Substituent Effects on the ^{13}C and ^{1}H Chemical Shifts of 1-Phenyl-1,3-butadiene and Phenylallene

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CMR and PMR spectra of *trans*-1-phenyl-1,3-butadiene (PBD) and phenylallene (PA) and their ring-substituted derivatives (*p*-CH_3, *m*-CH_3, *p*-Cl, and *m*-Cl) have been measured. The chemical shifts of side-chain carbons and protons were treated with a Hammett-type relationship. The carbon chemical shifts of the side chain gave alternately opposite sign of ρ values while those of PA showed little dependence on the ring substitution. The ^{1}H chemical shifts showed behavior different from that of the ^{13}C shifts. The mode of electron polarization along the side-chain of PBD and PA was discussed to interpret the observations.

It is well known that the efficiency of a C=C double bond in transmitting electronic effects is greater than that of a saturated CH_2 group.[1] The π-bond polarization may contribute to the greater transmission efficiency of double bond. Kajimoto and Fueno[2] have recently found that the alternation of substituent effects on the ^{13}C chemical shifts occurs along the conjugated framework of 1-substituted 1,3-butadienes. The electronic effects are transmitted mainly through successive π-bond polarization.

$$X \leftarrow \overset{\delta-}{C}=\overset{\delta+}{C}-\overset{\delta\delta-}{C}=\overset{\delta\delta+}{C}$$

However, because of direct substitution at the 1-carbon' additional factors may have contributed to the chemical shifts of unsaturated carbons. To avoid this complexity, we have measured CMR spectra of ring-substituted 1-phenyl-1,3-butadienes.

On the other hand, opposite polarization of π-electrons in the orthogonal p-orbitals of the acetylenic bond has recently been considered in an attempt to interpret the substituent effects on the ^{13}C chemical shift of 1-phenylpropyne.[3] In this connection, it is interesting to examine the mode of bond polarization of allene which has cumulative orthogonal π-bonds. Thus, we have measured CMR spectra of some ring-substituted phenylallenes.

Proton chemical shifts have also been measured for the sake of comparison.

Results

The ^{13}C NMR spectra of *trans*-1-phenyl-1,3-butadiene (PBD) and phenylallene (PA) and their derivatives were measured as a neat liquid or a 50% solution in carbon disulfide. The observed signals were assigned by comparison with the partially proton-decoupled spectra and by the aid of the additivity rule[4] in the same way as described previously.[2,3] The chemical shifts of side-chain carbons are listed in Tables 1 and 2 for PBD's and PA's, respectively, in ppm downfield from tetramethylsilane.

Proton spectra were recorded with a 10% solution in carbon tetrachloride at the frequency of 100 MHz. The assignment of signals was accomplished through the analysis of their mode of coupling. The ^{1}H chemical shifts assigned are included in Tables 1 and 2.

Discussion

Butadiene System. Figure 1 shows plots of the chemical shifts of various side-chain carbons of PBD's against Hammett's σ values. It clearly exhibits that the sign of slope changes alternately from the α- to δ-carbon. That is, ρ values for the α- and γ-carbons are negative while those for the β- and δ-carbons are positive as are given in Table 1. These results apparently show the alternation of polar effects in the conjugated system. An electron-donating group on the phenyl ring increases the electron densities at the β- and δ-carbons (unfield shift) while it does decrease the electron densities at the α- and γ-carbons (downfield shift) of PBD.

Another interesting finding is that the ρ values are essentially equal for the β- and δ-carbons, 5.07 and 4.74. That is, the attenuation factor of C=C double bond in transmitting the substituent effects is close to unity (0.93) in the conjugated system. These ρ values are comparable with the value for the β-carbon of

Table 1. Chemical shifts[a] of side-chain carbons and protons of substituted *trans*-1-phenyl-1,3-butadienes

Substituent	α-C	β-C	γ-C	δ-C	γ-H	δ-H (*cis*)	δ-H (*trans*)
p-CH_3	134.0	128.5	137.4	116.2	6.310	5.207	5.061
m-CH_3	133.0	128.8	137.3	116.6	6.390	5.208	5.075
H	133.0	129.3	137.3	117.3	6.401	5.237	5.092
p-Cl	131.4	130.0	136.9	118.2	6.388	5.266	5.138
m-Cl	130.8	131.4	136.9	118.7	6.380	5.259	5.142
ρ[b]	−5.80	5.07	−1.04	4.74		0.113	0.162
s[c]	0.49	0.65	0.17	0.24		0.029	0.019
r[d]	0.990	0.976	0.963	0.996		0.913	0.980

a) In ppm from TMS. b) In ppm/σ. c) Standard deviation of ρ. d) Correlation coefficient.

Table 2. Chemical shifts[a] of side-chain carbons and protons of substituted phenylallenes

Substituent	α-C	β-C	γ-C	α-H	γ-H
p-CH_3	95.7	210.7	79.9	6.031	5.044
m-CH_3				6.025	5.058
H	95.4	210.2	79.8	6.069	5.064
p-Cl	94.5	210.2	80.2	6.035	5.092
m-Cl	94.6	210.2	80.3	6.033	5.130
ρ[b]	−2.33	−0.80	0.88		0.151
s[c]	0.57	0.47	0.32		0.016
r[d]	0.944	0.769	0.890		0.984

a) In ppm from TMS. b) In ppm/σ. c) Standard deviation of ρ. d) Correlation coefficiemt.

