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Enolate Anions. II. Substituent Effects of Sodium Ethyl Phenylacetates in DMSO[1)]

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The UV-visible, IR, and ^{1}H-NMR spectra of the sodium enolates of ethyl phenylacetates (substituents; p-CH$_3$O, p-CH$_3$, m-CH$_3$, H, p-Cl, p-CH$_3$CO, m-CH$_3$CO, p-COOC$_2$H$_5$, p-CN, and p-NO$_2$) in DMSO were measured at room temperature. The derivatives with electron-attracting groups at the *para* position exhibit their absorption maxima with $\varepsilon > 10^4$ in visible regions above 400 nm. The visible spectra suggest the presence of a resonance between their electron-attracting groups at the para position and the enolate anion parts through the benzene ring. The carbonyl-stretching vibrations of the enolates in the IR spectra and the chemical shifts of the residual methine proton of the enolates in the ^{1}H-NMR spectra can be well explained by using the substituent constants, σ and σ^-. The ρ values of the *meta* and *para* lines are extremely different. In the case of the p-NO$_2$ derivative, the ^{1}H-NMR spectra of the benzene-ring protons indicate that the free rotation of the partially double bond between the benzene ring and the enolate-anion part is fixed at room temperature.

The methylene protons adjacent to the electron-attracting groups, such as the nitro, cyano, and ester groups, are acidic enough to give anions when treated with sodium hydride.[2)] Such an anion is not a localized carbanion, but a delocalized enolate anion, as well as one derived from ketone.[3)] Studies of the structure of the metal enolate anions are rapidly increasing in number, though they are almost entirely restricted to mono- and diketones.[4)] Zaugg *et al.* have pointed out that the reactivity of enolate anions depends on the states of the ions and ion-pairs. However, spectroscopic studies of enolate anions have not given more definitive results about the states of ions and ion-pairs than about those of carbanions.[5,6)]

The states of the ions and ion-pairs of enolate anions were mainly presumed on the basis of kinetic evidence. In the alkylation of enolate anions, the reaction rate was greatly accelerated by the addition of dipolar aprotic solvents, such as DMSO and DMF. The enhanced rate was explained on the basis of the presence of more dissociated species (free ions and solvent-separated ion-pairs) in the reaction.[5)]

In DMSO, the ^{13}C-NMR spectra of the enolate anions of some diethyl alkylmalonates apparently gave a simple pattern which could be assigned to only one species at room temperature.[1)] So long as sodium metal is used as a counter cation, the metal cation can be sufficiently solvated with the dipolar aprotic solvent. Therefore, the apparent species in the ^{13}C-NMR spectra seem to depend on the equilibrium among some predominant configurations of the enolate anion on an NMR time scale. The structure of the sodium enolate anions, derived from ethyl phenylacetates, may be determined by means of the steric and electronic stabilities of the configuration and/or the conformation of the enolate-anion part in DMSO.

In spite of the importance of the electronic perturbation in estimating the reactivity of enolate anions, the substituent effects have scarcely been investigated at all. This paper will deal with the substituent effects in the UV-visible, IR, and ^{1}H-NMR spectra of enolate anions and the correlation between the effects and their configurations.

Results and Discussion

Molecular spectroscopy (UV-visible and IR) can generally reflect the configurations and conformations of substrates in solution, while magnetic resonance spectroscopy gives some informations about structure, including the proportions of the configurations and dynamic information about the transformation process among the configurations. A systematic examination of substituent effects in the UV-visible, IR, and ^{1}H-NMR spectra of enolate anions can clarify the alteration in their structure by substituents.

UV-Visible Spectra. In writing the resonance structures for the benzylic anion, the coplanarity of the ring with the α-methylene group is implied, because there can be an effective overlap between the p-orbital of the α-carbon with the unshared pair of electrons and the p$_\pi$-orbitals of the benzene ring.[7)] The UV-visible spectrum of benzyllithium was observed at 330 nm ($\lambda_{\max}$) with an absorption intensity of log ε=3.98 (yellow color).[8)] The enolate anion of ethyl phenylacetate gave the absorption maximum at 345 nm. It can, therefore, be presumed that this enolate anion has a resonance structure, analogous to the benzyl anion.

