Enolate Anions. IV. The ^{13}C NMR Spectra of Sodium Enolates of Ethyl Phenylacetates in DMSO[1)]

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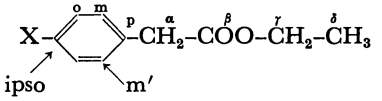
Synopsis. The ^{13}C NMR spectra of the sodium enolates of ethyl (*p*-substituted phenyl)acetates are presented. The polar interactions between the substituents and the anionic moiety in the sodium enolates are estimated by means of their ^{13}C chemical shifts.

In previous papers,[1)] the ^{13}C NMR data of sodium enolate from diethyl malonates were reported and the substituent effects on the structures of the enolate anions from ethyl phenylacetates and diethyl malonates in DMSO were investigated by means of their UV-visible, IR, and ^1H NMR spectra. The ^1H chemical shifts of the residual methine protons of the sodium enolates from ethyl phenylacetates were correlated to the σ^- constant as well as the carbonyl-stretching vibrations of the enolates. The substituent effects seem mainly to depend on the variation in the electron density of the delocalized-anion moiety. The studies of the IR and ^1H NMR spectra of sodium enolates prepared from ethyl phenylacetates found the existence of extremely different ρ values for meta-line and para-line against σ and σ^-, and suggested two different modes of explanation of the substituent-transmission mechanism. Many workers have reported on the correlations between the ^{13}C substituent chemical shifts (^{13}C SCS) and the relative electron densities on the carbon atoms of interest.[2)]

Table 1 shows the ^{13}C chemical shifts of the parent ester (A) and their sodium enolates (B) and the chemical-shift differences ($\Delta\delta$), which are given by $\delta_A-\delta_B$. These ^{13}C chemical shifts were assigned according to the additivity rule.[3)] In the case of the NO derivative, all benzene-ring ^{13}C signals of the enolate were distinguished because of the fixation of the partial double bond between the benzene ring and the enolate-anion moiety on the NMR time scale, as supported by ^1H NMR.[1b)] The nonequivalence of the two signals of C-m and C-m′ in the enolates with the CN and MeCO substituents is also supported by such a partial double-bond character.

The $\Delta\delta$ values at C-α and C-p were observed as downfield shifts, while those at C-γ and C-ipso were observed as upfield shifts, despite the kinds of substituents. The $\Delta\delta$ values at C-m and C-o are very small. The signs of the $\Delta\delta$ values at C-β are plus (downfield shifts) with electron-releasing substituents and minus (upfield shifts) with electron-attracting substituents. An analogous trend has also been found in

TABLE 1. THE ^{13}C NMR CHEMICAL SHIFTS (δ FROM TMS) OF ETHYL (*p*-SUBSTITUTED PHENYL)-ACETATES AND THEIR SODIUM ENOLATES IN DMSO-d_6



X		C-δ	C-γ	C-β	C-α	C-p	C-m	C-m′	C-o	C-ipso	X-part		
NO_2	A)[a)]	14.5	60.7	172.8	40.9	144.6	132.8		125.3	149.0			
	B)	16.0	57.5	168.4	88.4	152.1	{117.4	b)	121.1}	117.3			
	C)	+1.5	−3.2	−4.4	+47.5	+7.5	{125.6		126.4}	−31.7			
CN	A)	14.5	61.6	172.9	41.1	142.4	132.6		134.2	111.6	120.6		
	B)	16.6	56.3	167.8	74.9	152.3	133.2	124.5	131.7	89.9	103.6		
	C)	+2.1	−5.3	−5.1	+33.8	+9.9	+0.6	−8.1	−2.5	−21.7	−17.0		
MeCO	A)	14.5	61.5	173.1	41.1	142.1	131.6		130.2	137.7	200.3	27.2	
	B)	16.5	56.3	167.9	76.6	153.3	130.5	128.8	130.0	121.9	192.7	26.1	
	C)	+2.1	−5.2	−5.2	+35.5	+11.2	+1.1	−2.8	−0.2	−15.8	−7.6	−1.1	
COOEt	A)	14.4	61.6	172.9	41.2	141.9	{131.5	b)	131.1}	130.8	168.0	61.6	14.4
	B)	16.6	56.1	167.6	74.7	153.2	{130.1		130.2}	111.7	167.4	59.4	16.5
	C)	+2.2	−5.5	−5.3	+33.5	+11.3				−19.1	−0.6	−2.2	+2.1
Cl	A)	14.8	61.7	173.4	41.0	135.8	133.3		130.6	134.3			
	B)	19.5	56.9	178.2	45.8	139.6	132.1		128.5	127.7			
	C)	+4.7	−4.8	+4.8	+4.8	+3.8	−1.2		−2.1	−6.6			
H	A)	14.3	61.4	173.6	41.3	136.6	131.3		130.3	128.7			
	B)	19.5	56.9	176.4	46.9	140.7	130.2		128.6	126.0			
	C)	+5.2	−4.5	+2.8	+5.6	+4.1	−1.1		−1.7	−2.7			
Me	A)	14.5	61.2	173.7	41.1	133.6	130.1		130.1	138.1	21.1		
	B)	19.1	57.3	179.4	46.0	138.8	131.1		129.8	136.0	21.3		
	C)	+4.6	−3.9	+5.7	+4.9	+5.2	+0.1		−1.2	−2.1	+0.2		
MeO	A)	14.4	61.2	173.7	40.5	128.4	115.5		132.2	160.8	55.9		
	B)	19.3	57.4	180.0	46.0	133.9	115.3		132.5	160.0	56.2		
	C)	+4.9	−3.8	+6.3	+5.5	+5.5	−0.2		+0.3	−0.8	+0.3		

