Carbon-13 Nuclear Magnetic Resonance Spectroscopy. Quantitative Correlations of the Carbon Chemical Shifts of Acyclic Alkenes[1]

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An empirical method whereby the carbon chemical shifts of acyclic alkenes can be calculated is developed. The method is shown to be quite successful in predicting the chemical shift difference in acyclic alkenes. Correlations of substituent parameters of earlier work are discussed.

Carbon-13 nuclear magnetic resonance (cmr) spectroscopy has quickly become an important addition to the armory of structural spectroscopic methods available to the organic chemist. Using spectral accumulation and complete proton decoupling,[3] the measurement of carbon chemical shifts has become relatively routine,[4-8] even for rather large molecules at only moderate concentrations.[9-11] Of course, these measurements require somewhat more sophisticated equipment than does proton magnetic resonance (pmr) spectroscopy, and cmr spectra are often difficult to interpret, as is evidenced by the extensive discussions usually associated with the assignment of peaks.[4-11] In general, the secure assignment of the resonances of any particular compound requires the study of the cmr spectra of closely related compounds containing similarly substituted carbons.

Attempts to overcome the problems of assignments have led to the development of a number of methods, the most important of which involves taking advantage of more or less selective removal of the effects of proton coupling on the carbon resonances. In some cases it has been possible to use highly selective proton decoupling, in which the specific decoupling frequency of each carbon resonance is correlated to the resonance positions of the protons attached to the carbon nucleus.[7-8,12] A number of groups have also devised methods of "off-resonance decoupling," which produce perturbed multiplets which retain some information regarding the number of protons attached directly to the carbon nuclei.[9,13-14] Occasionally, it is possible to examine the cmr spectra in the absence of proton decoupling,[7-8,15-17] but this method is limited to only relatively simple spectra in which there are few peaks in a specific region of interest. The absence of proton decoupling also sacrifices the increased sensitivity due to the positive nuclear Overhauser enhancement,[18] a loss which is important in any but reasonably concentrated solutions. The nuclear Overhauser effect itself is occasionally useful in the assignment of ^{13}C resonances.[19] While it is to be hoped that continued instrumental advances, especially in higher resolution spectrometers and pulse techniques, will soon make interpretable proton-coupled cmr spectra routinely available, it is possible that the additional expense of such equipment will preclude its general availability.

Another method of some potential in assignment of carbon resonances has been explored. Using regression or least-squares analyses, it has been possible to derive systems of substituent parameters for a number of compound types.[4-8,20] The parameters can be used to estimate the chemical shifts of other related carbon nuclei, and such estimations have been useful in the assignments of mono- and oligosaccharides.[8,11] The purpose of the present paper is to discuss the possible extension of this method to alkene hydrocarbons. The large reservoir of published[15-17] chemical shift data for alkene carbons makes this group an especially attractive subject for such studies. Also, the success with which the chemical shifts of alkene protons are predicted by similar methods[21] suggests that analogous regularities in the chemical shifts of alkene carbon nuclei are also possible.

Experimental Section

A. Measurement of Spectra.—Carbon-13 chemical shifts measured in this study were obtained with the Varian digital frequency sweep spectrometer described previously.[3] The chemical shifts were measured relative to internal cyclohexane, a solvent which seems to have only minor solvent effects upon ^{13}C chemical shifts.[22] All chemical shifts were then referenced to external carbon disulfide, using the expression $\delta^{CS_2} = \delta^{C_6H_{12}} + 166.2$ ppm.

B. Referencing.—Since most of the carbon chemical shifts discussed below were taken from various literature sources and since the history of cmr spectroscopy has been plagued by a number of "standard" reference compounds, the following expressions were used to convert all chemical shifts to the external carbon disulfide reference.

$$\delta^{CS_2} = \delta^{1,4\text{-dioxane}} + 126.2 \text{ ppm}$$

$$\delta^{CS_2} = \delta^{C_6H_6} + 64.8 \text{ ppm}$$

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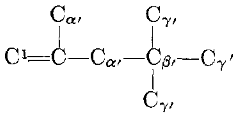
$$C_{\delta}—C_{\gamma}—C_{\beta}—C_{\alpha}—C_{A}=C—C_{\alpha'}—C_{\beta'}—C_{\gamma'}—C_{\delta'}$$

Figure 1a.—Definition of the substituent effects used in the calculation of the chemical shift of C_A.

$$C_{\beta}—C_{\alpha}—C^{3}=C—C_{\alpha'}—C_{\beta'}—C_{\gamma'}$$

Figure 1b.—The substituents of carbon 3 of 3-heptene.



$$\begin{array}{ccccc} & C_{\alpha'} & & C_{\gamma'} & \\ C^{1}= & C & —C_{\alpha'}— & C_{\beta'} & —C_{\gamma'} \\ & & & C_{\gamma'} & \end{array}$$

Figure 1c.—The substituents of carbon 1 of 2,4,4-trimethyl-1-pentene.

C. Least-Squares Solutions.—The least-squares solutions were obtained using an adaptation of LEASQ2[23] written for the CITRAN time-shared computer at the California Institute of Technology. The program computed the least-squares values for the substituent parameters, as well as their uncertainties.[24] The calculated and empirical chemical shifts were then compared and the sum of the squares of the residuals, the standard deviation, and the linear correlation coefficient computed. The last three criteria were used in judging the goodness of fit of the various shift relationships which were investigated. The results of the least-squares analyses were subsequently checked, using a standard subroutine for stepwise multiple regression analysis[25] and an IBM 360/75 computer.

Results and Discussion

A. The Monoenes.—The extant carbon chemical shift data for the monoenes are presented in Table I. It will be noted that for many of the monoenes only the chemical shifts of the unsaturated carbon nuclei are tabulated. The pioneering ^{13}C spectroscopists, limited by their dependence on the rapid-passage instrument and the lack of suitable methods of proton decoupling, were constrained to the study of relatively simple spectra. The alkenic region of the cmr spectra of monoenes satisfied the requirement of simplicity, and the residual proton coupling could be used to advantage in the assignment of resonances.[15-17] The present investigation seeks to generalize our knowledge of the chemical shifts of monoene carbons. We will first consider, however, the chemical shifts of the trigonal carbons.

In describing the chemical shifts of alkene carbons, the substituent effects in Figure 1a were used. It was initially assumed that the chemical shift of C_A would be dependent only upon the number of $\alpha,\beta\ldots\alpha',\beta'\ldots$ carbons in the molecule. Such a definition of substituent effects has analogy in other systems.[4-8] Using this method, the substituent effects experienced by carbon 3 of 3-heptene are represented by $\alpha + \beta + \alpha' + \beta' + \gamma'$; the substituent effects seen by carbon 1 of 2,4,4-trimethyl-1-pentene are $2\alpha' + \beta' + 3\gamma'$ (*cf.* Figures 1b and 1c). Using the chemical shift of ethylene[17] as the standard, these expressions can be used to calculate the chemical shift of any alkene carbon.

