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Carbon-13 Nuclear Magnetic Resonance Spectra of Olefins and Other Hydrocarbons

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The carbon-13 nuclear magnetic resonance (n.m.r.) method has been applied to the study of organic compounds by means of measurements on naturally occurring carbon-13. Spectra have been obtained principally to illustrate the advantages of the method in the study of carbons containing no hydrogen atoms as in substituted olefins, dienes, allenes, acetylenes, aromatics and carbonyls. For the olefins the spectra are sensitive to substitution on the olefinic carbon atoms or on carbon atoms α to the olefin carbons. Substituents on more remote carbon atoms have little or no effect on the spectra. In allenes the central carbon atom of the allene group has its resonance at extremely low fields, indicating a very strong paramagnetic deshielding. In aromatic derivatives an appreciable effect is found due to the branching on the α-carbon atom; the greater the branching the greater the paramagnetic deshielding of the substituted carbon atom. For aliphatic compounds fine structure produces complex spectra that are difficult to interpret. Spin-spin decoupling resolves much of this complexity.

Introduction

In the investigation of the molecular structure of complex organic materials the point of principal importance is usually the diagnosis of the skeleton; that is, the relative locations of the carbon atoms and hetero atoms in the substance. The location of the hydrogen atoms in the material is also of great importance, but in the spectroscopic investigation of the molecular structure of complex substances it is often true that some spectral methods are overly sensitive to the bond between hydrogen and carbon or hetero atoms. Thus much of the important information concerning skeletal structure is obtained indirectly by a study principally of structures involving hydrogen. This is partly true of infrared and completely true of proton nuclear magnetic resonance spectrometry.

The carbon-13 nuclear magnetic resonance method provides a potentially powerful tool for the direct investigation of the carbon skeleton of a complex material. With the initial researches of Lauterbur[3,4] the direct investigation of carbon compounds by means of the natural abundance of carbon-13, 1.108%, can be utilized to obtain spectra of compounds. The C^{13} spectra of increasing numbers of compounds are being investigated and already have shown the applicability of the method.[3–11]

All investigations of carbon-13 in natural abundance are based on the assumption that the distribution is random and that no isotope effect has occurred in the formation of the substance. The degree of validity of this assumption is not known; the carbon-13 technique may eventually become a powerful tool, complementary with mass spectrometry, for investigating possible isotope effects in the formations of complex molecules in nature.

The investigation of coal derivatives by utilization of the C^{13} nuclear magnetic resonance is being pursued in an effort to obtain direct information on the carbon skeleton of coal derivatives. The technique is difficult because of sensitivity limitations. Successful application of the C^{13} nuclear magnetic resonance technique to coal derivatives requires a preliminary study of the applicability of the method to pure compounds. The method is of the greatest potential value in the detection of carbon atoms that are completely substituted and have no hydrogen atoms. These carbon atoms cannot be investigated directly by such methods as infrared and proton magnetic resonance spectrometry. Groups of compounds that we have investigated in that category are: (1) hydrocarbons; olefins, dienes, allenes, acetylenes and aromatics; (2) non-hydrocarbons: tertiary butyl derivatives, carbonyls, ethers, halides, etc. The work on the hydrocarbons is described in the present article.

Quantitative techniques which have been worked out successfully for proton resonance are not applicable to C^{13} spectra. Very little quantitative work in this field has yet been done; Lauterbur has shown that intensities of carbon-13 lines are reasonably close to the predicted values.[5,6]

Experimental

The spectrometer used was a Varian high-resolution n.m.r. apparatus with the V-4311, 15.085 megacycle R.F. unit for carbon-13 work. Rapid-passage dispersion-mode spectra were obtained; experimental conditions were essentially those used by Lauterbur.[3,4] Carbon disulfide (δ_c, 0 p.p.m.) was used as the standard; the substitution method was employed. Chemical shift measurements were reproducible to better than 0.5 p.p.m. Many of the samples used were American Petroleum Institute standard samples. These compounds can be investigated without opening the ampoule, as the diameter of the tube is such that it can be placed directly in the carbon-13 probe.

The sweep rate was 1 gauss per minute. Forward and reverse sweeps were made and line positions and intensities were obtained from averaging the spectra. This technique is necessitated by changes in spectral fine structure with sweep direction. It can be seen in Fig. 1 that the C^{13} spectrum of benzene does not consist of two equally intense lines, but the last resonance encountered produces a line (b) less intense than the first (a). With reversal of the magnet sweep, toward decreasing field, (b) becomes more intense. Averaging the line heights and positions for the sweeps obtained at increasing and decreasing fields is always necessary to obtain the proper intensity ratio. Henceforth the figures will present only the sweep at increasing field; in all cases the reverse sweep has also been run.

The double resonance experiment was performed using the Nuclear Magnetic Resonance Specialties SD-60 spin decoupler.

Identification of Completely Substituted C^{13} Atoms; Differentiation from C^{13} Atoms Undergoing Carbon-Hydrogen Spin Splittings.—In complicated high-resolution nuclear magnetic resonance spectra, it is sometimes difficult to determine whether a resonance line is due to a nucleus in a unique electronic environment or whether the line is a component of a spin-spin multiplet. The usual solution to this problem in H^1 nuclear magnetic resonance is to obtain spectra at two different magnetic fields and radiofrequencies; spin-spin splittings are independent of the applied magnetic field, whereas chemical shifts are not. A simpler solution for C^{13} n.m.r. involves the study of spectra to determine whether relative line intensities change with direction of the sweep, as in Fig. 1, or remain constant. For example, in the spectrum of hexachloro-1,3-butadiene, two lines are observed in the olefinic region. The intensity ratio of these lines is the same for both increasing and decreasing field sweeps; the lines are due to two different olefinic carbons that are not identically shielded and do not represent a spin-spin multiplet.

