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CARBON-13 NMR SPECTRA OF SODIUM SALTS OF DIETHYL ALKYL-SUBSTITUTED MALONATES

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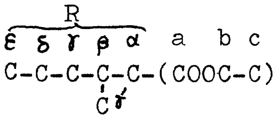
^{13}C chemical shifts of diethyl alkyl-substituted malonates and their sodium salts in dimethylsulfoxide are reported. The resonances of carbonyl carbons and α-carbons having an active hydrogen in the sodium salts were respectively found at 0.5∼1 ppm and 20 ppm lower fields than those of the original malonates did.

In carbanion chemistry, only a few ^{13}C NMR spectral data have so far been reported , although they have been suggested as necessary because ^{13}C NMR spectra can reflect the ionic character of the skeleton of a carbanion much greater than ^{1}H NMR spectra can.$^{1)}$ Earlier, Zaugg et al. found the marked acceleration by dimethylformamide (DMF) or dimethylsulfoxide (DMSO) of the rate of alkylation of the sodium derivative of diethyl n-butylmalonate with n-butyl halide in benzene solution.$^{2)}$ Recently,$^{3)}$ they studied the ^{1}H NMR spectra of the active hydrogen of the sodium and lithium derivatives of diethyl malonate in DMF to solve this problem, assuming that this solvent effect is produced by a specific solvation of the cation and the two species of ion-pairs of sodium derivative may be at equilibrium in DMF or DMSO. ^{13}C NMR spectroscopy is felt to be more useful in getting more direct insights.

Now, the measurements of ^{13}C NMR spectral data on several alkyl-substituted malonates$^{4)}$ and their sodium derivatives in DMSO-d_6. The measurement conditions were as follows. Diethyl alkyl-substituted malonates (0.1 cm^3) were combined with DMSO (0.3 cm^3) in an NMR tube. Sodium hydride was added into the mixture. After the generation of hydrogen gas ceased completely, the proton-decoupled natural-abundance ^{13}C FT NMR spectra of the sodium derivatives obtained at 25.15 MHz on a JEOL MH-100/PFT-100 spectrometer (pulse width, 31 μsec; spectral width, 6250 Hz ; data points, 4096; aquisition time, 327.8 msec) using benzene in a capillary as an external standard at a room temperature. The chemical shifts were converted to δ

Table I. ^{13}C chemical shifts of malonic derivatives and their sodium salts. Chemical shifts are indicated in δ (ppm downfield from TMS).



$$\overbrace{\overset{\varepsilon}{C}-\overset{\delta}{C}-\overset{\gamma}{C}-\underset{C\gamma'}{\overset{\beta}{C}}-\overset{\alpha}{C}}^{R}-(\overset{a}{C}OO\overset{b}{C}-\overset{c}{C})$$

Compounds (R)		a	b	c	α	β	γ	δ	ε	γ'
I Hydrogen	A	168.18	61.28	13.72	41.50					
	B	172.42	56.10	15.05	62.37					
	C	+4.24	-5.81	+1.33	+20.87					
II Methyl	A	171.33	61.16	13.59	45.63	13.11				
	B	171.57	56.43	15.29	66.62	12.02				
	C	+0.23	-4.73	+1.70	+20.99	-1.09				
III Ethyl	A	170.48	61.16	13.72	53.03	21.72	11.17			
	B	171.21	56.19	15.17	75.60	16.51	13.23			
	C	+0.73	-4.97	+1.45	+22.57	-5.21	+2.06			
IV n-Propyl	A	170.60	61.28	13.72	51.33	30.46	19.90	13.35		
	B	171.57	56.19	15.29	73.66	28.64	24.64	13.96		
	C	+0.97	-5.09	+1.57	+22.33	-1.82	+4.74	+0.61		
V iso-Propyl	A	170.12	61.28	13.96	58.61	28.40	20.03			
	B	171.45	56.19	15.17	79.85	24.88	23.18			
	C	+1.33	-5.09	+1.21	+21.24	-3.52	+3.15			
VI n-Butyl	A	170.36	60.92	13.47	51.33	27.79	28.64	21.60	13.23	
	B	171.09	55.82	14.93	73.47	25.36	33.86	21.85	13.84	
	C	+0.73	-5.10	+1.46	+22.14	-2.43	+5.22	+0.25	+0.61	
VII iso-Butyl	A	170.72	61.28	13.72	50.00	37.26	25.73	21.97		
	B	171.81	56.19	15.17	72.93	35.44	29.85	22.69		
	C	+1.09	-5.09	+1.45	+22.93	-1.82	+4.12	+0.72		
VIII sec-Butyl	A	170.12	61.28	13.96	57.16	34.46	26.58	11.05		16.14
	B	171.94	56.19	15.05	77.78	32.28	29.13	13.11		21.36
	C	+1.82	-5.09	+1.09	+20.62	-2.18	+2.55	+2.06		+5.22

A The chemical shifts of original malonates.
B The chemical shifts of sodium salts. C A - B.
Plus and minus signs mean a downfield and an upfield shift, respectively.

and reproduced within δ ±0.06 and scarcely affected by dilution of the solution.