Very early in this study it was recognized that alkenes which included cyclic structures fitted more poorly into these correlations. Part of the difficulty arises from the fact that it is difficult to apply the methodology introduced above to cyclic alkenes. The case of cyclobutene will serve as an example. There is some question as to what the chemical shift of the alkene carbons should be considered subject. One could express this chemical shift, for example, in any of the following ways: $\alpha + \beta$; $\alpha + \alpha'$; $\alpha' + \beta'$; $\alpha + \beta + \alpha' + \beta'$. It was found that the last case gave the best fit, but this is essentially counting each nonalkenic carbon twice, a procedure which tends to rankle the conscience. The presently adopted system of defining substituent effects also fails to explain the quite real differences (*cf.* Table I) in the alkene–carbon chemical shifts of the larger cycloalkenes where the aforementioned problem is not expected to be important. Discussion of those alkenes which include cyclic structures is therefore deferred to a later section.

The initial least-squares solutions indicated that the inclusion of the parameters δ and δ' had only a very small effect upon the least-squares solution. As indicated by the example of δ in solution 8 of Table II, these parameters were of smaller magnitude than the uncertainty of the experimental chemical shifts. In most cases, their deletion from the least-squares solutions had a negligible effect upon the standard deviation, and these parameters are therefore deleted from further considerations.

In Table II, a series of solutions for the acyclic monoenes is compared. Solution 1 involves consideration of only α, β, γ, α', β', and γ' substituent effects. While the value of the linear correlation coefficient (R) indicates that the correlation of empirical and calculated values is obviously significant, the standard deviation (σ) seemed rather high. Inspection of the original data indicated that the chemical shifts of trigonal carbons were, to some degree, dependent on the geometrical isomerism of the double bond, and a parameter designed to represent this dependence was sought. The increment "cis" was therefore introduced. This parameter was included once for each cis interaction between alkyl groups attached to the double bond. Hence, it was added once for cis 1,2-disubstituted alkenes, as well as for trisubstituted alkenes. In expressions representing the chemical shifts of the alkene carbons of tetrasubstituted olefins, it was added twice. The simplicity with which this parameter is applied probably precludes its accurate representation of the varying steric and conformational properties of variously substituted alkenes, but, as is seen in Table II, its inclusion results in a small improvement in the standard deviation of the solution.

In earlier studies,[4] it was found necessary to include correction factors to account for nonadditivity of parameters in highly branched systems. Consideration of the results of solution 2, Table II, showed that certain of the parameters defined in Figure 1 were also not properly additive. Thus, the α shifts observed in the monosubstituted alkenes are significantly larger than those observed in the 1,1-disubstituted alkenes. A new parameter, corr α, was accordingly introduced to correct for this nonadditivity. Comparison of solutions 2 and 3 (Table II) shows that the effect of the inclusion of this parameter upon the least-squares fit is quite dramatic. It was further discovered that similar correction increments were necessary for the β and α' shifts (see solutions 4 and 5), while there seemed no

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TABLE I

CARBON CHEMICAL SHIFTS[a] OF SOME ALKENE HYDROCARBONS

Compd	1	2	3	4	5	6	7	8	Other	Ref
Ethylene	70.4									17
A. Monosubstituted Alkenes										
Propene	77.8	57.5								17
1-Butene	80.4	53.5								17
1-Pentene	79.4	55.2								15
1-Hexene	79.3	55.0								15
1-Octene	79.2	54.3	159.3	(164.1)	(164.2)	161.3	170.5	179.5		This work
4-Methyl-1-pentene	77.9	55.2								15
3-Methyl-1-pentene	80.8	48.8								15
3-Ethyl-1-pentene	78.7	51.2								15
3,3-Dimethyl-1-butene	84.4	44.4								15
B. 1,1-Disubstituted Alkenes										
2-Methyl-1-butene	85.1	46.4								15
2-Methyl-1-pentene	83.9	49.2								15
2-Methyl-1-heptene	83.5	47.9	155.3	165.7	161.5	170.6	179.5		2-CH_3, 171.6	This work
2,4,4-Trimethyl-1-pentene	79.3	50.0	141.5	162.1	163.3				2-CH_3, 168.3	This work
2-Ethyl-1-butene	87.3	41.1								15
C. 1,2-Disubstituted Alkenes										
cis-2-Butene	181.6	69.1								This work
cis-2-Pentene	181.4	70.5	61.0	173.2	179.7					This work
cis-4-Methyl-2-pentene		71.9	54.9							15
cis-2-Hexene	181.1	69.7	62.8	164.3	171.1	180.0				This work
cis-3-Hexene			62.5							15
cis-2-Octene	181.0	69.9	62.5	166.4	163.8	161.6	170.6	179.5		This work
cis-3-Octene	179.2	172.8	61.9	64.1	166.4	161.7	170.9	179.6		This work
cis-4-Octene	179.8	170.3	163.9	63.5						This work
trans-2-Butene	176.1	67.7								This work
trans-2-Pentene		70.0	60.4							15
trans-4,4-Dimethyl-2-pentene		74.2	50.8							15
trans-2-Hexene	176.0	68.6	61.9	158.4	170.5	180.0				This work
trans-3-Hexene			62.4							15
trans-2-Octene	175.8	68.8	61.6	160.5	163.7	161.6	170.6	179.5		This work
trans-3-Octene	179.6	167.6	60.9	63.9	160.9	161.2	171.0	179.5		This work
trans-4-Octene	179.9	170.4	158.4	62.9						This work
D. Trisubstituted Alkenes										
2-Methyl-2-butene		62.4	74.9							15
2-Methyl-2-pentene		62.7	67.1							15
cis-3-Methyl-2-pentene		76.8	56.4							15
trans-3-Methyl-2-pentene		75.4	57.1							15
3-Ethyl-2-pentene		76.9	49.9							15
2-Methyl-2-hexene		62.6	67.4							15
cis-3-Methyl-2-hexene	180.5	74.2	57.7	159.8	172.3	179.7			3-CH_3, 170.4	This work
trans-3-Methyl-2-hexene	180.5	74.9	57.8	151.3	172.1	179.9			3-CH_3, 178.3	This work
2-Methyl-2-heptene	176.1 167.9	62.7	68.2	165.4	160.9	170.8	179.5			This work
E. Tetrasubstituted Alkenes										
2,3-Dimethyl-2-butene	174.8	70.9								15
2,3-Dimethyl-2-hexene		69.6	65.6							15
F. Cycloalkenes										
Cyclobutene	56.5		162.3							This work
Cyclopentene	62.9		160.9	170.4						This work
Cyclohexene	66.3		168.0	170.4						This work
Cycloheptene	61.0		164.1	165.7	161.0					This work
cis-Cyclooctene	63.3		167.7	166.7	163.9					This work
trans-Cyclooctene	59.7		158.2	(158.2)	(163.8)					This work
cis-Cyclododecene	61.8		160.9	166.8	(167.4)	168.1	(168.4)			This work
G. Methylenecycloalkanes										
Methylenecyclobutane	43.3	161.4	176.7						CH_2, 88.6	This work
Methylenecyclopentane	40.9	160.4	166.6						CH_2, 88.7	This work
Methylenecyclohexane	44.0	157.5	164.8	166.8					CH_2, 86.6	This work

[a] All chemical shifts were measured relative to external carbon disulfide.

