} \quad V$$
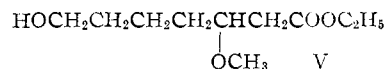
Extension of this study to derivatives of tetrahydropyran-2,3-diol[4] required the synthesis of certain new compounds. The known diacetate VIa was converted by means of hydrogen chloride into 3-acetoxytetrahydropyran-2-yl chloride (VIb).[5]

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