The Substituent Effects on the Chemical Shifts for Substituted Benzyl Acetates

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A number of studies of the NMR spectra of substituted benzene derivatives, with particular attention paid to substituent effects, have been reported in the literature.[1-6] The relative chemical shifts arising from substituent effects have been known to be affected primarily by changes in the local electron-charge-density distribution caused by the substituents. The substituent effects have been discussed in terms of electronic transmission for the system of X-C_6H_4-Y-H, where X = the substituent,

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C_6H_4-Y=the transmitting group, and H=the terminal proton in the side chain.[6,7] However, there has been no report on the molecules where the terminal proton is separated from the aromatic ring by four atoms.

This study will deal with substituted benzyl acetates ($Y=CH_2O\underset{\underset{O}{\|}}{C}CH_2$), which were originally studied as model compounds for side chains of poly-β-(*p*-substituted)-benzyl-L-aspartates.[8]

The insertion of the $-O\underset{\underset{O}{\|}}{C}-$ group between two methylene groups of ethylbenzene ($Y=CH_2CH_2$) was found to attenuate the electronic transmission to a lesser extent.

Experimental

Materials. The substituted benzyl acetates were prepared by the reaction of benzyl chlorides with potassium acetate. They were purified by distillation or recrystallization, and were checked by elementary analyses and by a study of their IR and NMR spectra.

Measurements. The NMR spectra were recorded on a Varian A-60 spectrometer. The magnet-gap temperature was 31°C. The chemical shifts were determined by the side-band technique relative to tetramethylsilane (TMS) as the internal standard. The concentrations were in the 0.2—0.15 mol/*l* range in a carbon tetrachloride solution; the dilution shifts were examined for in four compounds, but were not found. The data shown are the mean values of five measurements and are precise to ±0.2 cps.

Results and Discussion

The chemical shifts of the acetyl protons and the benzylic methylene protons of substituted benzyl acetates in a carbon tetrachloride solution are shown in Table 1. Figure 1 shows the plots of the relative chemical shifts against the Hammett σ constants. The relative chemical shifts have been correlated with several substituent constants, such as σ^0, σ^+, σ^-, σ_I, and σ_R. In the present study, however, the plottings against these constants do not improve greatly and lead to such correlations as are shown in Fig. 1.

TABLE 1. CHEMICAL SHIFTS FOR METHYL AND METHYLENE PROTONS OF BENZYL ACETATES IN CARBON TETRACHLORIDE

Substituent X	$-\nu_{CH_3}$ (in cps)	$-\nu_{CH_2}$ (in cps)	σ_p or σ_m
p-OCH_3	119.4	296.5	−0.268
p-CH_3	120.2	298.2	−0.170
p-Cl	121.6	299.5	+0.227
p-Br	121.8	298.6	+0.232
m-Cl	123.3	300.4	+0.373
H	121.8	301.5	0.000
p-CN	124.4	305.5	+0.628
p-NO_2	125.2	308.0	+0.778
m-NO_2	125.7	308.5	+0.710

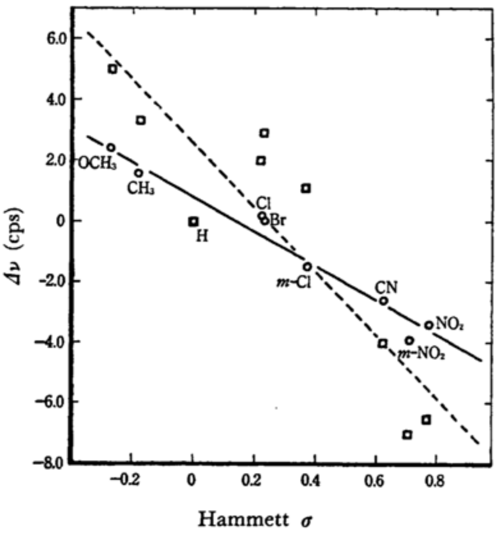

Fig. 1. Plots of the relative chemical shifts in substituted benzyl acetates against Hammett σ.
—○—: Acetyl methyl protons
---□---: Benzylic methylene protons

In the present study the substituent effects are examined in the form of the Hammett equation, $\Delta\nu=\rho\sigma+\Delta\nu_0$,[6] in order to make possible the comparison of the present data with those published for related series of compounds. The constants in this equation were obtained by the least-squares method. Table 2 lists the constants thus obtained, together with some of the published data. The ρ values in Table 2 represent a measure of the transmission of electronic effects of the substituent, X, through the side chain, Y, in the X-C_6H_4-Y-H type.