Table II

Substituent Parameters Derived from Various Least-Squares Solutions for All Acyclic Monoenes

Parameter	Solution no.							
	1	2	3	4	5	6	7	8
α (68)[a]	−7.67 ±0.07	−8.11 ±0.10	−10.37 ±0.11	−10.86 ±0.10	−10.62 ±0.08	−10.58 ±0.08	−10.59 ±0.07	−10.57 ±0.08
β (42)	−6.83 ±0.08	−6.65 ±0.08	−5.91 ±0.05	−6.02 ±0.04	−7.18 ±0.08	−7.17 ±0.08	−7.35 ±0.09	−7.15 ±0.08
γ (24)	0.38 ±0.12	0.49 ±0.11	0.79 ±0.05	0.94 ±0.05	1.47 ±0.04	1.45 ±0.04	1.79 ±0.08	1.47 ±0.05
δ (8)								−0.19 ±0.13
α' (68)	6.48 ±0.07	6.03 ±0.10	6.55 ±0.05	7.64 ±0.10	7.90 ±0.08	7.94 ±0.08	7.87 ±0.07	7.94 ±0.08
β' (42)	1.63 ±0.08	1.82 ±0.08	2.22 ±0.04	1.93 ±0.04	1.84 ±0.03	1.64 ±0.08	1.86 ±0.03	1.64 ±0.08
γ' (24)	−1.14 ±0.12	−1.03 ±0.11	−1.29 ±0.06	−1.45 ±0.05	−1.50 ±0.03	−1.41 ±0.04	−1.51 ±0.03	−1.42 ±0.04
Cis (38)		1.13 ±0.20	1.12 ±0.10	1.12 ±0.08	1.12 ±0.06	1.12 ±0.06	1.08 ±0.06	1.11 ±0.06
Corr α (18)			4.56 ±0.25	5.07 ±0.21	4.83 ±0.16	4.76 ±0.17	4.87 ±0.16	4.73 ±0.17
Corr α' (18)				−2.08 ±0.21	−2.51 ±0.16	−2.55 ±0.17	−2.48 ±0.16	−2.54 ±0.17
Corr β (7)					2.27 ±0.19	2.23 ±0.19	2.53 ±0.21	2.19 ±0.20
Corr β' (7)						0.39 ±0.19		0.39 ±0.19
Corr γ (3)							−0.85 ±0.28	
σ[b]	1.66	1.60	1.11	0.99	0.850	0.851	0.841	0.855
r[c]	209.74	193.05	91.65	71.82	52.02	51.43	50.16	51.23
R[d]	0.9883	0.9892	0.9949	0.9960	0.9971	0.9971	0.9972	0.9971

[a] Numbers in parentheses denote the number of occurrences of that parameter. [b] The standard deviation. [c] The sum of the squares of the residuals. [d] The linear correlation coefficient.

necessity to include a correction increment for the β' shift (solution 6). In solution 7, there is some suggestion that a correction increment for γ would be worthwhile. However, the low occurrence of this "corr γ" parameter does not presently justify its inclusion.

It is probable that solutions 5 and 7 are the best obtainable for the present data, using the method described above. In some studies of this type,[4,21] it was found that treating the standard or base chemical shift (in this case, that of ethylene) as a variable unknown led to solutions which gave better overall correlations between calculated and empirical chemical shifts. In the present case, however, the chemical shift of ethylene calculated by the least-squares method was indistinguishable from the measured value.[17] In any event, the standard deviation (0.85 ppm) for the fit of 80 chemical shifts does not much exceed the experimental uncertainty (±0.5 ppm) in the rapid passage data.[15] The literature reports only one such fit (to alkane ^{13}C resonances) with a lower standard deviation, and in that case all the chemical shifts considered were measured on the same machine using high-resolution techniques.[4]

At the inception of this research, it was thought probable that it would be of interest to divide the monoene data of Table I into the subgroups A, B, C, D, and E for separate least-squares solutions. If any substituent effects were dependent on structural or conformational effects, then it seemed likely that these effects would be heavily dependent upon the way in which the alkene group was substituted. Unfortunately, there are problems involved in such subdivision. In the case of the tetrasubstituted alkenes (Table I, E), there were insufficient data for a separate least-squares fit. Only ten chemical shifts are available in the 1,1-disubstituted alkenes (Table I, B), thereby diminishing the degrees of freedom to a rather low level. In all cases, the subdivision led to least-squares solutions based on smaller reservoirs of data, thus impairing the credibility of the result.

There were also further problems. The consideration of subgroups of similar compounds imposes greater symmetry upon the matrices used to obtain the least-squares solutions. Therefore, it was necessary to guard against the possibility of the determinant going to zero when the inversion of the normal matrix was attempted. Thus, the 1,2-disubstituted alkene chemical shift expressions all include one occurrence each of the α and α' effects. In such a situation, these two parameters can take any value, so long as their sum ($\alpha + \alpha'$) is appropriate. In other cases it was found that the correction increments occurred in repetitive combinations with the parent parameter, and it was therefore not possible to include the correction parameters in some fits. The methodology above therefore required some alterations before least-squares solutions for these subgroups could be obtained.

