Transmission of Substituent Effects through Oxygen and Sulfur Atoms. II. ^{13}C Chemical Shifts of Ring-Substituted Phenyl Vinyl Ethers and Sulfides

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The ^{13}C chemical shifts of ring-substituted phenyl vinyl ethers and sulfides were measured and discussed in relation to the change in electron distribution caused by the ring-substitution. The Hammett plots of the shifts for the terminal carbon confirm the greater transmission efficiency of sulfur atom. An "inverse" substituent effect was found for the α-carbon of both compounds. This suggests that the bond-polarization plays an important role in the transmission of electronic effect.

In the preceding paper,[1] transmission of substituent effects through oxygen and divalent sulfur has been investigated for proton-magnetic-resonance (PMR) chemical shifts. The usual Hammett $\rho\sigma$ treatment revealed that divalent sulfur atom, when interposed between two conjugated systems, behaves as a more efficient transmitter of the electronic effect than oxygen atom. It was then suggested that the d-orbital of sulfur may play an important role in the transmission of substituent effect by an additional resonance contribution termed "through-conjugation."

Critically speaking, however, some uncertainty attaches to the investigation of substituent effect based on PMR substituent chemical shifts. Proton chemical shifts do not reflect a unique physical quantity of molecules. They are affected by several factors such as the diamagnetic as well as paramagnetic shielding by electrons of the hydrogen atom in question and the adjacent atom.[2] On the other hand, ^{13}C chemical shifts can be definitely related to the electron density of the carbon atom of interest. Therefore, measurements of the ^{13}C substituent chemical shifts enable us to estimate directly the electronic effects of substituents on the electron densities of various carbon atom in molecules.

In this paper, we compare the ^{13}C chemical shifts of substituted phenyl vinyl ethers and sulfides. The substituent effects on the terminal carbon were found to be in line with the results of PMR studies.[1] Further, the substituent dependence of the chemical shifts of other carbon atoms offered an interesting information on the mechanism of the transmission of electronic effects.

Experimental

The ^{13}C NMR spectra (neat) were taken at 26°C on a JEOL C-60HL spectrometer equipped 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 carried out by a nuclear resonance single side-band technique; they were accurate to within ±0.2 ppm. CS_2 was used as an external standard; higher-field shifts were represented by positive δ values.

Results

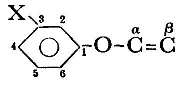
Assignments were based on the additivity rule[3] and on the splitting of peaks on partial decoupling. There are some uncertainties in the assignment of the peaks spaced within 1 ppm. All the peaks assigned are listed in Tables 1 and 2.

The ^{13}C chemical shifts δ of the α and β carbons were found to be linearly correlated with Hammett σ values, as shown in Figs. 2 and 3, respectively. The ρ values, defined by $\delta_X - \delta_H = \rho\sigma$, are listed in Table 3, together with correlation coefficients r and standard deviations s. It is noteworthy (1) that, with both the α- and β-carbons, PVS has the ρ values greater in

TABLE 1. ^{13}C CHEMICAL SHIFTS FOR RING-SUBSTITUTED PHENYL VINYL ETHERS (ppm from CS_2)

Substituent	Aromatic carbon[a)]						Vinyl carbon[a)]		Substituent carbon
	1	2	3	4	5	6	α	β	
p-CH_3O	42.5	74.6	78.4	37.5	78.4	74.6	43.6	99.5	137.7
p-CH_3	38.3	76.1	62.8	60.8	62.8	76.1	44.5	98.8	172.1
m-CH_3	34.6	75.2	53.7	69.1	63.7	79.0	45.0	98.2	171.3
H	36.5	76.1	63.4	69.9	63.4	76.1	45.2	97.8	—
m-CH_3O	35.3	89.7	32.3	84.3	63.0	84.2	45.3	97.7	138.0
p-Cl	37.6	74.6	63.3	64.8	63.3	74.6	45.3	96.8	—
m-Cl	35.8	75.5	58.0	69.7	62.6	77.8	46.0	96.3	—

a) The numberings of the carbons are as follows:



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1) T. Fueno, O. Kajimoto, K. Izawa, and M. Masago, This Bulletin, **46**, 1418 (1973).