Table 1 shows the data of the UV-visible spectra of the enolate anions. The absorption maxima of the

Table 1. UV-visible spectra of enolate anions of ethyl (p-substituted phenyl)acetates[a)]

Substituent	$\lambda_{\max}$	$\varepsilon_{\max}$	Color
MeO	340	—[b)]	yellow
Me	345	—[b)]	yellow
H	345	—[b)]	yellow
Cl	350	—[b)]	yellow
COOEt	428	0.84×10^4	yellow
CN	405	2.17×10^4	yellow-green
MeCO	453	1.73×10^4	yellow-red
NO$_2$	548	3.30×10^4	violet
	580	3.00×10^4	

a) These original esters have no absorption bands in the UV-visible region (300—700 nm). b) Accurate $\varepsilon_{\max}$ values could not be obtained at low concentrations (10^{-5} mol/dm^3).

enolate anion with electron-releasing substituents and hydrogen at the *para* position are present at the range of 340—350 nm. The overlaps between the p-orbital of α-carbon and the p_π-orbitals of the benzene ring are of nearly the same degree as in these enolate anions because of similar λ_{max}. The absorption maxima of these enolate anions are mostly extinguished by dilution with DMSO to a concentration of 10^{-5} mol/dm^3, so that the accurate ε_{max} can not be obtained. This may be attributed to the presence of an equilibrium between the enolate anions and DMSO.

On the other hand, the enolate anions which have electron-attracting substituents at the *para* position are stable at low concentrations (10^{-5} mol/dm^3) because of the high acidity enhanced by these substituents. The more bathochromic shifts of λ_{max} were observed in the region above 400 nm for the more electron-attracting groups, which are conjugated with the enolate-anion part through the benzene ring. The marked tendency of the enolate anions to show a bathochromic effect is similar to that of phenolate anions.[9] Hence, the pattern of the additional resonance of the enolate anions seems not to be far from that of the phenolate anions. Two adsorption maxima with nearly equal intensities were observed in the case of the enolate anions of ethyl *p*-nitrophenylacetate; these are characteristic of *para* nitro substituents.[10]

Table 2. IR spectra of ethyl phenylacetates and these enolate anions in DMSO
Carbonylstretching vibration (cm^{-1}).

Substituent	Original ester	Enolate anion
p-MeO	1727	1588
p-Me	1726	1588
m-Me	1726	1587
H	1724	1589
p-Cl	1725	1591
p-COOEt[a)]	1728	1617
p-CN[a)]	1728	1622
p-MeCO[a)]	1727	1618
m-MeCO	1726	1593
p-NO$_2$[a)]	1730	1640

a) The other characteristic absorption bands were observed in the enolate anions with electron-attracting substituents at the *para*-position.

p-COOE	1555, 1515 cm^{-1}
p-CN	1555, 1510 cm^{-1}
p-MeCO	1550, 1515 cm^{-1}
p-NO$_2$	1575, 1520 cm^{-1}

IR Spectra. Table 2 shows the wave numbers of the carbonyl (CO) stretching vibrations in the ethyl phenylacetates and their enolate anions. These wave numbers are very important in examining the electron density at the CO double bond. The original esters have definite wave numbers (1724—1730 cm^{-1}) in spite of the variation in the substituents. The CO stretching vibration bands of enolate anions are illustrated by some typical representative spectra (*p*-Cl and *p*-CN) in Fig. 1.