In Table III are compared representative solutions of the subgroups. In this comparison are selected solutions which are similar in number and identity of parameters, and in some cases the results in Table III do not represent the optimal solution for a subgroup (*vide infra*). It is seen from Table III that the solutions for the subgroups are all better than the analogous solution

Table III

Substituent Parameters Derived from Least-Squares Solutions for the Alkene Subgroups

	Monoene group				
Parameter	1 A	1 B	1 C	1 D	Solution 1[a]
α	-12.63 ± 0.18	-8.75 ± 0.43	[b]	-6.35 ± 0.07	-8.11 ± 0.10
β	-4.55 ± 0.06	-5.90 ± 0.81	-6.50 ± 0.05	-6.47 ± 0.22	-6.65 ± 0.08
γ	1.18 ± 0.07	1.10 ± 0.11	0.72 ± 0.10	0.66 ± 0.29	0.44 ± 0.11
α'	8.03 ± 0.18	6.59 ± 0.43		5.14 ± 0.07	6.03 ± 0.10
β'	1.95 ± 0.06	1.86 ± 0.81	1.82 ± 0.05	1.22 ± 0.22	1.82 ± 0.08
γ'	-1.41 ± 0.07	-1.99 ± 0.11	-0.93 ± 0.10	-1.20 ± 0.29	-1.03 ± 0.11
Cis			0.45 ± 0.08		1.13 ± 0.20
σ	0.579	0.716	0.794	0.811	1.60
r	4.02	2.05	16.379	7.90	193.05
R	0.9994	0.9997	0.9889	0.9966	0.9892

[a] See Table II. [b] $(\alpha + \alpha') = 2.61 \pm 0.12$.

for all acyclic monoenes. Furthermore, there are significant changes in the values of the parameters. The changes in the values of α and α' can be reasonably explained in terms of nonadditivity. Thus, α is largest when it occurs only once in the expression of chemical shifts. In group 1 B, wherein α always occurs twice, its value is smaller. It is interesting to compare the value of 2α (-17.50 ppm) from the solution for group 1 B with the value of 2α + corr α (-17.61 ppm) taken from solution 5 of Table II. The close correspondence of these two values gives further evidence of the relevance of the correction increments. There do not seem to be nonadditivities in the γ, β', and γ' parameters, and the variations observed in these increments in Table II will receive later comment.

For subgroups 1 B and 1 D, the solutions offered in Table III are the best which could be obtained. For the 1,1-disubstituted alkenes (1 B), the data were too few to allow inclusion of any other parameters into the least-squares solution. In the case of the trisubstituted alkenes (1 D), efforts were made to differentiate between the substituent parameters for the mono- and disubstituted alkene carbons. Unfortunately, none of the methods attempted had a significant effect on the standard deviation of the fit. Possibly the gathering of more data for this subgroup will lead to improved methods of estimating the chemical shifts of the alkene carbons.

The monosubstituted alkenes (1 A) solution can be improved somewhat by inclusion of a correction increment for the β' shift ($\sigma = 0.536$, $r = 4.02$, $R = 0.9995$). This parameter (*i.e.*, corr β') occurs but four times, however, and its magnitude (-1.37 ppm) may be attributable to experimental error. Introduction of a corr β parameter has a negligible effect on the solution.

The solution for group 1 C (the 1,2-disubstituted alkenes) is dramatically improved by inclusion of a corr β parameter (*cf.* Table IV), although its occurrence is low (2). The residual error in this solution is furthermore attributable to the inadequacy of the cis parameter, as is shown when the cis and trans 1,2-disubstituted alkenes are separately solved (Table IV). The excellent fit of these data may be due to the fact that the data for this subgroup are mostly (70%) derived from a single high-resolution instrument. It is noted from Table IV that there are significant differences in the substituent effects observed for cis and trans 1,2-disubstituted alkenes. This is an entirely reasonable result, because bond angles and conformations of side chains would be expected to be quite different in these cases. This matter will receive further comment below.

Table IV

Substituent Parameters for the 1,2-Disubstituted Alkenes

	All 1,2-disubstituted alkenes	Cis 1,2-disubstituted alkenes	Trans 1,2-disubstituted alkenes
$\alpha + \alpha'$	-2.36 ± 0.03	-1.348 ± 0.003	-2.566 ± 0.004
β	-7.78 ± 0.03	-7.992 ± 0.003	-7.428 ± 0.005
γ	1.65 ± 0.03	1.615 ± 0.004	1.507 ± 0.006
β'	1.92 ± 0.01	1.431 ± 0.002	2.161 ± 0.002
γ'	-0.92 ± 0.02	-0.634 ± 0.003	-1.119 ± 0.004
Cis	2.82 ± 0.02		
σ	0.360	0.091	0.110
r	3.234	0.083	0.121
R	0.99779	0.99985	0.99986

The data in Tables II, III, and IV may be used to predict, usually to within 1 ppm, the chemical shifts of the trigonal carbons of any acyclic monoene. It would also be of use, of course, to be able to estimate the chemical shifts of tetrahedral carbon in these compounds. One possible approach, and one which has been successful in other compound types,[6] is to compare the cmr spectra of the saturated carbons with those of the analogous alkanes. Because the carbon spectra of the latter compounds may be calculated,[4] the generalizations resulting from such comparisons provide a means of estimating the chemical shifts of the tetrahedral carbons of monoenes.

In Table V, the chemical shifts of the saturated carbons of those monoenes for which complete cmr spectra are available are referenced to the analogous carbon of the parent alkane. In most cases the spectra of the alkanes were available from previous work[4] or were measured in these laboratories. Calculated spectra[4] were used in those cases in which the parent alkane had not been studied. Examination shows that the chemical shifts of the δ, ϵ, and ζ carbons are nearly unchanged from their positions in the parent alkanes. The changes at the β carbon are generally larger, but there seems no discernible regularity in their signs or magnitudes. With the present data, we conclude that the chemical shift of the β carbon in monoenes is not significantly different from that of the analogous carbon in the parent alkane.

At the γ position, the chemical shift change associated with the introduction of the double bond is also small (*ca.* 0.5 ppm). In this case, however, the direction of the shift is invariably upfield. This generality

TABLE V

SHIFTS OF TETRAHEDRAL CARBONS MEASURED RELATIVE TO THE SAME CARBONS IN THE ANALOGOUS ALKANE

Compd	α	β	γ	δ	ε	ζ	Other
		A. Monosubstituted Alkenes					
1-Octene	−1.8	+0.3	+0.4	+0.2	0	0	
		B. 1,1-Disubstituted Alkenes					
2,4,4-Trimethyl-1-pentene	+2.4	+0.5	+0.8				2-CH_3, +1.1
2-Methyl-1-heptene[a]	+1.0	−0.8	+0.6	+0.2	−0.1		2-CH_3, +0.3
		C. 1,2-Disubstituted Alkenes					
cis-2-Butene	+1.3						
cis-2-Pentene	CH_3, +1.6 CH_2, +2.3	−0.1					
cis-2-Hexene	CH_3, +1.5 CH_2, +2.8	+0.5	+0.4				
cis-2-Octene	CH_3, +1.5 CH_2, +2.6	0	+0.5	+0.1	0		
cis-3-Octene	+2.3, +2.6	−0.3, 0	+0.4	+0.1			
cis-4-Octene	+2.8	−0.2	+0.3				
trans-2-Butene	−4.2						
trans-2-Hexene	CH_3, −3.6 CH_2, −3.1	−0.1	+0.4				
trans-2-Octene	CH_3, −3.7 CH_2, −3.3	−0.1	+0.5	+0.1	0		
trans-3-Octene	−2.9, −2.9	+0.1, +0.1	+0.5	0			
trans-4-Octene	−2.7	−0.1	+0.4				
		D. Trisubstituted Alkenes					
cis-3-Methyl-2-hexene[a]	C-1, −1.6 C-4, +5.2	−0.8	+0.4				3-CH_3, −3.5
trans-3-Methyl-2-hexene[a]	C-1, −1.6 C-4, −3.3	−1.0	+0.6				3-CH_3, +4.4
2-Methyl-2-heptene[a]	C-1, −3.4 C-4, −1.1	0	+0.4	−0.1			2-CH_3, +4.8
		E. Tetrasubstituted Alkene					
2,3-Dimethyl-2-butene	+0.6						