2) O. Kajimoto and T. Fueno, *Chem. Lett.*, **1972**, 103.

3) P. C. Lauterbur, *J. Amer. Chem. Soc.*, **83**, 1846 (1961).

Table 2. ^{13}C chemical shifts for ring-substituted phenyl vinyl sulfides (ppm from CS_2)

Substituent	Aromatic carbon[a]						Vinyl carbon[a]		Substituent carbon
	1	2	3	4	5	6	α	β	
p-CH_3O	69.1	58.8	77.8	33.5	77.8	58.8	58.8	80.1	137.6
p-CH_3	62.5	61.7	63.0	56.0	63.0	61.7	60.0	79.0	171.5
m-CH_3	58.6	61.8	54.2	65.3	63.8	64.9	60.5	77.9	171.2
H	58.5	62.6	63.8	66.0	63.8	66.0	61.2	77.4	—
p-Cl	59.8	61.5	63.6	59.6	63.6	61.5	61.5	76.5	—
m-Cl	55.7	63.6	57.9	65.9	62.7	65.3	62.2	75.3	—

a) For the numberings, see Table 1.

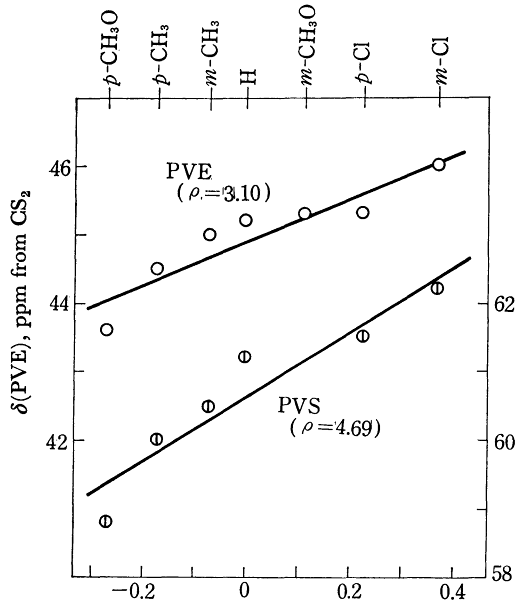

Fig. 1. Hammett plots of the ^{13}C chemical shifts for the α-carbons of phenyl vinyl ethers (PVE) and phenyl vinyl sulfides (PVS).

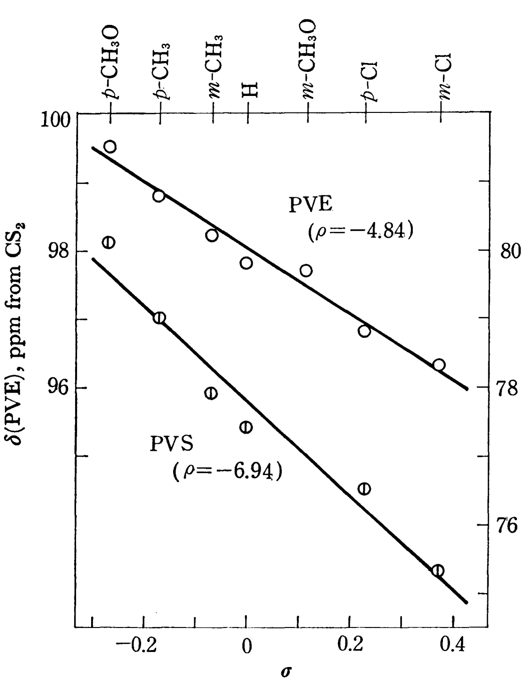

Fig. 2. Hammett plots of the ^{13}C chemical shifts for the β-carbons of phenyl vinyl ethers (PVE) and phenyl vinyl sulfides (PVS).

Table 3. Sensitivity constants ρ for the ^{13}C chemical shifts of phenyl vinyl ethers and sulfides (ppm/σ)

	α-Carbon		β-Carbon	
	-O-	-S-	-O-	-S-
ρ[a]	3.10	4.69	−4.84	−6.94
r	0.921	0.944	0.987	0.980
s	0.59	0.82	0.35	0.70

a) $\delta_X - \delta_H = \rho\sigma_X$.

magnitude than those of PVE and (2) that, for both PVE and PVS, the ρ values for β-carbons are positive while those for α-carbons, negative.