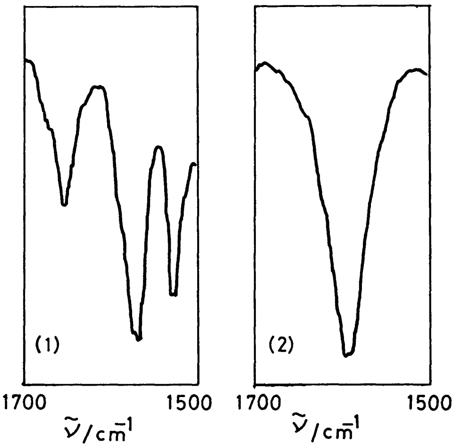
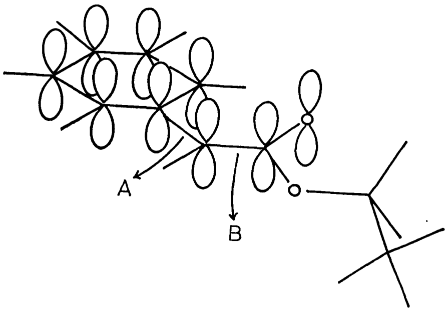


Fig. 1. The carbonyl streching vibration bands (1500—1700 cm^{-1}) of enolate anions; (1) *p*-CN derivative, (2) *p*-Cl derivative.

The enolate anions with substituents other than *para* electron-attracting substituents give only one absorption band with a strong intensity in the region of 1587—1593 cm^{-1}, like the *p*-Cl derivative in Fig. 1. In the enolate anion of ethyl phenylacetate, the CO absorption band was observed at a lower frequency, 135 cm^{-1}, than in the original ester. This low-frequency shift indicates an increase in the electron density of the polarized CO bond in the enolate anion.

In contrast, the enolate anions with *para* electron-attracting substituents gave one CO absorption band with a medium intensity, together with two other absorption bands (1575—1550 and 1520—1510 cm^{-1}) which seem to be attributable to the resonance. The stronger electron-attracting ability of the substituent shifts the CO stretching absorption band of the enolate anion to a higher frequency region; in the *para* nitro derivative, the absorption band was obtained 51 cm^{-1} higher than in the *para* hydrogen derivative. This high-frequency shift suggests that the delocalized electrons flow into the benzene ring rather than being present in the polarized CO bond.

^{1}H-NMR Spectra. The ^{1}H-NMR measurements of enolate anions are useful for the investigation of the structures in solution.[11] On the basis of a consideration of molecular models of the enolate anion derived from ethyl phenylacetate, one of the stable configurations is illustrated below:



In the above figure, the A bond forms the maximum overlap between the p-orbital of the enolate-anion part and the p_π-orbitals of the benzene ring, while the benzene ring is located at a position *trans* to the ethoxyl group with respect to B bond. For detailed descriptions

Table 3. ^{1}H-NMR chemical shifts of ethyl phenylacetates in DMSO-d_6

The chemical-shift values are indicated by means of a δ scale.

Substituent		$\overset{\alpha}{\text{X-C}_6\text{H}_4\text{-CH}_2}$ α	$\text{-COO-}\overset{\beta}{\text{CH}_2}$ β	$\overset{\gamma}{\text{-CH}_3}$ γ
p-MeO	a)	3.61	4.14	1.19
	b)	3.34	3.60	1.11
	c)	+0.27	+0.54	+0.08
p-Me	a)	3.69	4.14	1.18
	b)	3.38	3.98	1.13
	c)	+0.31	+0.16	+0.05
m-Me	a)	3.65	4.15	1.20
	b)	3.38	3.64	1.20
	c)	+0.27	+0.51	0.00
H	a)	3.71	4.41	1.18
	b)	3.45	3.59	1.14
	c)	0.26	+0.55	+0.04
p-Cl	a)	3.75	4.18	1.21
	b)	3.42	3.75	1.13
	c)	+0.33	+0.43	+0.08
p-COOEt	a)	3.83	4.18	1.21
	b)	4.01	3.54	1.11
	c)	−0.18	+0.64	+0.10
p-CN	a)	3.94	4.20	1.24
	b)	4.14	3.90	1.13
	c)	−0.20	+0.30	+0.11
p-MeCO	a)	3.85	4.18	1.23
	b)	4.28	3.90	1.13
	c)	−0.43	+0.28	+0.10
m-MeCO	a)	3.85	4.19	1.23
	b)	3.50	3.54	1.10
	c)	+0.35	+0.65	+0.13
p-NO_2	a)	3.94	4.22	1.24
	b)	4.75	4.01	1.18
	c)	−0.81	+0.21	+0.06

a) Chemical shifts of original esters. b) Chemical shifts of enolate anions. c) Differences (a—b). A plus sign represents a high-field shift.

of the configurations, these two partially double bonds (A and B) are very important.