This technique has also been used to make C^{13} line assignments in the spectra of monosubstituted benzenes. The spectrum of

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(3) P. C. Lauterbur, *J. Chem. Phys.*, **26**, 217 (1957).

(4) P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, **70**, 841 (1958).

(5) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).

(6) P. C. Lauterbur, *ibid.*, **83**, 1846 (1961).

(7) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

(8) H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 731 (1961).

(9) C. H. Holm, *ibid.*, **26**, 707 (1957).

(10) P. C. Lauterbur, "Determination of Organic Structures," Vol. II, ed. F. C. Nachod and W. D. Phillips, Academic Press, Inc., New York, N. Y., 1962, Chapter 7.

(11) R. A. Friedel and H. L. Retcofsky, paper presented at Symposium on Nuclear Magnetic Resonance Spectroscopy, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 5-9, 1962.

TABLE I
CHEMICAL SHIFTS OF OLEFINIC CARBONS

Terminal olefins			Internal olefins		Branched term. olefins			Branched inter. olefin		
	δ_c, p.p.m.			δ_c, p.p.m.		δ_c, p.p.m.			δ_c, p.p.m.	
Compound	$=CH_2$	$\overset{H}{=C-}$	Compound	$\overset{H}{=C-}$	Compound	$=CH_2$	$\overset{\vert}{=C-}$	Compound	$\overset{H}{=C-}$	$\overset{\vert}{=C-}$
$\mathrm{CCCC{=}C}$	79.3	55.2	$\mathrm{CCC{=}CCC}$ (*cis*)	62.5	$\mathrm{CC\overset{C}{C}{=}C}$	85.1	46.4	$\mathrm{C\overset{C}{C}{=}CC}$	74.9	62.4
$\mathrm{CCCCC{=}C}$	79.3	55.0	$\mathrm{CCC{=}CCC}$ (*trans*)	62.4	$\mathrm{CCC\overset{C}{C}{=}C}$	83.9	49.2	$\mathrm{CCC{=}\overset{C}{C}C}$	67.1	62.7
$\mathrm{C\overset{C}{C}CC{=}C}$	77.9	55.8	$\mathrm{CCCC{=}CC}$ (*cis*)	63.0 69.8	$\mathrm{CC\overset{\overset{C}{C}}{C}{=}C}$	87.3	41.1	$\mathrm{CC\overset{C}{C}{=}CC}$ (*cis*)	76.8	56.4
$\mathrm{CC\overset{C}{C}C{=}C}$	80.8	48.8	$\mathrm{CCC{=}CC}$	60.4 70.0				$\mathrm{CC\overset{C}{C}{=}CC}$ (*trans*)	75.4	57.1
$\mathrm{CC\overset{\overset{C}{C}}{C}C{=}C}$	78.7	51.2	$\mathrm{C\overset{C}{C}C{=}CC}$ (*cis*)	54.9 71.9				$\mathrm{CC\overset{\overset{C}{C}}{C}{=}CC}$	76.9	49.9
$\mathrm{C\overset{C}{\underset{C}{C}}C{=}C}$	84.4	44.4	$\mathrm{C\overset{C}{\underset{C}{C}}C{=}CC}$ (*trans*)	50.8 74.2				$\mathrm{CCC\overset{C}{C}{=}\overset{C}{C}C}$		65.6 69.6
								$\mathrm{CCCC{=}\overset{C}{C}C}$	67.4	62.6

the aromatic carbon atoms in isopropylbenzene consists of five lines, two pairs of which reverse their intensities upon reversal of sweep. It can easily be concluded that the single line that remains constant in intensity is due to the completely substituted carbon atom. The other lines can be assigned to the other five aromatic carbons.

Results and Discussion

Olefins.—The investigation of olefins is of considerable interest because of the difficulties encountered in studying highly substituted olefin structures by other methods. The infrared determination of olefinic groups is quite successful for terminal olefins and for unsubstituted internal olefins. However, in the case of internal olefin groups with one substituent, the infrared absorption becomes rather weak and the wave length position varies. Absorption depends essentially on the protons present, and there is only one proton on one of the double bond carbon atoms. For the disubstituted, *i.e*, completely substituted, internal olefins, there are no protons remaining on the carbon atoms and accordingly there is no possibility of a characteristic infrared band due to hydrogen vibrations.

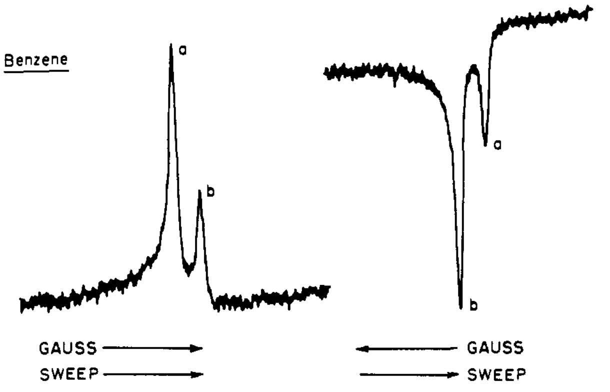

Fig. 1.—C^{13} n.m.r. spectrum of benzene, forward and reverse magnet sweeps.

Carbon-13 spectra of olefins have been investigated briefly by Holm,[9] who showed that olefins and aromatics absorb in the same general region. As shown in the present work it is possible to define the specific regions of absorption for various olefinic carbon atoms and substituents.

Representative spectra of five types of olefins are given in Fig. 2; chemical shifts appear in Table I. One sample, pentene-2, was a mixture of the *cis* and *trans* isomers. The olefinic carbons produce chemical shifts downfield from the chemical-shift positions for saturated carbon atoms. This is entirely analogous to the case of proton n.m.r. spectra. The fine structure in C^{13} spectra is predictable from the splitting rule which states that the number of fine-structure components is given by the quantity $(2NI + 1)$, where N is the number of spinning nuclei bonded to the C^{13} atom and I is the spin value of the substituent nuclei.

