

## Steric Effects on Chelation in $^{13}\text{C}$ Nuclear Magnetic Resonance Spectra of $\beta$ -Diketone Enolates

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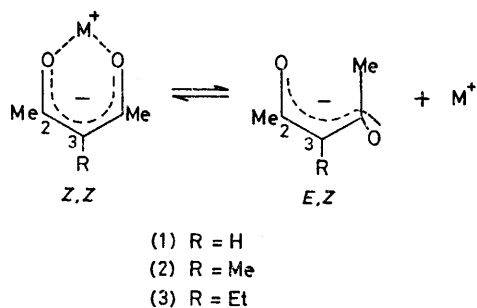
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*Summary* Low temperature  $^{13}\text{C}$  n.m.r. spectra of sodium and lithium enolates of  $\beta$ -diketones ( $\text{MeCOCHRCOME}$ ,  $\text{R}=\text{H}$ , Me or Et) provide evidence concerning ionic

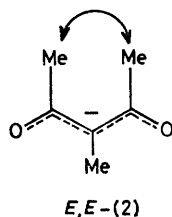
bonding and the effect of steric hindrance on alkali metal chelation.

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WHILE the  $^{13}\text{C}$  n.m.r. spectra of simple ketone enolates have been reported recently,<sup>1-5, 6a</sup> the low temperature  $^{13}\text{C}$  n.m.r. spectra of the enolates of  $\beta$ -diketones have not yet been described. These are of particular interest since  $^1\text{H}$  n.m.r. studies<sup>†</sup> have shown that associated and dissociated forms exist in an equilibrium which is slow on the n.m.r. time scale at low temperature. We report here on the low temperature  $^{13}\text{C}$  n.m.r. spectra of the enolates (1), (2), and (3), of pentane-2,4-dione, 3-methylpentane-2,4-dione, and 3-ethylpentane-2,4-dione, and on the effect of substitution at C-3 on the ability of the enolate anion to act as a chelating ligand for alkali metals.



The low temperature  $^{13}\text{C}$  n.m.r. spectrum of (1) ( $\text{M}=\text{Na}$ ) in methanol solution<sup>‡</sup> exhibits three carbonyl resonances and two methine (C-3) resonances reflecting the presence of the  $Z,Z$  and  $E,Z$  isomers in slow equilibrium (Table 4, Figure 1a). Two equally intense carbonyl resonances arise from  $E,Z$ -(1) while the less intense resonance is due to  $Z,Z$ -(1). The intensities of resonances of the two isomers afforded an estimate of the mole fraction of  $Z,Z$ -(1), 0.26, which is in good agreement with the value, 0.23, obtained from  $^1\text{H}$  n.m.r. spectra<sup>6b</sup> considering the possible errors arising from differential nuclear Overhauser effects and relaxation times. The two methine carbon resonances afforded nearly the same mole fraction for  $Z,Z$ -(1), *viz.* 0.25.



The low temperature  $^{13}\text{C}$  n.m.r. spectra of (2) and (3) exhibit similar non-equivalent carbonyl resonances which can be assigned to the  $E,Z$  configuration. Only a single C-3 quaternary carbon resonance was observed for each compound. Based upon the signal to noise ratio observed

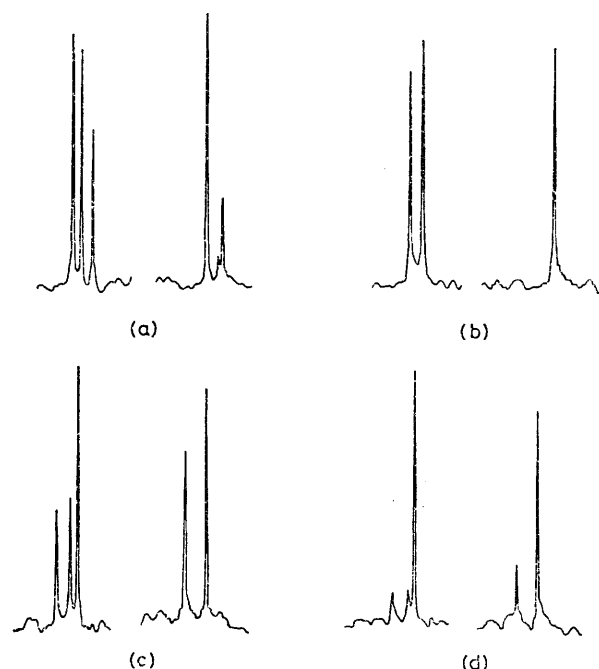


FIGURE. Carbonyl (left) and C-3 (right) regions of the  $^{13}\text{C}$  n.m.r. spectra of (1) and (2): a, (1); b, (2); c, (2) with 0.5 equiv. of added LiI; d, (2) with 1.0 equiv. of added LiI. Resonance positions are given in the Table.

we conclude that no more than *ca.* 3% of chelated  $Z,Z$ -(2) or  $Z,Z$ -(3) can be present. The 3-alkyl group destabilizes the  $Z,Z$  configuration by steric interactions with both acetyl methyl groups. The vicinal interaction between a single acetyl methyl and the methyl group on C-3 is, however, not destabilizing enough to lead to a measurable amount of  $E,E$ -(2), [or  $E,E$ -(3)], since the  $E,E$  configuration features fairly close contact between the two acetyl methyl

TABLE.