As the rotational barrier of the B bond in the enolates derived from ethyl phenylacetates is assumed to be of a similar degree to that of the partially double bond in lithio isobutyrophenone (>27 kcal mol^{-1}),[12] the rotation about the B bond may be restricted and fixed to a preferential *trans* configuration at room temperature. On the other hand, the A bond would be allowed to rotate at room temperature, because the analogous partially double bond in stryl anions has rotational barriers (11—14 kcal mol^{-1})[13] which are clearly connected with the delocalization of the negative charge into the benzene rings. Table 3 shows the ^{1}H-NMR chemical shifts of the alkyl parts in enolate anions derived from ethyl phenylacetates. From the simple pattern of the observed spectra of the alkyl parts, the species in the solution can be attributed to only one structure, which presumably corresponds to the *trans* configuration.[14] The chemical shifts of $-CH_2-$ and $-CH_3$ in the enolate anions are observed at higher fields (+0.2—+0.6 and <+0.1 ppm, respectively) than those of the original esters. The chemical shifts of the residual active methine proton are obtained at fields +0.2—+0.6 ppm higher than those of original esters; these shifts evidently show substituent effects.

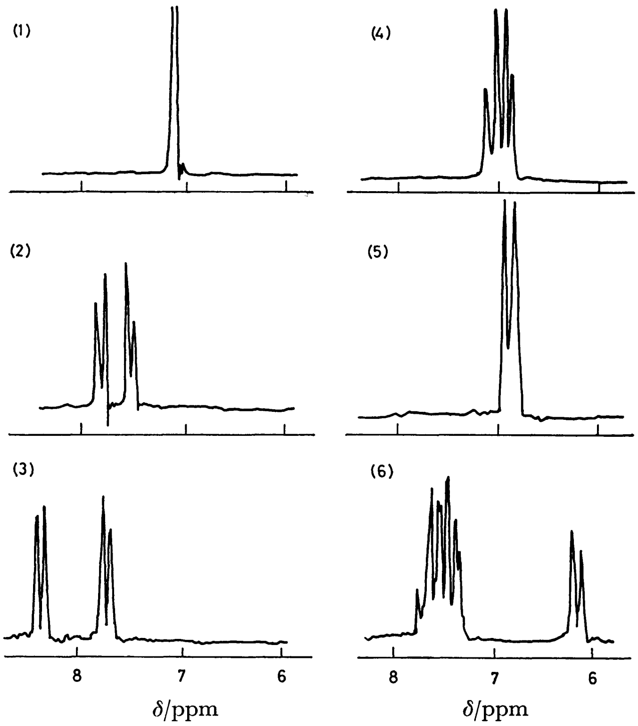


Fig. 2. The ^{1}H-NMR spectra of original esters [(1), (2), (3)] and enolate anions [(4), (5), (6)] at δ 6—8 ppm; (1), (4): *p*-Me derivative, (2), (5): *p*-CN derivative, (3), (6): *p*-NO_2 derivative.