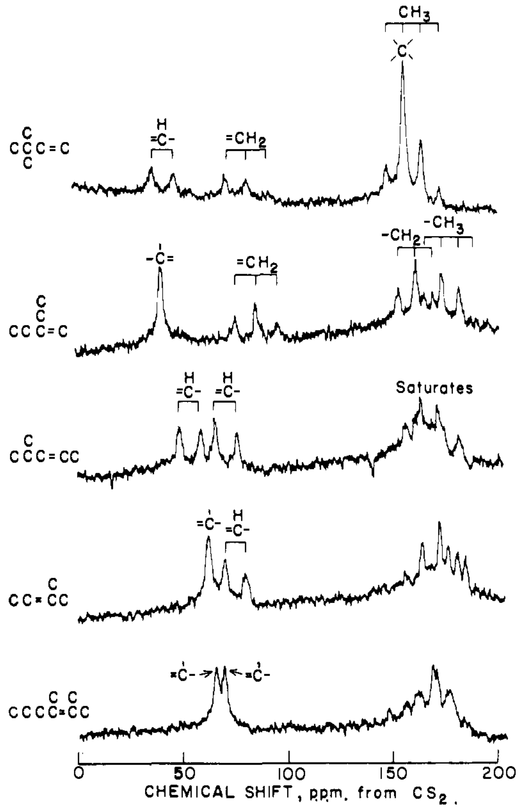

Fig. 2.—C^{13} n.m.r. spectra of olefins.

Terminal olefins produce the predicted fine structure, a doublet and a triplet, for the two olefinic carbon atoms that undergo spin–spin interaction with one and two protons, respectively (Fig. 2, the spectrum of 3,3-di-

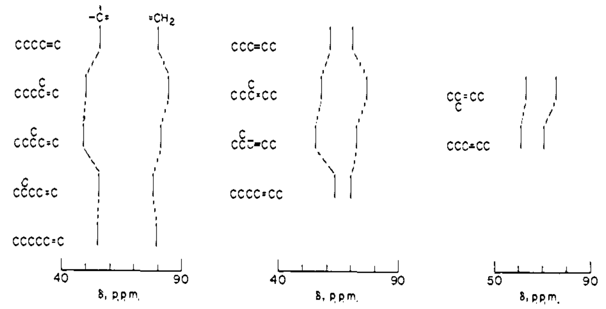

Fig. 3.—Effect of methyl substitution on C^{13} chemical shifts of olefinic carbon atoms. (For internal olefins, high field line is assigned to β-C.)

methyl-1-butene). Branched terminal olefins have two protons on the terminal olefinic carbons. Fine structure results from the interaction of the two protons with that carbon, producing a triplet (Fig. 2, 2-ethyl-1-butene); also near the position of the triplet is the single line due to the substituted carbon atom.

Ordinary unsubstituted internal olefins will consist essentially of two doublets for the two olefinic carbon atoms, each having one hydrogen (Fig. 2, 4-methyl-2-pentene). For 2-pentene two of the components are superposed. Intensity measurements can detect such superposition.

Monosubstituted internal olefins have only one hydrogen on one of the carbon atoms, resulting in a doublet. The completely substituted carbon atom will produce a singlet (Fig. 2, 2-methyl-2-butene). Again, intensity studies enable the correct assignment of superposed lines.

Completely substituted olefins having no hydrogens on the olefinic carbons may be expected to produce two singlets in the olefin region. Unsymmetrical molecules, such as 2,3-dimethyl-2-hexene, produce two singlets that are split by a small amount. As in the foregoing, a study of intensities from upfield and downfield magnet sweeps established that these two peaks are assignable to two completely substituted carbon atoms, rather than to a spin–spin interaction. The spectrum of a similar molecule, 2,3-dimethyl-2-butene, which is an olefin having complete symmetry about the olefinic bond, shows two equivalent carbon atoms in the bond. These carbons produce singlets that are superposed.

Branching Effects in Olefins.—The effect of branching on the olefinic carbon atoms of a terminal olefin, 1-pentene, is shown in Fig. 3. The substitution of a methyl group on the second carbon atom of the double bond produces a divergence of the peaks; the line spectra presented in this figure are the centers of the fine-structure patterns for the indicated carbon atoms. Further, column 1 shows that slightly less divergence is produced by substitution of a methyl group on the carbon atom α to the terminal olefin group. If a methyl group is substituted on the fourth carbon atom, that is, β to the double bond, the spectrum reverts to that of the original unsubstituted compound. Also, if substitution occurs beyond the β-carbon atom, the spectrum is that of the unsubstituted olefin. Thus, substitution on the olefinic group itself or on the carbon atom α to the olefinic group produces a significant effect on the spectrum; substitution at positions farther away has little or no effect. The same behavior is found for internal olefins (Fig. 3, columns 2 and 3).

The magnitude and direction of these substituent effects on olefinic carbon resonances appear to be strongly dependent upon the number and types of bonds through which they are transmitted. Effects transmitted through a single bond to an olefinic carbon atom produce downfield shifts; effects transmitted through a double bond produce upfield shifts. Both effects are small when transmitted through three single bonds or three single and a double bond. These results are summarized (the number of examples used is indicated in parentheses):

Structural change		Change in chemical shift, Δδ in p.p.m. C*	C†
—C*═C†—H (int.) → —C*═C†—CH_3 (int.)	(4)	4.4 to 6.8	−3.3 to − 7.3
—C*═C†—H (term). → —C*═C†—CH_3 (int.)	(3)	6.4 to 8.8	−9.5 to −10.4
—C*═C†—CH → —C*═C†—C—CH_3	(5)	0.1 to 2.2	−5.3 to − 7.8
—C*═C†—C—CH → —C*═C†—C—C—CH_3	(3)	−0.1 to −2.1	0.3 to 2.8

Further effects of branching on the carbon atom alpha to the olefin group are observed if two substituents are present. Figure 4 shows that a methyl substituent on the α-carbon produces a divergence of the olefin absorption. Two methyl substituents on the α-carbon (*tert*-butyl group) produce still greater divergence.