[a] Carbon-13 chemical shifts for analogous alkanes were calculated by the method described in ref 4. The chemical shift for methane adopted in these calculations was 196.0 ppm.

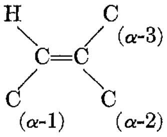

Figure 2.—Convention for designating the α carbons of a trisubstituted alkene.

is one which extends throughout the present data, regardless of the substitution of the double bond. It would seem, therefore, that the chemical shift of a carbon which is γ to a double bond can be estimated on the assumption that it will occur 0.5 ppm toward higher field than will that of the analogous carbon of the parent alkane.

The situation at the α position is more complex. In the single example of the monosubstituted group which is currently available, the α-methylene is deshielded by 1.8 ppm by the adjacent double bond. There are two complete spectra of 1,1-disubstituted alkenes available, and in these cases the α carbons are shielded with respect to the alkene analog. Furthermore, there is indication that α-methylenes are shifted by greater increments than are α-methyl groups, though the observed variation is large.

Most of the data in Table V concerns the 1,2-disubstituted alkenes. It is immediately apparent that the shifts at the α carbons are dependent on the geometrical isomerism of the double bond. In cis alkenes, the α carbons are shifted upfield from their positions in the alkane, while the opposite effect is observed for the trans cases. This is another example of the importance of steric effects in cmr spectroscopy.[4−8] More detailed examination of the data show that the magnitude of the shift at the α position is dependent on the extent to which the α carbon is substituted. Thus, the shift observed for an α-methyl carbon in a trans alkene is −3.8 ± 0.3 ppm, while the shift for an analogous methylene is −3.0 ± 0.3 ppm. For the cis examples, however, the shift shown by an α methyl (+1.5 ± 0.2 ppm) is of smaller magnitude than that of an α-methylene (+2.6 ± 0.3 ppm). At present there is no case in which the α carbon is tertiary or quaternary.

The case of the trisubstituted alkenes is complicated by the fact that there are three different types of α carbons. These are shown in Figure 2, wherein a system of differentiating between these α carbons is defined. The chemical shifts of α-1 carbons are observed to occur 1.1–1.6 ppm downfield from their positions in the alkanes. The shifts at the α-3 carbons are also downfield but are substantially larger (*ca.* 3.4 ppm). The α-2 carbons of trisubstituted alkenes, however, show large upfield shifts (+4.4 to +5.2 ppm) with respect to their alkane analogs. The significance of these data could be challenged on the basis that the alkane spectra for all three trisubstituted alkenes were estimated, but the semblance in the shifts of α carbons in similar environments is impressive.

For the tetrasubstituted alkenes, again only one example is available. The chemical shift of an α-methyl group in this case is 0.6 ppm higher field than in the parent alkane. The present data for the chemical shift changes associated with the introduction of an adjacent double bond are summarized in Table VI.

TABLE VI

CHEMICAL SHIFTS[a] OF α CARBONS OF MONOALKENES

Compd type		Chemical shift
Monosubstituted		CH_2, −1.8
1,1-Disubstituted		CH_3, +0.3 to +1.1
		CH_2, +1.0 to +2.4
Cis 1,2-disubstituted		CH_3, +1.5 ± 0.2
		CH_2, +2.6 ± 0.3
Trans 1,2-disubstituted		CH_3, −3.8 ± 0.3
		CH_2, −3.0 ± 0.2
Trisubstituted	α-1	CH_3, −1.6
		CH_2, −1.1
	α-3	*Ca.* −3.4
	α-2	CH_3, *ca.* +4.6
		CH_2, +5.2
Tetrasubstituted		CH_3, +0.6

[a] Measured in parts per million relative to the chemical shift of the analogous carbon in the parent alkene.

Though a paucity of data jeopardizes, to some degree, the conclusions of the above discussion, it will be seen in the next section that the results presented in Tables II, III, IV, and VI can be used with reasonable success in the correlation and assignment of the carbon resonances of alkenes. In many cases the carbon chemical shifts can be predicted quite accurately, and there are often quite obvious explanations for those cases in which the methods developed above fail.

B. Applications to Other Types of Compounds.—Also gathered in Table I are the carbon chemical shifts of ten dienes. Because these data are too few to justify a separate least-squares solution, the approach taken here is to use these chemical shifts in testing the general applicability of the methods developed in the previous section. There are, of course, difficulties in that the substituent parameters listed in Tables II through IV were developed for the case in which α, β, and γ carbons were tetrahedral. In the calculations below, any substituent other than hydrogen at these three positions was considered to have substituent effects identical with a tetrahedral carbon atom at the same position. Thus, the expression of substituent parameters for carbon 1 of 1,3-butadiene is taken to be $\alpha' + \beta'$. In estimating the chemical shifts of the saturated carbons, the effects due to both double bonds of the dienes were considered. Thus, carbon 4 of 2,6-*cis,cis*-octadiene was considered to be $2 \times 2.6 = 5.2$ ppm (*cf.* Table VI) higher field than carbon 4 of *n*-octane.