The ^{1}H-NMR spectra of benzene-ring protons are shown in Fig. 2 (*p*-CH_3, *p*-CN, and *p*-NO_2 compounds). In the *p*-CH_3 derivative, the apparent singlet pattern of benzene-ring protons in the original ester is changed to the AB pattern in the enolate anion. In the *p*-CN derivative, the apparent AB pattern of benzene-ring protons in the original ester is changed to a doublet pattern with a large high-field shift in the enolate anion. The ^{1}H-NMR patterns of the benzene-ring protons in these enolate anions are symmetrical, as has been mentioned above. Such observations suggest that the partially double bond A has a free rotation because of the equivalence in the magnetic environments of two *ortho* protons and two *meta* protons. In the *p*-NO_2 derivative, however, the symmetric AB pattern of the benzene-ring protons in the starting ester changed to a dissymmetric pattern with an extreme high-field shift (at 6.32 ppm) of one proton, distinguished from three benzene-ring protons, in the enolate anion. The partially double bond A in the *p*-NO_2 enolate anion is assumed to be almost fixed on the basis of this observation.[14] Such a greatly enhanced double-bond character of the A bond is also supported by the chemical shift (4.75 ppm) of the residual methine proton in the *p*-NO_2 enolate anion, measured in the olefinic regions.

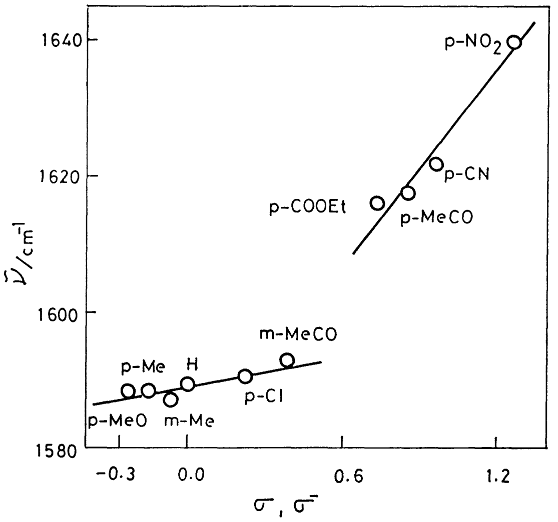


Fig. 3. Hammett plot of the frequencies of carbonyl stretchings in enolate anions of ethyl substituted phenylacetates.

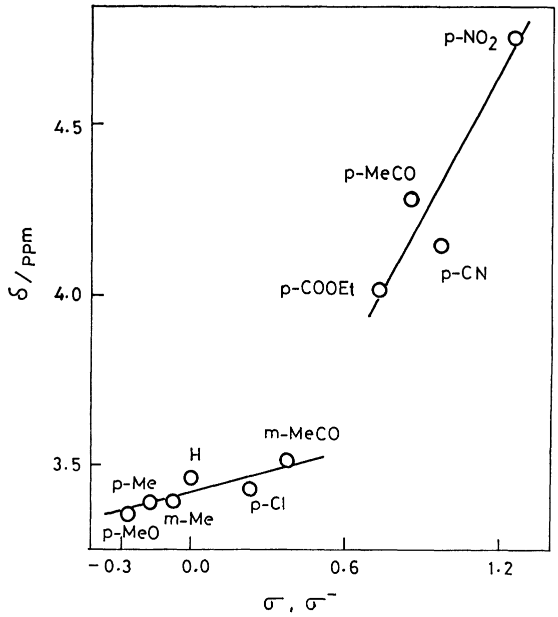


Fig. 4. Hammett plot of the chemical shifts of residual methine proton in enolate anions of ethyl substituted phenylacetates.

Substituent Effects. It has been reported[15] that there is a good linear correlation between the CN stretching-vibration bands of the anions derived from substituted benzyl cyanides and the substituent constants, σ^-. The substituent effects related to anion system are generally correlated by σ^- constants.[16] The CO stretching-vibration bands of the enolate anions derived from ethyl phenylacetates are plotted against σ and σ^- in Fig. 3, which shows two characteristic lines. The plot of the chemical shifts of the residual methine protons *vs.* σ and σ^- is similar to that of the CO wave numbers, as is shown in Fig. 4.

These two lines, which constitute a meta-line of both meta substituents and para electron-releasing substituents for σ and a *para*-line of *para* electron-attracting substituents for σ^-, have extremely different ρ values, suggesting that two different mechanism are required to account for the substituent effects in a sodium-phenylacetate system. The behavior promoted by *para* electron-attracting substituents is consistent with all the observations of the UV-visible, IR, and ^{1}H-NMR spectra of the enolate anions presented above.

