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Carbon-13 NMR Spectra of 1-Arylpropynes and 1-Arylpropenes. Transmission of the Electronic Effects of Substituents through Carbon-Carbon Triple and Double Bonds

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It has been customary to use the Hammett $\rho\sigma$ relationship for the analysis of substituent effects on the side-chain reactions of benzene. The magnitude of reaction constant ρ usually diminishes with the increasing number of bonds intervening between the substituent and the reaction site.[1] This attenuation of the ρ value allows us to evaluate the efficiency of the intervening group in transmitting the electronic effect of substituents. A similar treatment is applicable to the ground-state properties; various spectral data have been analyzed on this basis.[2]

In the present work, we have investigated the effects of ring substituents on the ^{13}C chemical shifts of 1-phenylpropyne (**1**) and 1-phenylpropene (**2**) in order to compare the efficiencies of the $\mathrm{C{=}C}$ and $\mathrm{C{\equiv}C}$ bonds in transmitting the substituent effects. The $\mathrm{C{\equiv}C}$ bond has been found to be a less efficient transmitter.

Results

The ^{13}C NMR spectra of 1-phenylpropyne (**1**), *cis*- and *trans*-1-phenylpropenes (**2c** and **2t**) and their ring-substituted derivatives have been recorded in neat liquid. The chemical shifts were expressed in ppm *downfield* from tetramethylsilane as the standard.

The assignment of the α- and β-carbon signals of **1** was accomplished by the partial proton-decoupling technique. White and Levy[3] have recently reported the CMR spectral data of **1** and assigned the signals at 85.7 and 79.8 ppm to the α- and β-carbons, respectively, without any sound basis. On the other hand, Frei and Bernstein[4] observed the β-carbon signal at 86.8 ppm, using a ^{13}C-enriched sample. We have found that the signal at 86.4 ppm splits into quartet by partial proton-decoupling. The observed splitting must be due to the methyl protons. Although the spin coupling constants between ^{13}C and ^{1}H which are separated by more than one bond do not necessarily attenuate with an increase in the number of intervening bonds,[5] we have a good reason to say that $J_{\mathrm{C-C-H}}$ is greater than $J_{\mathrm{C-C-C-H}}$ in **1**. It is reported that the coupling constants between the methyl protons and the acetylenic carbons of propyne, $J_{\mathrm{C-C-H}}$ and $J_{\mathrm{C-C-C-H}}$, are 10.6 and 4.8 Hz, respectively.[6] Thus, the quartet signal can be assigned to the β-carbon, to which the methyl group is bonded. The assignment is compatible with the observation reported by Frei and Bernstein.[4]

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[1] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[2] Y. Yukawa and Y. Tsuno, "Bunkokagaku 1968-B," ed. by Y. Morino, T. Shimanouchi, S. Fujiwara, and M. Oki, Nankodo, Tokyo, (1968), pp. 87—112.

[3] D. M. White and G. C. Levy, *Macromolecules*, **5**, 526 (1972).

[4] K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **38**, 1216 (1963).

[5] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, (1966), p. 1027.

[6] J. N. Shoolery, *J. Mol. Spectrosc.*, **63**, 110 (1960).

The assignment of the α- and β-carbon signals of **2c** and **2t** was carried out with the aid of the additivity rule of Savitsky *et al.*[7] A methyl substitution of ethylene causes 12.9 ppm downfield and 7.4 ppm upfield shifts of the carbons α and β to the substitution, respectively.[7] In the same way, a phenyl substitution results in 13.0 ppm downfield and 10.5 ppm upfield shifts of the α- and β-carbons, respectively.[8] Using these shift values and the chemical shift of the ethylene carbon (122.8 ppm), we estimate the chemical shifts of the α- and β-carbons of **2** to be 128.4 and 125.2 ppm. Thus, the signals appearing at *ca.* 130 and 126 ppm of both **2c** and **2t** can be assigned to the α- and β-carbons, respectively.

Chemical shifts of sp and sp^3 carbons are substantially different from those of sp^2 carbons. Assignment of the signals of ring carbons was worked out, using both the partial proton-decoupling technique and the known additivity rule.[9]

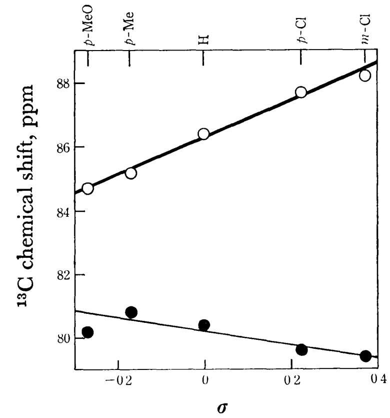

Fig. 1. Hammett plots of the ^{13}C chemical shifts of the α- (●) and β-carbons (○) of 1-phenylpropynes.

Table 1. ^{13}C chemical shifts[a] of the α- and β-carbons of ring-substituted **1**, **2c**, and **2t**

Substituent	**1**		**2c**		**2t**	
	α	β	α	β	α	β
p-CH_3O	80.2	84.7	130.2	125.2	131.7	123.6
p-CH_3	80.8	85.6	130.1	125.9	132.1	124.6
H	80.4	86.4	130.7	126.9	132.2	125.7
m-CH_3O					131.9	126.1
p-Cl	79.6	87.7	129.4	127.8	130.9	127.1
m-Cl	79.4	88.2				

a) In ppm downfield from TMS.