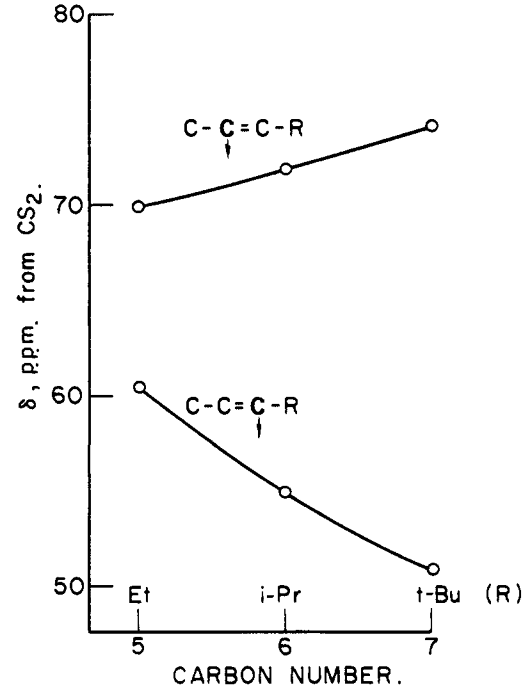

Fig. 4.—C^{13} n.m.r. chemical shifts of 2-pentene and its methyl derivatives.

Dienes.—The spectra of the olefinic carbons of terminal dienes are identical with the spectra of terminal olefins. Figure 5 shows the spectra of three dienes: 1,3-butadiene, 1,4-pentadiene and 1,5-hexadiene. Chemical shifts are presented in Table II. One of

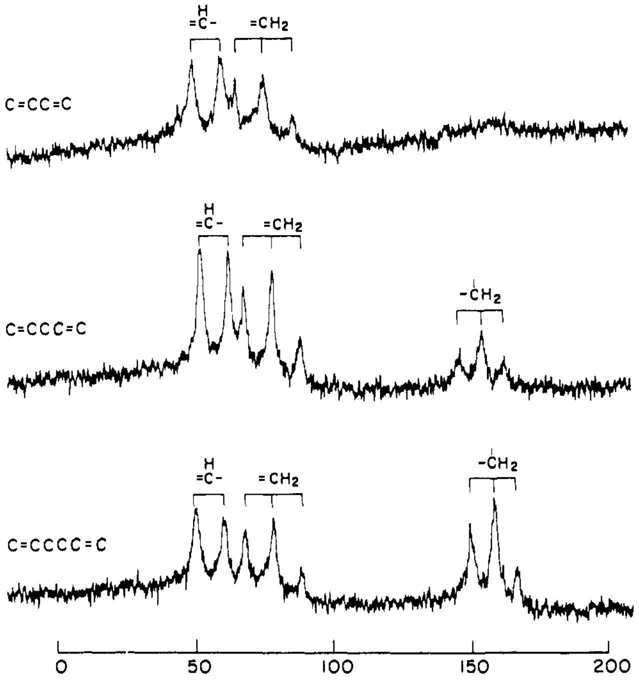

Fig. 5.—C^{13} n.m.r. spectra of dienes containing conjugated or isolated double bonds.

these, butadiene, is a conjugated diene. The olefinic peaks are practically identical in the presence or absence of conjugation; in aromatic systems also conjugation has no effect.[5] In other spectral methods there is usually a tremendous difference between the spectra of conjugated and unconjugated systems.

TABLE II

CHEMICAL SHIFTS OF DIENES, ALLENES, ACETYLENES AND AROMATICS

Dienes	δ_c, p.p.m. =CH₂	δ_c, p.p.m. H =C—	δ_c, p.p.m. =C—	Aromatics	δ_c, p.p.m. C—
C=CC=C	76.2	55.6		C_6H_6	64.9
C=CCC=C	77.8	56.4		C_6H_5C	56.3
C=CCCC=C	78.7	55.5		C_6H_5CC	49.6
CC C=CC=C	81.2		50.4	C C_6H_5CC	45.7
C C C=CCCC=C	82.7		48.3	C C_6H_5CC C	42.2

Allenes	=CH₂	H =C—	=C=	Acetylenes	≡CH	≡C—
C=C=CC	119.6	109.3	−16.7	C≡CCC	125.5	107.8
C=C=CCC	118.4	102.0	−15.2	CC≡CC		118.9
CC=C=CC		108.3	−13.4	C_6H_5C≡C	115.2	108.9

The diverging effect of methyl substitution on the second carbon atom of terminal olefins (Fig. 3) is also observed in the spectra of both conjugated and unconjugated dienes (Fig. 6).

Figure 7 presents spectra of three allenes. The C^{13} spectrum of an allene when compared with that of a diene containing conjugated or isolated double bonds reveals spectral differences of a much greater magnitude than the differences found in other spectral methods. The olefinic peaks for 1,3-butadiene extend over a chemical shift range of about 40 p.p.m., but in the 1,2-butadiene the 1- and 3-carbons of the cumulative olefinic structure extend over a range from 100 to 125 p.p.m., and the middle carbon atom is shifted all the way to $\delta_C = -15$ p.p.m. The total spread for the allenic carbon atoms is 140 p.p.m. With the exception of carbonyl groups and CS_2, there are as yet no known structures having carbon atoms that will absorb in the same region as the center allenic carbon atom. Obviously C^{13} n.m.r. can be an important tool for the investigation of molecular structures of this type. The method is complementary with other spectral methods.

