

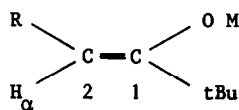
METAL ENOLATES : CARBON -13 MAGNETIC RESONANCE SPECTRA.

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In connection with a study on the stereochemistry of the aldol condensation, we have used  $^{13}\text{C}$  NMR spectroscopy, a more pertinent technique than  $^1\text{H}$  NMR, to elucidate certain structural problems for metallic enolates (1) of the type



This method permits a direct examination of the carbon  $\text{C}_2$  and an estimate of its electron density and hybridization state (3).

We report here new results concerning the effect of substitution by alkyl groups and the reality, or not, of C-metalated forms, already established (4) for symmetrical magnesium derivatives (i.e. :  $\text{R} = \text{Me}$ ,  $\text{M} = \text{Mg}_{1/2}$ ). The table presented below gives the spectral characteristics of the enolate I (5) and of the enolates derived from I by a change of metal M, for II and III, or alkyl substituent R, for IV (5).

Enolate	M	R	$\delta\text{C}_1$	$\delta\text{C}_2$	$^1\text{J}_{\text{CH}}$	$\delta\text{H}_\alpha$
I	MgBr	Me	162.4	95.5	154	4,54
II	$\text{Mg}_{1/2}$	Me	162.4	95.1		(3)
II			166.1	83.2		
III	Na	Me	172.3	78.2	152	3.84
IV	MgBr	iPr	158.9	110.3	153	4.29

Solvent :  $\text{Et}_2\text{O} - \theta$  :  $20^\circ\text{C}$  - reference : TMS -  $\delta$  (ppm) - J (Hz), presence of 1,4-dioxane for II.

As the metal becomes more electropositive (Na instead of MgBr) the carbon  $C_2$  is shifted upfield ( $\Delta\delta_2 = -17.3$ ), as is the proton  $H_\alpha$  ( $\Delta\delta = 0.70$ ), while the  $C_1$  signal is shifted to low field ( $\Delta\delta_1 = +9.9$ ). This corresponds to increased electron donation through resonance of the oxygen and an increase of the  $\Pi$  charge density on  $C_2$ . It is interesting to note that  $C_2$  is more shifted than  $C_1$ , in contrast with House's observation (2) concerning the enolates  $\psi CH = C(Me) OM$  (i.e. :  $\Delta\delta_1 = -1.9$  ;  $\Delta\delta_2 = +4.6$  in passing from Li to Na in DME) where the negative charge is delocalized on the phenyl ring. On the other hand, the coupling constant  $^1J_{CH}$  scarcely changes and the carbon  $C_2$  keeps its planar configuration. This is in agreement with the observation of stable stereoisomeric enolates of lithium (7) and sodium (8).

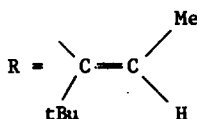
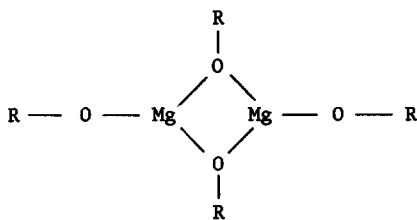
The use of a more polar solvent bringing about a better solvation of the metal should produce the same effects. This has been confirmed by House (2).