Compound	$\delta(^{13}\text{C})/\text{p.p.m.}$			
	$EZ$		$ZZ^a$	
	C(2)/C(4)	C(3)	C(2)/C(4)	C(3)
(1)	194.4 192.3	102.2	190.4 <sup>b</sup>	99.2 <sup>b</sup>
(2)	193.6 190.9	106.7	189.4	102.7
(3)	192.6 191.5	114.0	189.7	110.2

<sup>a</sup> For compound (1) the chemical shifts of the  $Z,Z$ -conformer refer to the sodium chelate. For compounds (2) and (3) the chemical shift for the  $Z,Z$ -conformer refers to the chelate which appears upon addition of LiI. <sup>b</sup> The chemical shifts for the lithium chelate of  $Z,Z$ -(1) obtained upon addition of an excess of lithium ion were 190.9 p.p.m. for C(2) and 99.7 p.p.m. for C(3).

<sup>†</sup>  $^1\text{H}$  N.m.r. studies of  $\beta$ -diketone enolates have been described in refs. 5 and 6. The  $^1\text{H}$  n.m.r. spectra of enolates of  $\beta$ -ketoaldehydes and  $\beta$ -ketoesters have also been studied extensively; see ref. 7.

<sup>‡</sup> All spectra reported here were measured using a JOEL FX-60 spectrometer (15 MHz) on 0.40 M solutions in methanol and are expressed in  $\delta$  units relative to external  $\text{Me}_4\text{Si}$  which together with the lock compound,  $(\text{CD}_3)_2\text{CO}$ , was present in a coaxial tube. *Ca.* 2000 FID were collected using 16,384 data points and a spectral width of 4 kHz. Spectra were measured at  $-60^\circ\text{C}$  for (1) and  $-85$  to  $-95^\circ\text{C}$  for (2) and (3). The signals due to the acetyl methyl carbons were partially obscured by the  $(\text{CD}_3)_2\text{CO}$  multiplet and are not reported. Small flip angles ( $3\ \mu\text{s}$  pulse width, 1.5–2 s repetition time) were used to minimise incomplete relaxation of carbonyl and other unprotonated carbon atoms with long transverse relaxation times.

groups. Based on these fragmentary results, it seems reasonable to suppose that the 1,3 steric interaction in *E,E*-(**2**) is more destabilizing than the 1,2- interaction in *E,Z*-(**2**).§

Although the chelation of sodium by *Z,Z*-(**2**) [or *Z,Z*-(**3**)] is not strong enough to overcome the unfavourable steric interactions, chelation of lithium is more stabilizing.<sup>1,6,7</sup> Thus, *Z,Z*-(**2**) and *Z,Z*-(**3**) could be formed by 'configurational titration'<sup>8</sup> of (**2**) or (**3**) with lithium iodide. Addition of the lithium salt resulted in the appearance of a new carbonyl resonance, upfield from the two resonances of the *E,Z* configuration. Similarly, new C-3 quaternary carbon and C-3 methyl resonances were apparent (Figure 1c,d, Table 4). Addition of increasing amounts of lithium ions resulted in a progressive increase in the intensity of these signals attributable to the *Z,Z* form.

In all three cases the *Z,Z* carbonyl resonance is shifted *upfield* from the average of the *E,Z* carbonyl resonances [by 3.1 p.p.m. in (**1**), 2.9 in (**2**), and 2.4 in (**3**)], as is the C-3 resonance [3.0 p.p.m. in (**1**), 4.0 in (**2**), and 3.8 in (**3**)]. The similarity in these shifts indicates that a similar structural change in all three cases is observed, *i.e.*, a change of configuration and a change from dissociated ions to chelated ion pairs. These results are in contrast to the types of shifts observed in 3-phenylpentan-2-one enolate studied by House and his co-workers<sup>2</sup> which were attributed to closer ion pairing. In that system change of the gegenion from sodium to lithium resulted in a *downfield shift* of 6 p.p.m. for the carbonyl resonance, but an *upfield shift* of 3.5 p.p.m. for the  $\alpha$ -methine resonance [which corresponds to the C-3 methine resonance in (**1**) or the C-3 quaternary carbon resonance in (**2**) or (**3**)]. These shifts were rationalized by considering the lithium salt as a stronger ion pair

and further from the dissociated ion structure. Thus the  $\alpha$ -carbon of the lithium salt was said to resonate at lower field because of lesser  $\pi$ -electron density relative to the sodium salt.

Change of the gegenion in *Z,Z*-(**1**) from sodium to lithium results in a small *downfield* shift (0.5 p.p.m.) for C-3 while dissociation (and change to the *E,Z* configuration) results in a much larger *downfield* shift (2.5 p.p.m.). Thus the shift on going from contact ion pairs to dissociated ions is in the opposite direction from that which results from the change in gegenion from lithium to sodium. The changes in shifts of the carbonyl resonances of diketone enolates are also different from those of the simple enolates described by House.

On the basis of these results any interpretation of small gegenion effects on <sup>13</sup>C chemical shifts in enolates should be treated with caution. Especially in conformationally mobile enolates such as those discussed here, conformational factors can overwhelm any possible  $\pi$ -density shifts and even in the absence of conformation changes diketone enolates exhibit behaviour different from that of simple enolates.

This work was supported by the National Science Foundation and the National Institute of General Medical Sciences. We also thank the National Science Foundation for an institutional grant for the purchase of the JOEL FX-60 spectrometer used. One of us (M.R.) thanks the departments of Structural Chemistry and Isotope Research of the Weizmann Institute of Science for their hospitality during a Sabbatical visit during which some of this work was carried out.

(Received, 25th July 1978; Com. 803.)

§ For discussions of the relative importance of these two types of steric interactions in the isoelectronic amides see E. A. Noe and M. Raban, *J. Amer. Chem. Soc.*, 1975, **97**, 5811; G. Tetu, J.-C. Duplan, N. Pellissier, and E. Laurent, *J. Chem. Research*, (S) 1978, **98**; (M) 1247.

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