The ρ values for methylene and methyl protons of benzyl acetates are −10.45 and −5.63 respectively. This may indicate that substituent effects are decreased to about a half by the side-chain, $-O\underset{\underset{O}{\|}}{C}CH_2-$, group. On the other hand, the ρ value for methyl protons of ethylbenzene is about a half of that for toluene (ρ-ethylbenzene/ρ-toluene=0.53), as shown in Table 2. This means that the methylene group in the side chain transmits about a half of the electronic effects. For the carbonyl group, the transmission of electronic effects may be estimated to be 0.65 from the ρ values for the methyl protons of acetophenones and toluenes. On the other hand, the insertion of an oxygen atom into toluene, that is, anisole, increases the electronic effects (ρ-anisole/ρ-toluene=1.26). The oxygen atom is known to be a superconducting

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TABLE 2. ρ VALUES OBTAINED FROM HAMMETT EQUATION FOR NMR CHEMICL SHIFTS

$X\text{-}C_6H_4\text{-}Y\text{-}H$	Number of atoms in Y	$-\rho$[a]	$\Delta\nu_0$[b]	r[c]	S[d]	Ref.
$Y=CH_2$	1	12.8	2.0	0.884	2.56	6
CH_2CH_2	2	6.76	0.6	0.967	0.789	5
OCH_2	2	16.2	−0.61	0.891	0.044	4
$\underset{\overset{\|}{O}}{C}CH_2$	2	8.34	1.5	0.975	0.895	6
$CH_2O\underset{\overset{\|}{O}}{C}CH_2$	4	5.63	0.77	0.974	0.531	
$(X\text{-}C_6H_4\text{-}\underline{CH_2}O\underset{\overset{\|}{O}}{C}CH_3)$	—	10.45	2.56	0.898	2.133	

a) ρ Values are given in the units of cycle per second per Hammett σ unit.
b) The intercept. c) The correlation coefficient. d) The standard deviation.

group.[6] For the methyl protons of substituted benzyl acetates, the ρ value is found to be similar to that reported for the methyl protons of substituted ethylbenzenes, even though benzyl acetate corresponds to the insertion of an ester group $(-O\underset{\overset{\|}{O}}{C}-)$ between the methylene and methyl groups of ethylbenzene. If the ester group can be regarded simply as a combination of oxygen and the carbonyl group in relation to the transmission of electronic effects, the ester group may somewhat decrease the electronic transmission $(1.26\times0.65=0.82)$. The ρ value of benzyl acetates can, then, be estimated as about -5.54 $(=0.82\times\rho\text{-ethylbenzene})$. This value is very close to the ρ value of -5.63 observed for benzyl acetates.

The methylene group of the side chain attenuates about a half for the transmission of the electronic effects of substituents, while the ester group does so slightly. The latter can be accounted for by a combination of the transmission properties of the oxygen atom and the carbonyl group.[9] The present study shows that the substituent effects on the chemical shifts of the terminal proton in the side chain of benzyl acetates can be estimated, if only roughly, by a simple combination of the transmission property of each group involved in the side chain.

Anomalous behavior in halogen substituents, deviating from the correlation line, has been established.[10] As is evident from Fig. 1, considerable deviations were found for the methylene protons, whereas slighter deviations were found for the methyl protons. The deviations observed for the latter are decreased more than was to be expected from the decrease in the ρ value. Slighter deviations similar to these can be estimated for the methyl protons of acetophenones.[8,6] These facts suggest that the deviation of halogen substituents is primarily due to anisotropy and to field effects, which are consistent with the following finding. It should be noted that good linear correlation-lines, even including halogen substituents, were found among the chemical shifts of three series of benzylic protons: toluenes *vs.* ethylbenzenes $(\Delta\nu_{CH_2\text{-ethylbenzene}}=+1.08\Delta\nu_{CH_3\text{-toluene}}-1.08,\ S=0.605,\ r=0.995)$, toluenes *vs.* benzyl acetate $(\Delta\nu_{CH_2\text{-benzyl acetate}}=+0.84\Delta\nu_{CH_3\text{-toluene}}+0.61,\ S=0.156,\ r=0.996)$. This finding indicates that the anomalous effects of halogen substituents are almost identical among the protons attached to the α-carbon atoms, even in different side-chains.[10]

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[9] This is consistent with the kinetic results that similar σ values have been found for the saponifications both of substituted benzyl benzoates $(\sigma=0.990)$ and of substituted ethyl phenylacetates $(\sigma=0.978)$; Y. Yukawa, Y. Tsuno and M. Sawada, *ibid.*, **39**, 2274 (1966).

[10] In private discussion, Dr. Yuho Tsuno suggested that he and his coworkers have found similar evidences for other series of compounds.