TABLE VII

CALCULATED AND OBSERVED CHEMICAL SHIFTS[a] FOR DIENE CARBON RESONANCES

Compd	Carbon	δ_{obsd}	δ_{calcd}	Residual
1,3-Butadiene	1	76.2	80.4	−4.2
	2	55.6	53.2	+2.4
2,3-Dimethyl-1,3-butadiene	1	81.2	85.5	−4.3
	2	50.4	47.0	+3.4
1,4-Pentadiene	1	77.8	79.0	−1.2
	2	56.4	54.4	+2.0
1,5-Hexadiene	1	78.7	79.0	−0.3
	2	55.5	54.4	+1.1
2,5-Dimethyl-1,5-hexadiene	1	82.7	83.5	−0.8
	2	48.3	48.1	+0.2
1,7-Octadiene	1	79.0	79.0	0.0
	2	54.6	54.4	+0.2
	3	159.4	159.3	+0.1
	4	164.7	164.3	+0.4
2,6-*cis,cis*-Octadiene	1	180.9	181.0	−0.1
	2	69.4	69.8	−0.4
	3	63.0	62.7	+0.3
	4	166.4	166.4	0
2,6-*cis,trans*-Octadiene	1	180.9	181.0	−0.1
	2	69.4	69.8	−0.4
	3	63.0	62.7	+0.3
	4	166.2	166.4	−0.2
	5	160.6	160.8	−0.2
	6	62.1	61.8	+0.3
	7	68.4	68.8	−0.4
	8	175.7	175.7	0
2,6-*trans,trans*-Octadiene	1	175.7	175.7	0
	2	68.4	68.8	−0.4
	3	62.1	61.8	+0.3
	4	160.4	160.8	−0.4
3,5-*cis,cis*-Octadiene	1	179.3	179.5	−0.2
	2	172.5	173.1	−0.6
	3	60.2	61.9	−1.7
	4	70.0	64.1	+5.9

[a] All chemical shifts were referenced to external carbon disulfide.

The results of calculations based on these suppositions are compared to the empirical chemical shifts in Table VII. It is seen that the agreement between empirical and calculated chemical shifts becomes reasonably good in those cases wherein the two double bonds are separated by at least two tetrahedral carbons. Indeed, the residuals observed for 1,7- and the 2,6-octadienes are of the same magnitude as is observed in the monoenes. The situation becomes worse, however, when the double bonds are conjugated or separated by only one tetrahedral carbon. In these cases there is a noticeable "leveling effect," which tends to bring the chemical shifts of the trigonal carbons closer together than would be predicted by our methods. It is interesting to note, however, that the chemical shifts of the tetrahedral carbons are predicted equally well regardless of the proximity of the double bonds. The data are extremely limited, however, and at the present time there is available no complete cmr spectrum of a compound in which the double bonds are separated by only one tetrahedral carbon.

It is also interesting to note that this method of estimating chemical shifts is satisfactory in the cases of some simple terpenes (Chart I). Hence, the chemical shifts of the carbons of squalene can be calculated with a standard deviation of empirical[26] and calculated values of 0.6 ppm (*cf.* Table VIII). Only the calculated chemical shifts of carbons 6 and 10 are in poor agreement with the empirical values, and even in these cases the residuals do not exceed 1.7 ppm. The present method would therefore seem to be quite satisfactory for predicting the chemical shifts of the carbons of acyclic polyenes in which the double bonds are isolated from one another.

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(26) M. Jautelat, J. B. Grutzner, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **65**, 288 (1970).

CHART I
STRUCTURES OF COMMON ACYCLIC TERPENES DISCUSSED IN THIS WORK

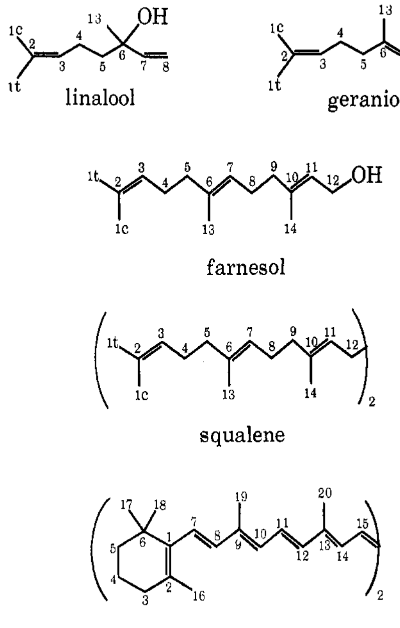


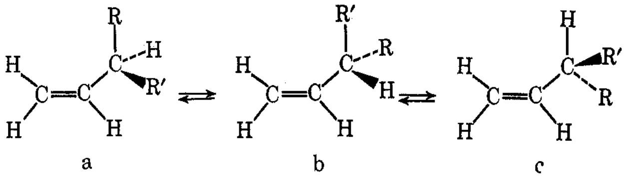
TABLE VIII
COMPARISON OF OBSERVED[a] AND CALCULATED CARBON CHEMICAL SHIFTS[b] OF SOME COMMON ACYCLIC TERPENES

Carbon	Linaool	Geraniol	Farnesol	Squalene
1c	175.9 (175.7)	175.9 (175.8)	175.9 (175.8)	175.9 (175.7)
1t	167.9 (167.6)	167.9 (167.7)	167.9 (167.8)	167.9 (167.7)
2	62.7 (62.5)	62.7 (62.0)	62.7 (61.9)	62.7 (62.6)
3	68.4 (68.0)	68.4 (68.3)	68.4 (68.2)	68.4 (68.3)
4	171.8 (165.4)	167.5 (166.6)	167.0 (166.3)	167.0 (166.2)
5	151.3 (150.5)	152.8 (153.5)	152.7 (153.5)	152.7 (153.3)
6	122.7 (120.6)	58.1 (55.9)	56.9 (58.3)	56.9 (58.4)
7	45.2 (47.2)	67.7 (68.7)	68.4 (68.9)	68.4 (68.6)
8	84.0 (81.9)	132.0 (134.5)	167.1 (167.6)	167.0 (166.6)
9			152.6 (153.4)	152.6 (153.3)
10			58.1 (56.1)	56.9 (68.6)
11			67.7 (68.5)	68.4 (68.6)
12			132.0 (134.6)	164.3 (164.8)
13	166.2 (170.3)	178.3 (177.1)	178.0 (179.5)	178.0 (177.3)
14			178.3 (177.3)	178.0 (177.3)

[a] Observed chemical shifts[26] are in parentheses. [b] All chemical shifts referenced to external carbon disulfide.

The introduction of a single hydroxyl function into the molecule has a slightly deterimental effect upon the correspondence of empirical and calculated chemical shifts (*cf.* Table VIII). The largest residuals are observed to occur at those carbons which are near the hydroxyl group. Doubtless, our simplifying approximation of considering a hydroxyl group to have the same substituent effect as a methyl group in the calculation of the chemical shifts of trigonal carbons was unwarranted. In the calculations of the chemical shifts of the tetrahedral carbons, the approximations involved with the prior estimation of the cmr spectra of the saturated alkanols[6] add greater uncertainty into the approximations defined in Table VI. Hence, the presence of a heteroatom in the alkene molecule requires that the present method of calculating carbon chemical shifts be used with some care, if not skepticism.

SCHEME I
STABLE ROTATIONAL CONFORMATIONS OF ALKENES AS DETERMINED BY PMR SPECTROSCOPY[a]



[a] See ref 36.