Experimental

Materials. Substituted phenylacetic acids and the ethyl esters were prepared according to the following routes:

1. The phenylacetic acids (*p*-CH_3O, *p*-CH_3, and *m*-CH_3) were synthesized by the Willgerodt reaction of the acetophenones[17,18] derived from the corresponding substituted benzoic acids.
2. The ethyl phenylacetates (*p*-CH_3CO and *m*-CH_3CO) were synthesized by the acetylation[19] of ethyl phenylacetate.
3. The phenylacetic acids (*p*-Cl, *p*-NO_2, *p*-CN, and *p*-$COOC_2H_5$) were synthesized by the nitration[20] of phenylacetonitrile, hydrolysis,[21] reduction,[22] and a Sandmyer reaction.[23] Thease synthesized compounds were identified by means of the IR and ^{1}H-NMR spectra and by CHN elementary analysis. The bp's or mp's of the esters are shown in Table 4, together with the literature values.

Preparation of Enolate Anions. Sodium hydride (NaH), the mineral oil having been washed out with dry DMSO, was added to DMSO (2—3 cm^3) in a 50 cm^3 three-necked flask equipped with a gas-inlet tube, a condenser, and a magnetic stirrer. Under an argon atmosphere, ethyl phenylacetates, equivalent to the NaH, in dry DMSO (1 cm^3) were added to the solution, and the resulting mixture was stirred for 30 min at room temperature. According to the above

Table 4. Physical constants of ethyl phenylacetates

Compound	Bp or mp
p-MeO	bp 120 °C/4 mmHg[g] (bp 143—144 °C/11 mmHg)[a,b]
p-Me	bp 88—90 °C/4.5 mmHg (bp 134—135 °C/25 mmHg)[b]
m-Me	bp 90—94 °C/5 mmHg (bp 122—123 °C/18 mmHg)[b]
p-Cl	bp 100—102 °C/2 mmHg (mp 33—33.5 °C)[b,c]
p-COOEt	bp 144—146 °C/3 mmHg (bp 312—313 °C)[d]
p-CN	mp 93 °C (mp 87—88 °C)[c]
p-MeCO	bp 110—117 °C/2 mmHg (mp 67—68 °C)[e]
m-MeCO	bp 156 °C/5 mmHg (bp 118 °C/0.5 mmHg)[e]
p-NO_2	mp 64 °C (mp 63 °C)[f]

a) Ref. 18. b) R.O.C. Norman, G.K. Radda, D.A. Brimacombe, P.D. Ralph, and E.M. Smith, *J. Chem. Soc.*, **1961**, 3247. c) Ref. 22. d) M. Fileti and G. Basso, *Gazz. Chim. Ital.*, **21**, 52 (1891). e) Ref. 19. f) Ref. 21. g) 1 mmHg = 133.322 Pa.

procedures, the solution of the enolate anions was about 0.5 mol/dm^3. Spectral-grade DMSO (Dojinyaku Kagaku) was used for the measurements of the visible and IR spectra, and DMSO-d_6 (Merck), for the measurements of the ^{1}H-NMR spectra.

Measurement of Visible Spectra. The prepared enolate solution was diluted to 10^{-4} mol/dm^3, transferred into a crystal cell (d=1 cm), covered with argon, and measured over the range of 300—700 nm, using a Hitachi 557 Double-wavelength Double-beem Spectrophotometer.

Measurement of IR Spectra. The prepared enolate solution was diluted to 0.2 mol/dm^3, transferred into a liquid cell (d=0.2 mm), and measured using a JASCO A-302 Diffraction Grating Infrared Spectrophotometer.

Measurement of ^{1}H-NMR Spectra. The prepared enolate solution (0.5 mol/dm^3) was transferred into a NMR tube (ϕ=5 mm) filled with argon, sealed, and measured using a JEOL MH-100 NMR Spectrometer (100 MHz). The proton signals present in the solvent, 99% DMSO-d_6, were employed as an internal standard for the chemical shifts.

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