The simple mode of the ^{13}C NMR spectra obtained suggested that the assumed ion-pairs[3)] are rapidly equilibrating on the NMR time scale. The active proton signals in diethyl malonate were shifted to a slightly lower field and the ester-part proton signals to a slightly higher field by the formation of the sodium salt. On the other hand, the carbon (α-carbon) possessing an active hydrogen in the salt resonates at a field much lower than that of the original malonate does, and the carbonyl carbon does at a slightly lower field. Further, peak intensities of carbonyl carbons were

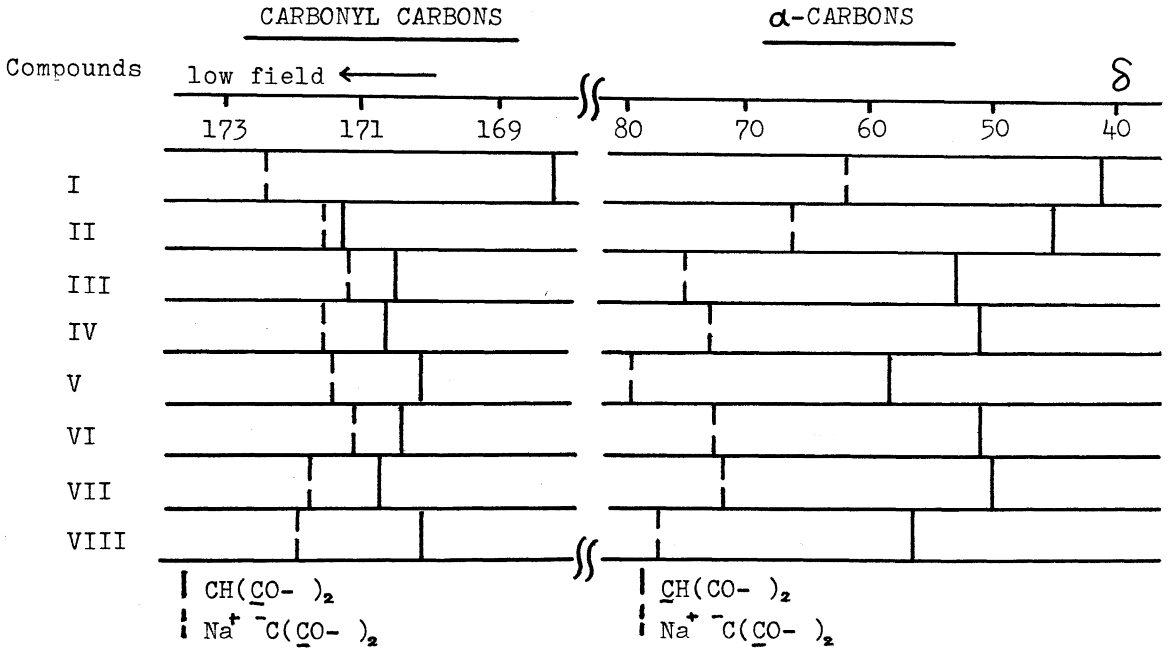


Fig. 1. ^{13}C chemical shifts of carbonyl carbons and α-carbons of the malonic derivatives and their salts.

found to be enhanced by the formation of a sodium salt under the present experimental conditions; this phenomenon apparently corresponds to shortening of the relaxation time of the carbonyl carbon. Table 1 lists the ^{13}C chemical shifts of substituted alkyl groups. When the sodium derivatives were produced, the chemical shifts of the β-carbons exhibited upfield shifts (about 2 ppm), whereas that of the γ-carbons exhibited downfield shifts (about 4 ppm). The ^{13}C chemical shift of the carbon, $-O\underline{C}H_2CH_3$, was δ 61 and that of the carbon, $-OCH_2\underline{C}H_3$, was δ 13.7. Then, the salt formation caused upfield shifts (5 ppm) for the former and downfield shifts (1.5 ppm) for the latter. The electronic and stereochemical influences of the substituted alkyl groups were found in the ^{13}C chemical shifts of the ethyl carbons of the ester group. The signals of α-carbons having a chain branching at the β-position such as iso-propyl or sec-butyl groups were observed at a lower (5~7 ppm) field than that of normal alkyl groups (see Fig. 1). This result may be due to a so-called β-substituent effect.$^{5)}$ The α-carbon signals of the salts were shifted downfield by 22 ppm in comparison with those of the original malonates. The downfield shift may be due to the partial sp^2 hybridization of the α-carbon; this seems to correlate with a downfield trend for organolithium derivatives of a series of phenylmethanes.$^{6)}$ Moreover, the chemical shift of carbonyl carbon was little affected by the alkyl groups.

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