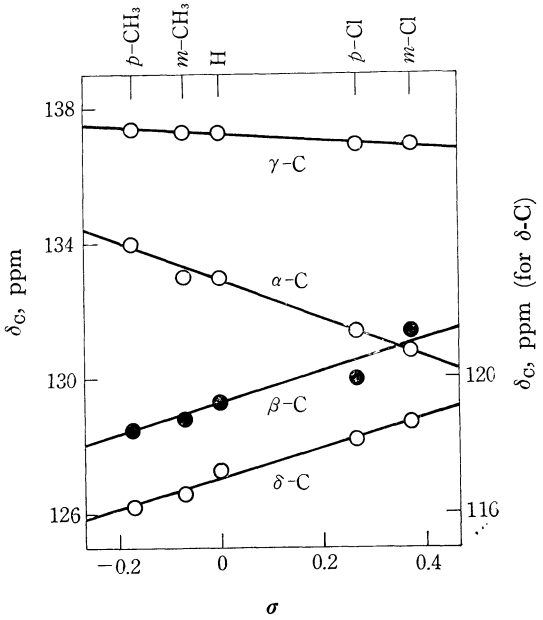


Fig. 1. Hammett-type plots of the ^{13}C chemical shifts of the side-chain carbons of *trans*-1-phenyl-1,3-butadienes.

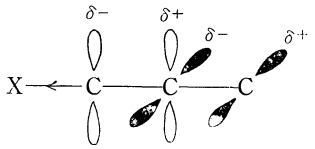
styrene (4.73).[5]

As for the PMR data, a fairly good linear correlation was obtained between the *trans*-δ-proton chemical shifts and Hammett's σ values with $\rho=0.162$ ppm/σ. The sign is the same as that for the δ-carbon shift. The attenuation factor of the $C_\gamma=C_\delta$ bond is, however, *ca.* 0.5; the ρ value for the *trans*-β-proton shift of styrene is 0.335.[6]

The different efficiencies of the carbon chain in transmitting the substituent effects on the ^{13}C and ^{1}H chemical shifts contradict the earlier suggestion that ^{1}H shift mainly reflects the electron density of the attached carbon.[7] The ^{13}C shift was concluded on a sound basis to be determined predominantly by the electron density on the carbon atom of question.[8] Therefore, it is very likely that some other factors contribute to the determination of ^{1}H shift. Kajimoto and Fueno[9] pointed out that ^{1}H chemical shift is influenced by electron densities on both the hydrogen atom in question and the carbon atom directly bonded to it and that they very often show different dependence on a structural perturbation. This type of anomaly between ^{13}C and ^{1}H chemical shifts is becoming apparent as CMR data are accumulated.

Allenic System. The chemical shifts of side-chain carbons of PA's summarized in Table 2 show little dependency on the ring substitution. The ρ values were calculated and included in Table 2. The ρ values for the α-, β-, and γ-carbons are negative, nearly zero, and slightly positive, respectively.

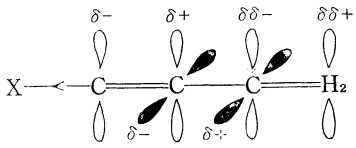
These observations might be explained by considering the polarization of π-electrons like



The opposite sign of ρ values between the α- and γ-carbons is understandable by this polarization. The net change in the electron density at the β-carbon would be very small owing to the cancellation of contributions from two orthogonal p-orbitals. This could be a reason for the low ρ value for the β-carbon shift.

On the other hand, chemical shifts of the γ-protons of PA show a fairly good linear correlation with Hammett's σ values. The ρ value is not very small (0.151 ppm/σ), being comparable with that for the δ-proton of PBD.

This distinctive difference between ^{13}C and ^{1}H shifts at the γ-position of PA seems to suggest that some special mechanism of electron polarization is operative in the side-chain bonds of PA. One possible explanation is a hyperconjugative model like



That is, electrons in the orbitals parallel to α-β π-orbitals are alternately polarized like conjugated diene, using the pseudo π-orbital of the γ-hydrogens. This may also explain the small ρ value for the γ-carbon shift. The hyperconjugative interaction may be effective because of the rigid structure of allene with favorable orientation of the γ-hydrogens.

Experimental

Materials. Preparations of *trans*-1-phenyl-1,3-butadiene (PBD) and phenylallene (PA) and their ring-substituted derivatives were described previously.[10,11]

NMR Measurements. The CMR spectra of a neat liquid of PBD derivatives and of a 50% solution in CS_2 of PA derivatives were recorded at 24 °C on a JEOL C-60 HL spectrometer with a 15.09 MHz RF unit as described previously.[2,3]

The PMR spectra were obtained on a JNM 4H-100 spectrometer at room temperature (~22 °C). A 10% solution of a sample in CCl_4 was used for the measurement. TMS was used as internal standard.

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