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PMR SPECTRA OF SODIUM ENOLATES OF SOME β-DICARBONYL COMPOUNDS

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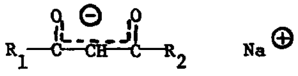
Recently House and coworkers[1] have examined the structures of certain metal enolates of monoketones in solution by nmr spectroscopy. The nmr spectra of some metal acetylacetonates[2-4] and of malonaldehyde anion[5] have been reported. We have made a comparative study of the pmr spectra of the sodium salts (Ia-c) of acetylacetone, ethyl acetoacetate, diethyl malonate and (Id) of ethyl cyanoacetate in order to gain insight into their structures and their dynamic behaviour.



I

a. $R_1 = R_2 = Me$
b. $R_1 = Me$, $R_2 = OEt$
c. $R_1 = R_2 = OEt$

The sodio-derivatives were prepared from the active methylene compounds under dry nitrogen using equimolar quantities of sodium hydride in dimethylformamide (DMF). The mixtures were filtered and the final concentrations of the enolates were 1.7 M. Pmr chemical shifts for Ia-d are given in the Table. They are compared with those of the corresponding resonances for the parent compounds and, where appropriate, for the enols of the latter at the same concentration by reporting the differences between these δ values. There were no variations outside experimental error in chemical shifts of protons of Ib in the concentration range 0.42-1.7 M.

The Table shows that there are remarkable uniformities in the chemical shifts for corresponding resonances of Ia-d relative to their conjugate acids. For example, the methine values for Ia, Ib, Ic and for the enols of Ia and Ib showed a constant upfield shift of approximately 0.59 ppm for replacement of each $-COCH_3$ group by $-CO_2Et$. The results appear to indicate that similar shapes[6] and similar patterns of delocalization of negative charge occur in the enolate ions studied. As far as charge distribution is concerned, this is surprising since the influence of a carbethoxyl group would be expected to be different to that of a keto group. The δ values for methyl groups in R_1 of Ia and Ib may not be consistent with the above conclusion since R_1 in Ia is more shielded compared to its enol than in Ib. This could arise from a greater negative charge on the oxygen atom next to R_1 in Ia relative to its enol than in Ib. None of the spectra showed separate peaks due to more than one geometric isomer[7] or conformer. We conclude that in each case there is either only one major species present or a rapid equilibrium prevails between cis-trans isomers.[8]

On heating solutions of Ia or Ib the sharp singlet due to the methine proton broadened near 100-105° and collapsed at approximately 120°. The other peaks were unchanged. This effect was totally reversible. There was evidence of decomposition above 158°. In contrast, the spectrum

Table. PMR Chemical Shifts[a] for Anions I in DMF

Cpd	R_1	R_2[b]		C$\underline{H}$	Differences between corresponding resonances δ keto (enol) — δ anion			
		CH_2	CH_3		R_1	R_2		C$\underline{H}$
	(s)	(q)	(t)	(s)		CH_2	CH_3	
Ia	1.68			4.93	+0.49			-1.22
					(+0.38)			(+0.72)
Ib	1.67	3.86	1.07	4.36	+0.53	+0.29	+0.15	-0.86
					(+0.29)	(+0.29)	(+0.15)	(+0.70)
Ic		3.86	1.07	3.77		+0.30	+0.19	-0.37
Id		3.83	1.07	c		+0.36	+0.18	c

[a] δ values (±0.01 ppm) obtained on Varian A60D instrument at 41° for centres of each resonance.

[b] J for the ethyl groups of all the anions and the parent dicarbonyl compounds was 7.0±0.5 Hz.

[c] Not measured since peaks obscured by other resonances.

of Ic did not change from 41 to 160°. It seemed likely that exchange between the anions and traces of their unreacted conjugate acids was responsible for the change in the methine signals of Ia and Ib.

At 41° the addition of 0.02-0.04 equivalent of the parent β-dicarbonyl compounds to Ia and Ib caused considerable broadening of the methine signals, while 0.1 equivalent led to their collapse. On the other hand, the addition of 0.4 equivalent of diethyl malonate to Ic had no effect on its spectrum, but the presence of 1.0 equivalent collapsed the methine resonance. The changes in the methine peaks of Ib and Ic were accompanied by some broadening[1] of the methyl singlet of Ib and of the ethyl resonances of Ic. The spectrum of Ia in the presence of 0.5 equivalent of acetylacetone showed a methyl singlet at 1.90 δ, a value intermediate between that for Ia and acetylacetone enol (see Table). Similarly the enol hydroxyl peak of acetylacetone at 14.2 δ was replaced by a very broad resonance at 10.2 δ for the mixture with Ia. This is further evidence for the proposed rapid exchange between the enols and the enolate ions. As expected, the exchange process is not so facile for the less acidic[6] diethyl malonate as for acetylacetone and ethyl acetoacetate. Similar effects have been observed by Crews[9] in the fast exchange of an ylide with its conjugate acid.

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