Discussion

Electron Distributions in PVE and PVS. There have been several treatments of the relation between ^{13}C chemical shift and the electron density of the carbon atom. Spiesecke and Schneider[4] measured the ^{13}C chemical shifts δ for $C_5H_5^-$, C_6H_6, $C_7H_7^+$, and $C_8H_8^{++}$ and proposed the empirical relation

$$\delta = 160(q_\pi - 1) \text{ ppm} \tag{1}$$

where q_π is the π-electron density of the carbon atom in question. Karplus and Pople[5] justified the above equation on the basis of π-molecular orbital calculations.

Recently, Tokuhiro and Fraenkel[6] calculated the ^{13}C chemical shifts of nitrogen heterocycles using the Karplus-Pople equation coupled with all-valence-shell-electron SCF–MO's. They found that, even though the observed shifts are roughly linear with the π-charge, the linearity is considerably improved when δ is plotted against the total electronic charge. Using the CNDO wave functions of Bene and Jaffé,[7] they obtained the equation;

$$\delta = 155(q_{\pi+\sigma} - 4) \text{ ppm} \tag{2}$$

where $q_{\pi+\sigma}$ is the total electron density on the carbon atom of interest. Bloor and Breen[8] also obtained linearity between δ and *total charge* using CNDO/2 MO's.

In reality, however, many approximations are invoked for the derivation of Pople's equation from the

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4) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, **1961**, 468.

5) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

6) T. Tokuhiro and G. Fraenkel, *J. Amer. Chem. Soc.*, **91**, 5005 (1969).

7) J. D. Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968).

8) J. E. Bloor and D. L. Breen, *J. Phys. Chem.*, **72**, 716 (1968).

formal expression of Ramsey. Therefore, one should be careful in applying the above linear relationship to carbon nuclei of much different environment. In such cases, chemical shifts may be largely affected by factors other than electron density. For the compounds treated in this paper, however, all the carbon nuclei are situated in so similar a condition that it would be reasonable to assume a roughly linear relationship. In what follows, therefore, we will consider the ^{13}C chemical shift as a measure of the electron density on carbon atom.

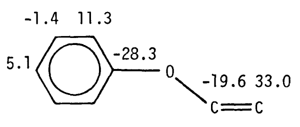
Table 4. Side chain ^{13}C chemical shifts (ppm from CS_2)

Compound	Carbon	Chemical shifts -O-	-S-	$-CH_2-$
C_6H_5-Y-CH_3	methyl	138.8[a]	177.0	179.4[b]
C_6H_5-Y-CH=CH_2	α	45.2	61.2	55.6
	β	97.8	77.4	77.6

a) Ref. 10.
b) G. B. Savitsky and K. Namikawa, *J. Chem. Phys.*, **67**, 2430 (1963).

Table 4 summarizes the side-chain ^{13}C chemical shifts of anisole, PVE and their sulfur analogs. The methyl carbon of anisole shows a shift considerably lower than that of thioanisole. This implies that oxygen attracts electron through σ-bond more strongly than does sulfur. On the other hand, the ethylenic β-carbon of PVE is observed at δ about 20 ppm higher than that of PVS. This reflects a strong π-donating character of oxygen. These results confirm the validity of our conclusion which was previously drawn on the basis of ^1H chemical shifts of the same compounds.

Illustrated below are the ^{13}C chemical shifts of the various carbons of PVE and PVS with respect to benzene. Because of the parallelism between δ and electron density, these shifts may be regarded as representing the electron distribution over the molecules. Positive values correspond to excess electron.