TABLE IX
CALCULATED AND OBSERVED[a] CHEMICAL SHIFTS[b] OF SOME OF THE CARBONS OF β-CAROTENE

Carbon	δ_{calcd}	δ_{obsd}
7	66.4	57.8
8	57.1	66.8
9	56.9	56.4
10	68.4	67.8
11	66.6	60.3
12	57.1	64.2
13	56.9	61.8
14	68.4	63.0
15	63.3	55.7
19	178.0	180.5
20	178.0	180.5

[a] Reference 26. [b] All chemical shifts referenced to external carbon disulfide.

Problems are also introduced by an extended chain of conjugated double bonds. In view of the difficulties encountered above for conjugated dienes, this result is not surprising. The example of β-carotene (*cf.* Scheme I) is presented in Table IX. Inspection of these tabulated data shows that the agreement of calculated and empirical chemical shifts would be much improved by interchanging the previous assignments[26] of carbons 7 and 8, as well as those for carbons 11 and 12. Even if these reassignments are accepted, it is apparent that the calculated and empirical values are still in considerable disagreement near the center of the chains of conjugated double bonds. This is not surprising, considering that the method is derived from data for acyclic monoenes.

Still greater problems are involved in the application of our system of calculating chemical shifts to cyclic alkenes. All prior quantitative correlations of carbon chemical shifts of cyclic compounds have been limited to cases involving rings of the same size,[5-8] and even then the correlations were successful only when the compounds concerned existed in similar conformations.[8] There are available a few data[26] which suggest that chemical shift differences in variously substituted cyclohexenes will be successfully accounted for by methods similar to ours. Such analyses would require the gathering of many more data for such compounds.

Despite these limitations, the methods devised in the previous section hold great promise of being of aid in future investigations of the cmr spectra of alkenes. Furthermore, the generalities emerging from these analyses may contribute to the better understanding of the sources of carbon chemical shift differences. The next section will investigate this possibility.

C. Correlation with Structural and Conformational Factors.

—In previous studies, the substituent parameters derived from methods similar to the above have been correlated with the electronic, structural, and conformational properties of the molecules concerned.[4-8,11,27-30] It is therefore of interest to seek

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

(28) P. C. Lauterbur, *ibid.*, **38**, 1415 (1963), and earlier papers.

(29) (a) J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 7107 (1970); (b) see also M. Christl, H. J. Reich, and J. D. Roberts, *ibid.*, **93**, 3463 (1971).

(30) D. M. Grant and B. V. Cheney, *ibid.*, **89**, 5315, 5319 (1967).

similar correlations in the present case. It will be worthwhile, however, to preface our discussion with a brief review of other results.

Substituent Parameters in Cmr Spectroscopy.—In the several studies[4–8,15,16] in which substituent parameters for calculation of carbon chemical shifts were derived, the α and β shifts are uniformly downfield. For substituents composed only of first-row elements, the α shift seems to increase in magnitude with the increasing electronegativity of the substituent. Thus, while substitution of a methyl group generally effects an approximately 10-ppm downfield shift in the resonance of the directly substituted carbon, the analogous chemical shift change for the hydroxyl group is -40 to -50 ppm.[6] The corresponding β shift, however, seems relatively independent of the nature of the substituent.[6,31] Thus, the β effects of the methyl and hydroxyl groups differ by only about 0.5 ppm.[6] The β shift is also broadly independent of the identity of the atom through which it is transmitted.[31] The β shift observed upon methylation of the heteroatoms of methanol, methylamine, dimethylamine, and the methylphosphines is quite uniformly -10 ppm,[31] a shift which is also observed for the acyclic alkanes.[4]

It has been pointed out, however, that the magnitudes of these downfield α and β shifts are diminished when the substituted region is highly branched.[29] This effect appears in the form of correction terms in case of the acyclic alkanes,[4] the correction terms in every case counteracting the downfield α and β shifts. In very highly branched bicyclic systems, the β shift was found to approach a limiting value, while the α effect, in rare cases, became upfield in nature.[29] These results were explained in terms of bond perturbations which would tend to lengthen the carbon–carbon bonds. Such perturbations are predicted by valence–bond theory to lead to upfield shifts.[32] The opposition of these upfield shifts to the fundamentally downfield α and β effects would therefore lead to shifts of smaller magnitude.

The γ shift has been demonstrated by several studies[4–11] to be correlatable to steric effects. Furthermore, valence–bond theory has been used with some success in the explanation of these shifts.[30] The substituent effects associated with the δ and ϵ positions are generally small and downfield.[4,5,7,8] Because the δ and ϵ effects were found negligible in the present study, their discussion is not important at the present time.

Substituent Effects in the Acyclic Alkenes.—The α, β, and γ shifts encountered for the acyclic alkenes parallel closely those encountered for the acyclic alkanes. Thus, the α shift is approximately -9 ppm in both types of compound. As has been mentioned above, and will be discussed at greater length below, most of the variations observed in the α shift (Tables II and III) can be attributed to the imperfect additivity of this parameter. The other single and notable deviation in the α shift is observed for the C-2 resonance of propene. Comparing the chemical shift of this resonance with that of ethylene, one concludes that the α shift in this case is nearly -13 ppm. The magnitude of this α effect seems unprecedented.

It is to be noted that the correction term for this parameter is quite large, having nearly half the magnitude of the α shift itself, and that it is of the opposite sign. This correction term may therefore result from a mechanism similar to that which is operative in saturated systems.[4,29] The results of microwave[33] and other techniques indicate that the lengthening of bonds must be very small. However, the bondlength dependence of ^{13}C chemical shifts, like that of energy,[34] may be rather steep. But the microwave results also show significant changes in bond angles upon substitution of a second methyl group, and the unusually low chemical shift of the trigonal carbons of cyclobutene may indicate that such angular changes have a large effect on chemical shift. It is impossible to separate these effects with the present limited data.

The β shift for the alkenes is also similar to those observed for other systems, though the magnitude of the shift seems somewhat smaller than that observed for the alkanes. The introduction of a β substituent into an alkene, however, is always accompanied by the development of steric interactions, which, as described above, could lead to an upfield shift which would oppose the fundamental downfield β shift. Because the addition of more β substituents could serve to increase these shielding interactions, one might expect that the β shift accompanying the addition of the second and third β substituents would be even smaller in magnitude. Such an explanation would rationalize the importance of the corr β term (*cf.* Table II).