a) A; Ethyl phenylacetates. B; Enolate anions. C; $\Delta\delta=\delta_A-\delta_B$. A plus sign denotes a downfield shift.
b) These chemical shifts could not be assigned to any carbons in the benzene ring.

the $\Delta\delta$ values of the residual methine protons.[1b] The $\Delta\delta$ values at C-γ and C-δ are affected by the negative moiety of the enolate anions in the same pattern as those of the malonate system.[1a]

In the case of benzyl methyl ketone, the $\Delta\delta$ value at benzyl carbon has been reported to be +42.5 ppm (a downfield shift), and the chemical-shift difference of the sodium enolate from the enol acetate, to be −23.2 ppm (an upfield shift).[4] By anion formation, the hybridization of the benzyl carbon changes from sp^3 to sp^2, accompanied by a large downfield shift of the ^{13}C chemical shift; *e.g.*, ethylene carbon resonates at a point downfield by more 117 ppm than that of ethane carbon; simultaneously, the increase in the pi-electron density on the carbon atom is forced to shift the chemical shift upfield.[5] These two opposing effects seem to cancel each other out and to give an apparent $\Delta\delta$ value to such an anionic carbon. The $\Delta\delta$ value at C-α of ethyl phenylacetate was +5.6 ppm. This small value appears to be attributable to the above-mentioned cancelling. Consequently, the small downfield shift at C-α seems to be associated with the increase in the electron density on the carbon rather than with the decrease based on sp^2 hybridization. The sign of the $\Delta\delta$ value at C-β in ethyl phenylacetate shows a downfield shift, while those at C-p and C-ipso show downfield and upfield shifts respectively. The $\Delta\delta$ values indicate the existence of pi-interaction between the benzene ring and the anion moiety (C⋯C⋯O$^-$), even in a nonsubstituted case.[6]

Several studies of ^{13}C SCS have been reported.[7] The purpose of this ^{13}C SCS study is to clarify the direction of the ^{13}C SCS on the carbons in the enolates against σ^- and σ. Such an anion system attached directly to a benzene ring is very rare in ^{13}C SCS studies.[8]

In Fig. 1, the ^{13}C chemical shifts at C-α, C-β, C-p, and C-ipso of sodium enolates are plotted against σ^-; those at the other carbons are scarcely affected at all by any substituents. The effect by the electron-attracting groups is quite different from that by the electron-releasing groups, as has been suggested by other physical data.[1] The electron-releasing groups act much like an H substituent, without any strong interaction between the substituents and the anion moiety, while the electron-attracting groups conjugate strongly with the anionic moiety through the benzene ring.

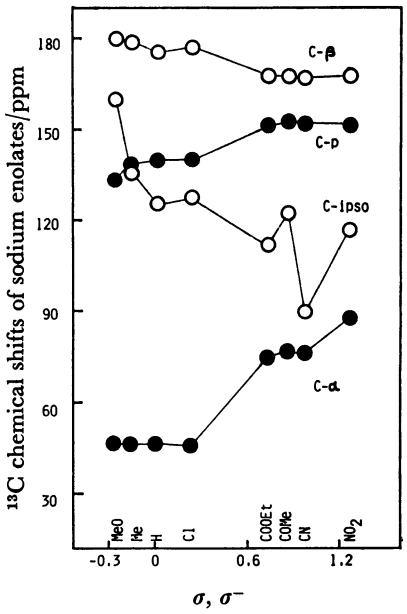


Fig. 1. Plots of the ^{13}C chemical shifts at C-α, C-β, C-p, and C-ipso of the sodium enolates derived from ethyl phenylacetates in DMSO-d_6 against σ^- and σ constants.

Experimental

The proton-decoupled ^{13}C FT NMR spectra were measured at 25.15 MHz on a JEOL MH-100/PFT-100 spectrometer (pulse width, 31 μs; spectral width, 6250 Hz; data points, 4096; aquisition time, 327.8 ms). The spectra were observed on 0.5 M solutions in DMSO-d_6 in 5-mm tubes at 35—45 °C. The chemical shifts were obtained using the signal of DMSO in a 99% d-enriched solvent as the internal standard (δ 40.5 ppm), and were then converted to the TMS scale.

The sodium enolates of ethyl (p-substituted phenyl)acetates were prepared in a manner similar to that described in a previous report.[1b]

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