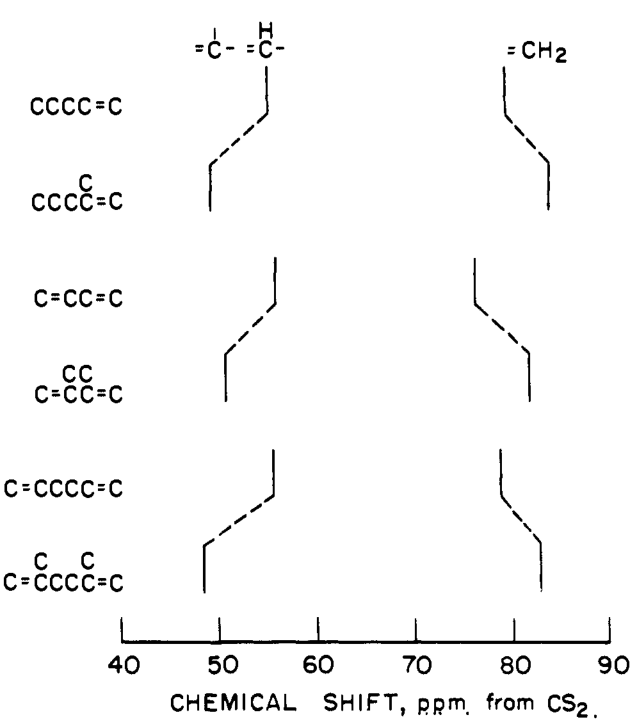

Fig. 6.—Effect of methyl substitution on C^{13} chemical shifts of olefins.

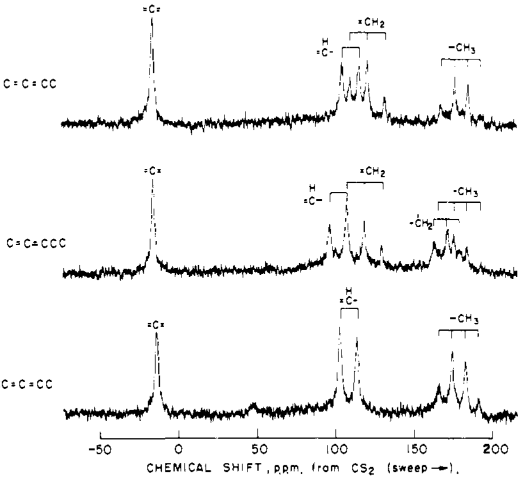

Fig. 7.—C^{13} n.m.r. spectra of dienes with cumulative double bonds (allenes).

Figure 7 also indicates allenic structures with various substituents. The expected changes in fine structure are observed. Chemical shifts for three allenes are given in Table II. Substituent effects summarized below are similar to those in monoölefins, but additional information was obtained on effects transmitted through more than one multiple bond:

Structural change	Change in chemical shift, Δδ in p.p.m. C*	C†	C‡
C—C‡=C*=C† → C—C‡=C*=C†—C	3.3	−11.3	−1.0
C‡=C*=C†—C → C‡=C*=C†—C—C	1.5	− 7.3	−1.2

Small downfield shifts are observed when the substitution effect of a methyl group for a hydrogen atom, or an ethyl group for a methyl group, is transmitted through two double bonds. Methyl groups in these

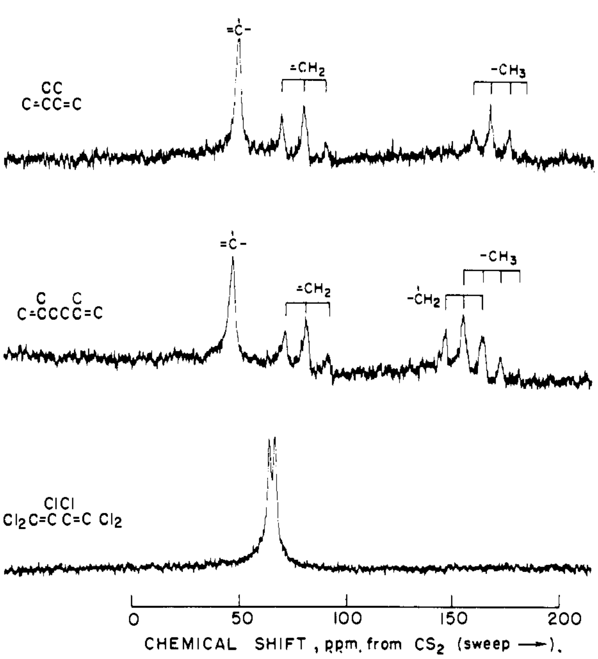

Fig. 8.—C^{13} n.m.r. spectra of substituted dienes.

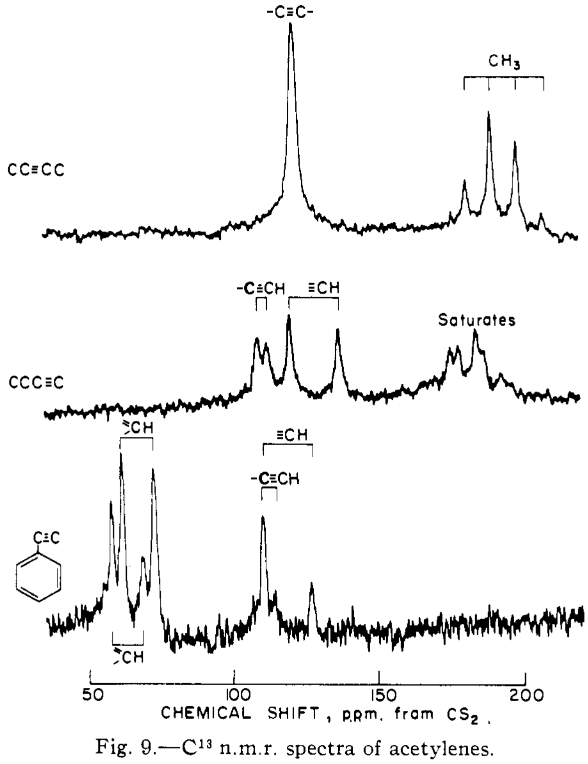

Fig. 9.—C^{13} n.m.r. spectra of acetylenes.

compounds have their shifts at about 179 p.p.m. whether or not they are bonded to an olefinic carbon atom.