As is observed for all saturated systems, the γ shift is positive for the acyclic alkenes. It is interesting, however, that the size of this shift is rather small. It has been inferred from pmr data that the three rotational conformations a, b, and c of Scheme I are nearly equally populated.[35] In alkanes, of course, the prevalent form would be trans, in which the dihedral angle is 180°. The interactions between the γ substituent and the nearer trigonal carbon will therefore be quite different from the γ-gauche interactions[5,30] in alkanes. Furthermore, it is not yet clear how steric perturbation will affect trigonal carbons. There is some indication, for example, that interactions between methyl groups and the π electrons of double bonds lead to shielding of the trigonal carbons.[29] It is therefore not surprising if our γ shifts do not quantitatively parallel the results of the alkane study.[4]

There seems no immediate precedent for the α', β', and γ' shifts observed for the alkenes. Both the α' and β' effects are shielding, and, in the case of the former parameter at least, the magnitude of the shift is rather large. Examination of the definition of this parameter in Figure 1 shows that an α' substituent is actually in the β position with respect to the alkene carbon in question. This is important because β shifts in other compounds are very generally deshielding in character.

Because of the relative rigidity of the alkene group,

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(31) (a) F. J. Weigert, Ph.D. Thesis, California Institute of Technology, 1968. (b) More recent research by C. Marzin and D. E. Dorman on n-butyl derivatives has revealed a definite electronic component to the β effect. The trends are for *smaller* β effects by groups which are strongly electron attracting especially by the resonance effect (one measure of which is Taft's σ_R): J. D. Roberts, paper presented at the IUPAC Congress, Boston, Mass., July 27, 1971.

(32) W. M. Litchman and D. M. Grant, *J. Amer. Chem. Soc.*, **90**, 1400 (1968).

(33) Y. Morino and E. Hirota, *Ann. Rev. Phys. Chem.*, **20**, 139 (1969), and references therein.

(34) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7036 (1967).

(35) (a) A. A. Bothner-By and C. Naar-Colin, *ibid.*, **83**, 231 (1961); (b) A. A. Bothner-By, C. Naar-Colin, and H. Günther, *ibid.*, **84**, 2748 (1962); (c) A. A. Bothner-By and H. Günther, *Discuss. Faraday Soc.*, **34**, 127 (1962).

one might consider the possibility of correlating the α' shift with steric effects. A formulation such as that derived by Grant and Cheney,[30] however, cannot succeed in rationalizing this shift because the cosine factor approaches zero. Furthermore, there are available incomplete but suggestive results from studies of alkynes which indicate that a similar α' effect holds for these compounds.[36] Because a steric effect in linear alkyne is impossible to envisage, it seems certain that some other explanation must obtain for the α' shift.

Another possible explanation of this parameter is that an α' substituent polarizes the π electrons of the double bond, thus shielding the more distant trigonal carbon. Explanations of this nature have been advanced several times to interpret the chemical shifts of substituted alkenes.[17,37] This explanation is certainly attractive, but at present it is constrained by theoretical limitations to a rather qualitative role.

At present, the explanation of the α' shift is not obvious. Any explanation of the α' effect itself will be required to rationalize the fact that its correction term, corr α', is deshielding in character. It seems probable that the underlying cause of the α' effect, like that of the fundamental β effect, is more subtle than either steric or electronic effects.

The β' effect is also shielding but is of rather smaller magnitude. Although its associated correction term, corr β', is of dubious experimental significance, it is of interest to note that when it is included, it is of the same sign as the β' shift (*cf.* solutions 6 and 8, Table II). Unlike the α' shift, the β' effect can be interpreted in terms of formulations such as derived for the alkanes.[30] Furthermore, microwave studies[38] would seem to indicate that steric interactions between an alkene carbon and its β' substituent are significant. We are inclined to believe that this parameter is likely to be due to steric effects.

The γ' effect, like that of the β' shift, defies any present explanation. It is surprising that this parameter is so large, considering the distance between a trigonal atom and its γ' substituent. It is interesting that this parameter tends to counterbalance the β' shift, a result which suggests that the effect of the γ' substituent is to inhibit the steric interactions between the trigonal carbon and the β' group.

The original purpose of the "cis" parameter was to account in part for the differing steric and conformational effects of the various subgroups of alkenes. Subsequent results have shown that this parameter is too simple in definition to serve this purpose. Although comparison of the chemical shifts of the trigonal carbons of cis and trans 1,2-disubstituted alkenes shows that there is some dependence of chemical shifts upon geometrical isomerism, it is also apparent that this dependence varies with the size of the molecule. Thus, *cis*- and *trans*-2-butene differ in chemical shift of alkene carbons by 1.4 ppm, while the analogous 3-hexene carbons are only 0.1 ppm different. The analogous effect for the 4-octenes is 0.6 ppm. Obviously, the "cis" parameter is inadequate to explain all of these results.

Finally, we may consider the chemical shift differences encountered for the tetrahedral carbons of alkenes. In the absence of steric effects, it was observed that the adjacency of a double bond brought about a downfield shift relative to the analogous alkane. One possible explanation of this is that the α effect of direct substitution by a trigonal sp^2 carbon is larger in magnitude than that of saturated sp^3 carbons. Since the α effect seems dependent on electronegativity, this indicates that an sp^2 carbon is more electronegative than an sp^3 carbon.

The only other regular change in the chemical shifts of tetrahedral carbons associated with the double bond is the +0.5 ppm observed at the γ position. Because this shift is quite constant for a variety of cases, it is difficult to attribute it to simple steric effects. It has been noted, however, that the γ shift in a variety of compounds is directly proportional to the increasing electronegativity of the substituent.[39] Though it is too early to comment further on this interesting possibility at this time, its presence may signal a heretofore unrecognized presence of a inductive contribution to the γ effect.

Registry No.—1-Octene, 111-66-0; 2-methyl-1-heptene, 15870-10-7; 2,4,4-trimethyl-1-pentene, 107-39-1; *cis*-2-butene, 590-18-1; *cis*-2-pentene, 627-20-3; *cis*-2-hexene, 7688-21-3; *cis*-2-octene, 7642-04-8; *cis*-3-octene, 14850-22-7; *cis*-4-octene, 7642-15-1; *trans*-2-butene, 624-64-6; *trans*-2-hexene, 4050-45-7; *trans*-2-octene, 13389-42-9; *trans*-3-octene, 14919-01-8; *trans*-4-octene, 14850-23-8; *cis*-3-methyl-2-hexene, 10574-36-4; *trans*-3-methyl-2-hexane, 20710-38-7; 2-methyl-2-heptene, 627-97-4; cyclobutene, 822-35-5; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; *cis*-cyclooctene, 931-87-3; *trans*-cyclooctene, 931-89-5; *cis*-cyclododecene, 1129-89-1; methylenecyclobutane, 1120-56-5; methylenecyclopentane, 1528-30-9; methylenecyclohexane, 1192-37-6.

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