The important upfield shift that we have observed for the proton  $H_\alpha$ , when the substituent R varies from Me to Et, iPr and tBu, cannot be interpreted in the same terms as metal or solvent effects (9); that will be shown by our  $^{13}C$  NMR observations. When the alkyl substituent R changes from Me to iPr, the upfield shift of the proton  $H_\alpha$  ( $\Delta\delta = -0.25$ ), in contrast to the preceding case, is accompanied by a lowfield shift of  $C_2$  ( $\Delta\delta_2 = +14.8$ ) and an upfield shift of  $C_1$  ( $\Delta\delta_1 = -3.5$ ) (10). We note that the same substituent variation with R on  $C_2$  produces similar effects on olefines such as cis R CH = CH Me ( $\Delta\delta_1 = -2.4$  ;  $\Delta\delta_2 = +14.6$ ) and trans ( $\Delta\delta_1 = -4.7$  ;  $\Delta\delta_2 = +18.7$ ) as well as the corresponding alkane RCH<sub>2</sub>CH<sub>2</sub>Me ( $\Delta\delta_1 = -4.3$  ;  $\Delta\delta_2 = +16.8$ ). Thus it appears that a change in the alkyl substituent in the  $\alpha$  position relative to an olefinic  $sp^2$  carbon is affected essentially in the  $\sigma$  electron distribution, in agreement with the charge variations reported by Miyajima (11). On the other hand, the  $\Pi$  electron density is significantly affected when a hydrogen attached to an  $sp^2$  carbon is replaced by an alkyl group ; this conclusion is reached from an examination of the substituent parameters reported by Stothers (12) for alkanes and alkenes, and supported by an analysis of the chemical shifts of the enolates  $Me_2C = C(OLi)Me$  and  $CH_2 = C(OLi)tBu$  studied by House (2).

In passing from R = Me to iPr we point out, once more, the invariance of the coupling constant  $^1J_{CH}$ , characteristic of a trigonal carbon. Thus it is clear that the interpretation of the stereochemistry of the aldol condensation as a function of the alkyl substituent (13) cannot be envisaged in terms of a more or less important hybridization change at  $C_2$  accompanying substitution by more electron donating groups, as has been suggested for related structures derived from RCHClCO<sub>2</sub>R' (14).

The spectrum of the symmetrical magnesium derivative  $(RO)_2Mg$  of tBuCOEt (6) reveals a mixture of two O- metallated entities IIa and IIb, which should be the enolates described by Maroni (4) and characterized by  $\delta_H = 4.49$  and 3.92 ppm. The difference between IIa and IIb is not attributable to 1,4-dioxane, a more basic solvent than ether (15): a large excess or the absence (17) of dioxane in the solution leaves the  $sp^2$  carbon signals unchanged. Thus, it

seems reasonable to exclude a solvation of magnesium by dioxane, and, a fortiori, by ether. On the other hand, we find, in all these cases, an equipartition of the enolate part on two non equivalent sites. These observations leads us to consider for the symmetrical enolate the following structure - where metal is tricoordinated - analogous to that proposed by Pinkus (18) for the bromomagnesium enolate of methyl mesityl ketone.



The most important fact to retain is however that this spectrum does indicate unambiguously the absence of any C - metalated species in solution within the limits of detectability of the  $^{13}\text{C}$  - NMR method.

#### NOTES AND REFERENCES

- (1) While this work was still in progress the first publication on the  $^{13}\text{C}$  - NMR of ketone enolates appeared. (House and al (2) ).
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- (5) J.E. Dubois and P. Fellmann, *C.R. Acad. Sc. Paris*, **274C**, 1307 (1972).
- (6) The bromomagnesium enolates were prepared by the reaction of magnesium with the appropriate  $\alpha$  - bromoketone in ether. The symmetrical magnesium enolate was obtained by addition of 1.4 equivalents of 1,4 - dioxane to an ethereal solution of the bromomagnesium enolate. The sodium enolate was prepared by the reaction

of sodium amide on the ketone.

The NMR spectra were recorded, for  $^1\text{H}$  at 60 MHz using a JEOL spectrometer model C-60-HL, and for  $^{13}\text{C}$  at 100 MHz using a JEOL Fourier transform spectrometer, model JNM-PS-100, with  $\text{D}_2\text{O}$  internal lock.

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- (15)  $\Delta\delta_1$  and  $\Delta\delta_2$  between IIa and IIb would be consistent with solvation of IIa by ether and IIb by dioxane, in line with their relative basicities (16) and the solvent effects observed by  $^{13}\text{C}$  - NMR (2).
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- (17) The solution of the symmetrical derivative  $(\text{RO})_2\text{Mg}$ , free of dioxane, was obtained by the addition of 0.5 equivalents of dioxane to the magnesium enolate  $\text{ROMgBr}$ , a part of which remained in solution (its spectrum is very slightly different from that of IIa).
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