In Fig. 8 spectra of substituted dienes with two terminal olefinic bonds are shown. The first two are substituted on both internal olefinic carbon atoms. One is conjugated, the other is not; as indicated before, the presence or absence of conjugation has no apparent effect on the C^{13} spectrum of the olefin carbons. The last spectrum is that of a completely substituted compound. The substitution of Cl for H in this molecule removes all fine-structure splitting. The center of absorption for the olefinic carbons is nearly identical with that for the hydrogen-containing compound, 1,3-butadiene. This is consistent with the small shielding effect of chlorine reported for chlorobenzene.[8]

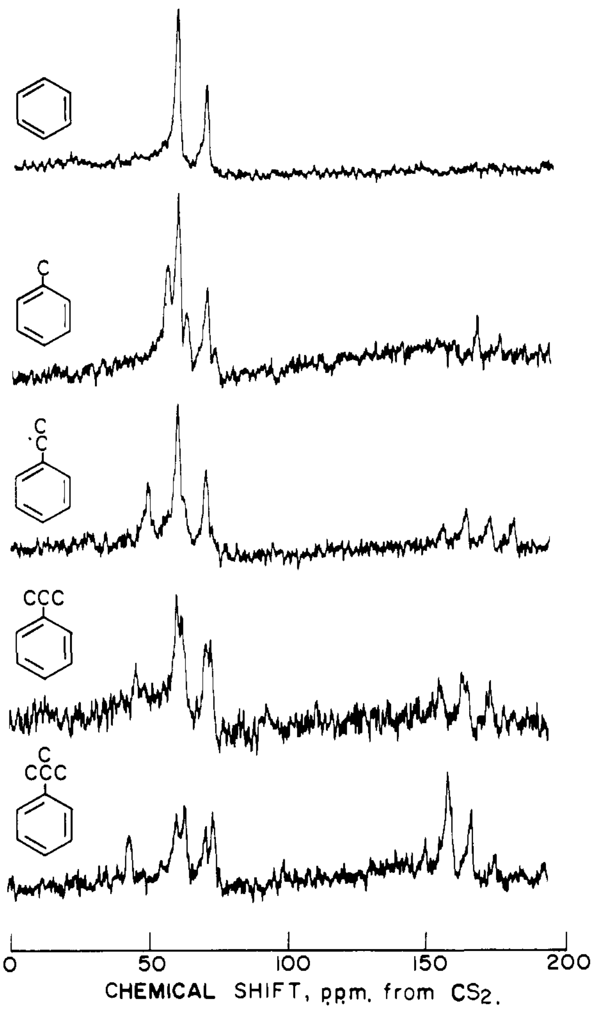

Fig. 10.—C^{13} n.m.r. spectra of aromatic compounds.

Acetylenes.—The spectra of acetylenes are of interest in both H^1 and C^{13} n.m.r. In the early development of H^1 n.m.r. it was expected that the chemical shift position for acetylenes would be at low field and would follow the relationship: alkyl–olefinic–acetylenic protons. But, contrary to this prediction, the acetylene chemical shift came in between the alkyl and olefinic proton shifts (Table II). This position was subsequently explained by Pople[12] on the basis of paramagnetic and diamagnetic circulations in unsaturated systems. It appears that a similar relationship exists in the case of C^{13} n.m.r. spectra of acetylenes (Fig. 9); the acetylenic carbon atoms (~ 115 p.p.m.) lie between the positions for olefinic (~ 65 p.p.m.) and alkyl carbons (~ 175 p.p.m.). In fact, the chemical-shift position for acetylenes is found to be very nearly the same as that of the two terminal olefinic carbon atoms in allenes. This is expected on the basis of the high degree of unsaturation of allenes and acetylenes, and the similar electronic shielding that results. Further, it is interesting to note that the vibrational frequencies in the infrared spectrum for these two classes of compounds are also similar.

Fine structure resulting from distant coupling of C^{13} and H^1 has been observed in C^{13} spectra of acetylenes. Coupling of the proton on the first acetylenic carbon atom, 1-butyne, with the second carbon atom, —C≡CH, has been observed (Fig. 9). The coupling constant obtained for methylacetylene from H^1 n.m.r. data was

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(12) 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.

found to be 50.8 c.p.s.,[13] in close agreement with our value for ethylacetylene from C^{13} spectra of 47 c.p.s. Lauterbur has observed this coupling in other acetylenes and in acetaldehyde. It is not observed in alkanes, olefins, allenes or aromatics under present instrumental conditions. The same coupling can be discerned in the spectrum of phenylacetylene.

Substituent effects in the C^{13} spectra of acetylenes cannot be evaluated from these data; however, Lauterbur has studied the effect in triply bonded alcohols.[10] The internal acetylenic carbon in 2-methyl-3-butynyl-2-ol has its resonance 6.5 p.p.m. lower than that in propargyl alcohol or about −3.2 p.p.m. per methyl group, whereas the effect on the terminal acetylenic carbon resonance is about +2 p.p.m. It can be concluded that alkyl substituent effects in acetylenes are of the same sign as the corresponding effects in monoölefins, but that they are somewhat smaller in magnitude. It is interesting to note that the methyl resonance in dimethylacetylene is found at higher field than the corresponding shift in both toluene and 2,3-pentadiene.