Table 2. Sensitivity constants for the ^{13}C chemical shifts of the β-carbons in **1**, **2c**, and **2t**

	1	**2c**	**2t**
ρ[a]	5.38	5.21	6.64
r[b]	0.993	0.992	0.991
s[c]	0.364	0.47	0.516

a) $\delta_X(\mathrm{ppm}) - \delta_H(\mathrm{ppm}) = \rho\sigma_X$. b) Correlation coefficient.
c) Standard deviation of ρ.

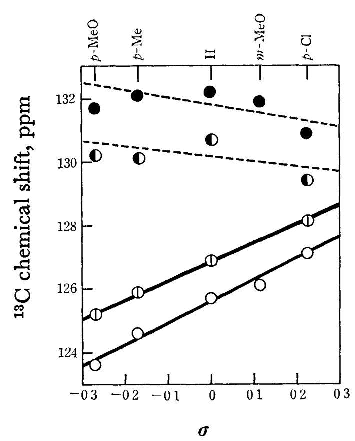

Fig. 2. Hammett plots of the ^{13}C chemical shifts of the α- and β-carbons of *cis*- and *trans*-1-phenylpropenes. **2c**; α(◐), β (⦶), **2t**; α (●), β(○).

Listed in Table 1 are the ^{13}C chemical shift data obtained for the α- and β-carbons in the derivatives of **1**, **2c**, and **2t**. They are plotted against the Hammett σ constants in Figs. 1 and 2. In any case studied, the β-carbon shows a better linearity than does the α-carbon. The ρ values for the former carbon are given in Table 2, together with the related data.

Discussion

According to the present CMR data given in Table 2, the transmission efficiency of the unsaturated bond in either of **1** or **2c** is lower than that observed for **2t**. The low efficiency in **2c** may be due to the conformational effect arising from its nonplanar structure.[10] Since our specific aim here is to compare the electronic effects of the C=C and C≡C bonds in transmitting the substituent effect, the transmission efficiency of a C=C bond should be evaluated from the results for **2t**, which is coplanar and hence is free from the conformational problem. This leads to a conclusion that the efficiency of a C≡C bond is smaller than that of a C=C bond free from steric strain. The same trend is discernible in the comparison of the ρ values for the β-carbon shifts of phenylacetylene (ρ=3.6 ppm/σ[11]) and styrene (ρ=4.73 ppm/σ[8]).

It is known that ^{13}C chemical shifts well reflect the electron density (especially the π-electron density) of the carbon atom.[12] Savitsky *et al.*[7] have shown from CMR observations that the polarization of a C=C bond by an electron-donating group should effect an increase (upfield shift) in electron density at the β-carbon and a decrease (downfield shift) at the α-carbon. Most likely, the polarization effect of substituents will be the greater, the greater their electron donating or withdrawing property. The view is in line with our

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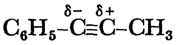
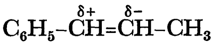
finding that, in both **1** and **2**, the signs of the ρ values for the α- and β-carbons are opposite to each other (Figs. 1 and 2). The small ρ-values of the β-carbon in phenylacetylenes as compared with those in styrenes may then be taken as an indication that a C≡C bond is less sensitive than a C=C bond to a perturbation in bond-polarity due to the introduction of polarizing substituents. This low sensitivity of a C≡C bond seems to be ascribable to the opposite polarization of orthogonal π-electrons in the triple bond.

The chemical shifts themselves of the α- and β-carbons seem to deserve brief comment. The polarization argument leads to the result that the side-chain unsaturated bonds of **1** and **2** are polarized in opposite directions.



$C_6H_5\text{-}\overset{\delta-}{C}\equiv\overset{\delta+}{C}\text{-}CH_3$



$C_6H_5\text{-}\overset{\delta+}{C}H=\overset{\delta-}{C}H\text{-}CH_3$

That is, for the acetylenic bond, the phenyl group appears to be less electron-donating than the methyl group, while the former is more electron-donating than the latter in the olefinic bond. However, this difference in the direction of polarization has no bearing with the lower sensitivity of the triple bond to the electronic effect of ring substituents.

Experimental

Preparation of the ring-substituted 1-phenylpropenes and 1-phenylpropynes will be described elsewhere.[13]

The ^{13}C NMR spectra of a neat liquid in an 8 mm ϕ sample tube were recorded at 25 °C on a JEOL C-60HL spectrometer with a 15.09 MHz RF unit. The signal to noise ratio of the spectra was enhanced by the ^{13}C–H noise decoupling. The chemical shift measurements were performed with a nuclear-resonance single-side-band technique, their accuracies being within ±0.2 ppm. CS_2 was used as an external standard. The chemical shifts are given in ppm downfield from TMS by using the chemical shift of CS_2 of 193.7 ppm.

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13) K. Izawa, T. Okuyama, and T. Fueno, to be submitted for publication.