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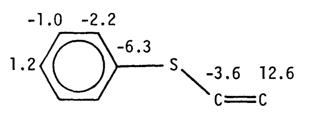
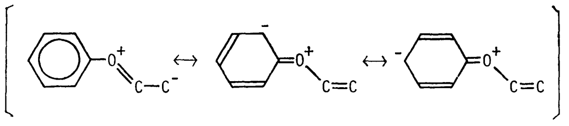


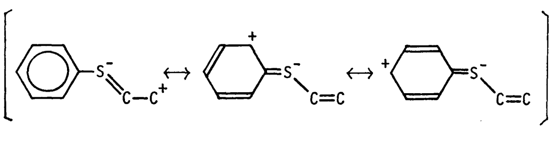
II

It is seen that the presence of oxygen atom increases the electron densities of the β carbon of the vinyl moiety as well as the *ortho* and *para* carbons of the benzene ring. The tendency is in accord with the prediction which can be made on the basis of classical canonical structures.



III

On the other hand, the charge distribution is rather uniform in PVS. This can also be rationalized by considering the canonical forms in which the sulfur atom acts as a π-electron accepter.

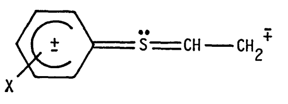


IV

Participation of such structures in resonance should neutralize the charge alternation caused by III, resulting in a flat distribution of electrons.

Substituent Effects on the Chemical Shifts of α and β Carbons. The Hammett-type substituent effects on ^{13}C chemical shifts were first reported by Spiesecke and Schneider[9] for monosubstituted benzenes. Later on, Dhami and Stothers[10] measured the ^{13}C chemical shifts of ring-substituted styrenes, anisoles, acetophenones, and methyl benzoates. Side-chain ^{13}C chemical shifts of these compounds, however, did not show clear dependence on Hammett's σ except for the β-carbon of styrenes. Our present work provides additional examples of fairly good Hammett dependence of ^{13}C chemical shifts. Moreover, it gives us interesting informations concerning the transmission of electronic effects.

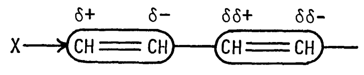
First, we compare the magnitudes of ρ between PVE and PVS. Thus, the ρ values for PVS are about 1.5 times greater than thoes of PVE with both the α and β carbons, indicating an enhanced transmission of substituent effects through sulfur atom. As has been described previously, this is considered to have been caused mainly by the through-conjugative participation of sulfur d-orbitals in π-conjuagtion. The presence of pπ-orbitals in both sides of sulfur atom is the essential condition for it. The concept can best be represented pictorially by the structure



V

Next, the signs of ρ enable us to deduce the mechanism of transmission. For the β-carbons of both PVE and PVS, the observed peaks tend to show lower-field shifts with the increase in the σ-value of substituent groups. This means that the electron density on carbon atom decreases as the electron-withdrawing ability of substituents increases. For the α-carbon, however, the chemical shift shows an "inverse" dependence on substituents; an electron-withdrawing substituent increases the electron density on the α-carbon.

One explanation for these facts may be given in terms of bond polarization. It is not unreasonable to consider that the substituent effects are transmitted by successive polarization of -CH=CH- units.



In the *p*-CH_3O derivatives for instance, the increments in the ^{13}C chemical shifts caused by the ring substitu-

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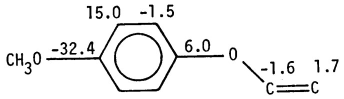
9) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

10) K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, **43**, 479 (1965); *ibid.*, **43**, 510 (1965); *ibid.*, **44**, 2855 (1966); *ibid.*, **45**, 233 (1967).

tion are as follows:



Successive bond polarization can clearly be seen.

Thus, the direction of substituent effect on the α-carbon should be the reverse of that on the β-carbon. Validity of this concept has already been proved for the case of *trans*-1-substituted-1,3-butadienes by comparing the observed ^{13}C chemical shifts with the electron distribution calculated by the CNDO/2 method.[11] Similar theoretical treatments of PVE and PVS will be given in a subsequent paper.

In conclusion, sulfur atom transmits the electronic effect of substituents more efficiently than oxygen atom, primarily through its pπ-dπ-pπ conjugation. Substituent effects on the ^{13}C chemical shifts of the α and β carbons of a vinyl group are opposite in direction, indicating polarization of the vinyl π-bond.

The authors are indebted to Mr. H. Okuda, this Faculty, for the ^{13}C NMR measurements.

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[11] O. Kajimoto and T. Fueno, *Tetrahedron Lett.*, **1972**, 3329.