Aromatics.—Benzenoid hydrocarbons have been extensively studied by Lauterbur[5] and by Spiesecke and Schneider.[8] In the present work the C^{13} spectra of monosubstituted benzenes have been investigated in order to determine the effect of branching in the aliphatic chain (Table II). The spectra shown in Fig. 10, benzene to *tert*-butylbenzene, illustrate a definite effect of branching on the chemical shift of the substituted carbon atom in the benzene ring. The singlet from this carbon atom appears in the toluene spectrum at a chemical-shift value lower than that of benzene. In ethylbenzene the chemical shift decreases further; for *n*-propylbenzene and *n*-butylbenzene (not shown) the relative positions of these lines are the same. For isopropylbenzene, however, the chemical shift decreases further, and in *tert*-butylbenzene it decreases still more. The alkyl absorption lines follow somewhat the same trend with increased branching of the substituent group.

The absorption lines for the other aromatic carbon atoms also undergo appreciable changes as a result of the branching of the substituent. In the spectrum of toluene the two lines corresponding to the doublet in the benzene spectrum are assignable to the absorption of *o*- and *m*-carbons. The weak doublet at higher chemical shifts is assignable to the *p*-carbon.[8] For ethylbenzene (and for *n*-propyl and *n*-butylbenzene) the *para* peaks move closer to the respective components of the *ortho–meta* doublet. As branching increases, in isopropylbenzene, the *para* peaks have shifted farther into, or past, the *ortho–meta* peaks. In *tert*-butylbenzene the apparent shift is even greater. It is not possible as yet to make definite assignments for isopropyl and *tert*-butylbenzene, as the *o*- or *m*-carbon absorption may shift due to the branching.

Aliphatic Compounds.—The chemical shifts of fine-structure components have been given for some aliphatic hydrocarbons.[7,10] The shifts that result from various configurations are appreciable. The centers of absorption for tetraethylmethane are spread over a range of chemical shifts of 29.3 p.p.m. Also the symmetrical compound 2,3-dimethylbutane shows a difference of 13.9 p.p.m. for the shifts assignable to CH and CH_3. Two interesting correlations have appeared from the study of alkanes. Table III shows the chemical shifts for highly substituted carbon atoms in $C^*(CH_3)_4$, $C^*H(CH_3)_2(i\text{-}C_3H_7)$ and $C^*(CH_2CH_3)_4$. Small downfield shifts appear to be due to the total number of substituent C-atoms. The chemical shifts of the methyl groups are also given and show sizable shifts in the opposite direction. The divergence of the spectra with size of the molecules may prove to be an important structural parameter.

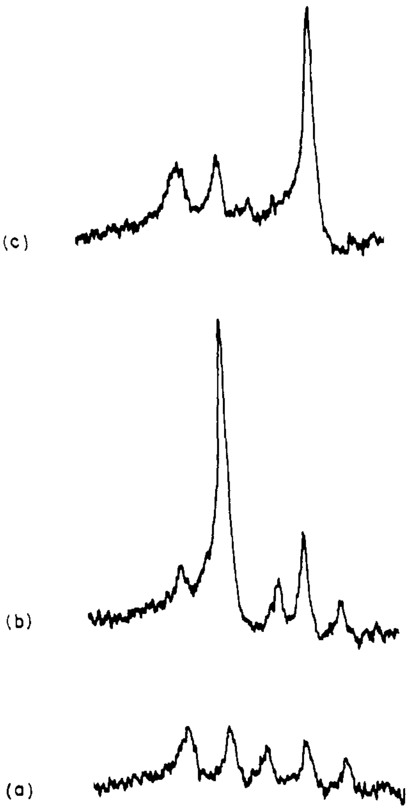

Fig. 11.—C^{13} n.m.r. spectra of 3,3-diethylpentane: (a) normal, (b) methylene protons decoupled, (c) methyl protons decoupled.

TABLE III

CHEMICAL SHIFTS OF HIGHLY SUBSTITUTED C ATOMS, AND OF C IN CH_3 GROUPS

C atom	No. of substd. C atoms	Chem. shift, p.p.m.	C atom	Chem. shift, p.p.m.
$C^*(CH_3)_4$	4	165.9	$C(C^*H_3)_4$	161.8
$C^*H(CH_3)_2(i\text{-}C_3H_7)$	5	159.9	$(CH)_2(C^*H_3)_4$	173.8
$C^*(CH_2CH_3)_4$	8	156.7	$C(CH_2C^*H_3)_4$	186.0

Comparison of Substituent Effects in the C^{13} Spectra of Hydrocarbons.—The effects of substitution on the chemical shifts of olefins, dienes, allenes and aromatic compounds presented here can be very useful in the analysis of C^{13} spectra. Reasonable predictions of C^{13} spectra for compounds not yet studied can be made. A comparison of these effects with corresponding effects on other compounds may provide groundwork for future theoretical explanations.

In the case of alkanes the data in the previous section have shown interesting substituent effects. In general these data follow the results of Spiesecke and Schneider,[7] who found the methyl resonance in propane to be 11.5 p.p.m. below that in ethane. Similarly, Lauterbur[4] reported a decrease of 9–10 p.p.m. in going from ethyl–X to isopropyl–X compounds (X = Cl, Br, I). The corresponding aliphatic alcohols and nitroalkanes produce somewhat smaller downfield shifts.

For olefins and dienes the effect of substituents transmitted through single, double and allenic bonds has also been presented. The effect on triple-bonded carbons has been noted. These data suggest that alkyl substituent effects transmitted through one single bond

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(13) J. N. Shoolery, L. F. Johnson and W. A. Anderson, *J. Mol. Spectry.*, **5**, 110 (1960).

produce downfield shifts that decrease in magnitude as the carbon under study becomes more unsaturated. When transmitted through a double bond the effect is an upfield shift.

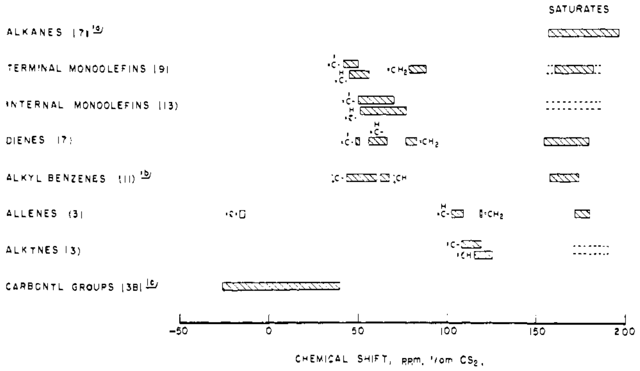

Fig. 12.—Correlation chart for C^{13} n.m.r. spectra; hydrocarbons and carbonyls: ====, range for saturate groups. Partly Bureau of Mines work; contains data from: 1a ref. 7, 8, 1b ref. 5, 1c ref. 10.

In the case of aromatic compounds the chemical shift of the *o*- and *m*-carbons in toluene differs only slightly from the ring carbon resonance in benzene.[6,8] This small effect in the intermediate aromatic system appears reasonable in view of these findings. Effects transmitted through two single bonds are very small, but produce upfield shifts when one of the bonds is multiple or small downfield shifts when both are double.

Spin-Spin Coupling.—Fine structure in n.m.r. spectrometry can be both an advantage and a disadvantage. In the study of complex substances by C^{13} n.m.r. fine structure is sometimes a disadvantage, and it is desirable to utilize a method for collapsing the fine structure. A method of achieving this has been described by Bloom and Shoolery[14]; apparatus for performing such experiments is now available. By means of 60-megacycle radiation of the hydrogens bonded to the carbon atoms, the coupling interaction between them is eliminated while the carbon-13 resonance is being recorded; in this way the fine structure is collapsed. The effect of this is shown (Fig. 11) by comparison of the spectra of $C(CH_2CH_3)_4$ taken under ordinary C^{13} conditions and under spin-decoupling conditions with radiation of the protons at 60 megacycles. The values used in Table II for this compound were obtained by utilizing this technique. For a methyl group producing a quartet with relative intensities of 1:3:3:1 the total absorption will collapse into a single peak with a relative intensity of at least 8. Thus an appreciable gain in sensitivity is achieved. The increased sensitivity and the decrease in spectral complexity will be very useful in the study of complex materials. This technique promises to be particularly helpful in the case of coal spectra in which fine structure is more of a detriment than an advantage. Fine structure is so prolific in coal derivatives that the result is no structure at all; this is similar to the case of mass spectra of complex molecules. If some of the structure can be eliminated (in the case of mass spectrometry the answer was low-ionizing-voltage spectra) then it will be possible to produce informative spectral bands where previously no information was available. It may be possible to find absorption bands in the spectra of coal derivatives where presently, under ordinary conditions, there is only broad diffuse absorption.

Chemical Shift Chart.—A spectra-correlation chart (Fig. 12) summarizes the work described and illustrates the possible application to hydrocarbon structures. For comparison purposes the range of shift data for carbonyl groups is also given.

[14] A. L. Bloom and J. N. Shoolery, *Phys. Rev.*, **97**, 1261 (1955).

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Hammett's Relations in Anionic Copolymerizations

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The absolute rate constants of anionic homo- and copolymerization in THF were determined for the monomers: styrene, α-methylstyrene, *p*-methylstyrene, *p*-methoxystyrene, *p*-*t*-butylstyrene, *p*-fluorostyrene, *p*-chlorostyrene, 4-vinylbiphenyl, *o*-methylstyrene, 2,4-dimethylstyrene and vinylmesitylene. It was shown that the Hammett relation is obeyed by the rate constants of copolymerization of *p*-substituted styrenes with living polystyrene. The respective $\rho = +5.0$, while for the radical polymerization $\rho = 0.5$ and in a coördination polymerization $\rho = -0.95$. The effect of polar factors and steric effects upon the rate constants of these reactions was discussed.

A technique for determining the absolute rate constants of propagation of anionic homo- and copolymerization was described in previous communications from this Laboratory.[1,2] Anionic polymerization, if carried out under suitable conditions, yields living polymers,[3,4] *i.e.*, polymeric species which resume their growth when mixed with additional monomer. The concentration of living ends may be determined by a suitable analytical or spectrophotometric technique and, in a properly conducted experiment, this concentration remains constant during the course of polymerization. Since most of the anionic polymerizations proceed extremely rapidly in tetrahydrofuran, studies of such reactions require special techniques; *e.g.*, the fast flow technique, originally described by Hartridge and Roughton[5] could be adopted for this purpose.[1] The solutions of living polymers and of the investigated monomer are mixed in a suitable chamber, the mixture is then passed through a capillary, and finally the polymerization quenched at the capillary outlet by flowing the reacting solution into wet tetrahydrofuran. In this arrangement the time of polymerization may be varied from 0.05 sec. to about 2 sec. by changing the rate of flow or the volume of the capillary. The concentration of the residual monomer is then determined

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[1] C. Geacintov, J. Smid and M. Szwarc, *J. Am. Chem. Soc.*, **84**, 2508 (1962).

[2] D. N. Bhattacharyya, C. L. Lee, J. Smid and M. Szwarc, *ibid.*, **85**, 533 (1963).

[3] M. Szwarc, M. Levy and R. Milkovich, *ibid.*, **78**, 2656 (1956).

[4] M. Szwarc, *Nature*, **178**, 1168 (1956).

[5] H. Hartridge and F. J. W. Roughton, *Proc. Roy. Soc.* (London), **B104**, 376 (1923).