zene, 106-38-7; 3-methyl-1-buten-3-ol, 115-18-4; 1-buten-3-ol, 598-32-3; 3-buten-1-ol, 627-27-0; 4-penten-1-ol, 821-09-0; 3-methyl-3-buten-1-ol, 763-32-6; 5-methyl-5-hexen-2-ol, 50551-88-7; 4-methyl-4-penten-2-ol, 2004-67-3; 4-methyl-4-penten-1-ol, 22508-64-1; bromobenzene, 108-86-1; iodobenzene, 591-50-4; β-terpineol, 138-87-4; 1-methyl-3-cyclohexene-1-methanol, 50552-10-8.

References and Notes

(1) A. J. Chalk and S. A. Magennis, *J. Org. Chem.*, **41**, 273 (1976).
(2) R. F. Heck and J. B. Melpolder, *J. Org. Chem.*, **41**, 265 (1976).
(3) R. Asano, I. Moritani, Y. Fujiwara, and S. Teranishi, *Bull. Chem. Soc. Jpn.*, **46**, 2910 (1973).
(4) J. M. Davidson and C. Triggs, *J. Chem. Soc. A*, 1324 (1968).

The Chemistry of Carbanions. XXVIII. The Carbon-13 Nuclear Magnetic Resonance Spectra of Metal Enolates[1]

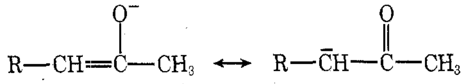
Herbert O. House,* Ananth V. Prabhu, and William V. Phillips

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Received September 12, 1975

The natural abundance ^{13}C NMR spectra of several metal enolates **5–10** have been measured in various aprotic solvents including Et$_2$O, THF, and DME. The chemical shifts of the enolate α-carbon atoms are readily measured and have been compared with the chemical shifts of the same carbon atoms in the corresponding enol acetates **17–22** and trimethylsilyl enol ethers **23–26**. The observed chemical shift differences ($\Delta\delta$) between the enolates and the enol acetates appear to be related both to the π-electron density and the reactivity at the enolate α-carbon atom. The following changes increase the magnitude of the chemical shift differences (and presumably the π-electron charge density) in metal enolates: (1) changing the metal cation from Li$^+$ to Na$^+$ to K$^+$; (2) changing the solvent from Et$_2$O to THF to DME; (3) addition of 4 molar equiv of HMP to a Li$^+$ enolate; and (4) addition of 1 molar equiv of dicyclohexyl-18-crown-6 polyether to a Na$^+$ enolate. The magnitudes of the chemical shift differences at the enolate α-carbon atoms are relatively insensitive to the presence or absence of α-alkyl or α-phenyl substituents.

In an early study[2] of the properties and reactions of solutions of metal enolates **1** derived from ketones **2**, comparison of the ^{1}H NMR spectra for a related set of compounds **1–4** (R = Ph) showed that the vinyl H atom signal moved progressively upfield in the order enol acetate **3** (δ 5.80), trimethylsilyl enol ether **4** (δ 5.32), and lithium enolate **1** (δ 5.02 in Et$_2$O, 4.93 in THF, and 4.83 in DME). Among the various cations and solvents studied with this enolate system, the cation–solvent combinations that resulted in the greatest upfield shift of the vinyl H atom NMR signal were also the combinations that resulted in the greatest proportion of O- to C-acylation of the enolate anions and corresponded qualitatively to conditions that favored most rapid reaction of the enolate anion with alkylating agents. Thus, the location of the ^{1}H NMR signal appeared to offer a useful measure of the reactivity of a metal enolate under various reaction conditions. However, two experimental problems dissuaded us from further study of the ^{1}H NMR spectra of metal enolates. First, the total range of ^{1}H NMR values observed for a particular enolate system was rather small (ca. 0.3 ppm) so that changes in chemical shift arising from nearby anisotropic substituents were likely to be as large as chemical shift differences arising from changes in the degree of association and charge distribution of metal enolates. Even more troubling was the interference from the ^{1}H NMR signals of the various solvents (Et$_2$O, THF, DME, DMF, etc.) commonly used with metal enolates.

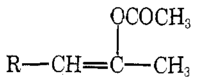


$\mathrm{R{-}CH{=}\overset{O^-}{C}{-}CH_3} \longleftrightarrow \mathrm{R{-}\bar{C}H{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$

1a **1b**

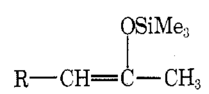
RCH$_2$COCH$_3$

2



$\mathrm{R{-}CH{=}\overset{OCOCH_3}{C}{-}CH_3}$

3



$\mathrm{R{-}CH{=}\overset{OSiMe_3}{C}{-}CH_3}$

4

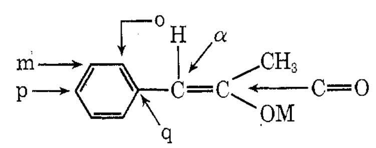
It appeared that both of these problems could be largely alleviated by studying the natural abundance ^{13}C NMR spectra of metal enolate solutions. Because of the much larger range of chemical shift values in ^{13}C NMR and the relatively narrow linewidths obtainable, problems arising from interference between solvent peaks and peaks from the metal enolates would be more easily avoided. Of equal importance is the fact that electron densities at carbon and the atoms bonded to it, but not shielding from neighboring anisotropic substituents, are dominant in determining ^{13}C NMR chemical shift values.[3]

To explore this possibility, a series of metal enolates **5–10** (Scheme I) of ketones **11–16** were prepared. Also included in the study were the corresponding enol acetates **17–22** as well as selected enol silyl ethers **23–26**, one enamine **27**, and the sodium enolate **28** of diethyl malonate.

Although relatively high concentrations (0.5–1.0 M) of metal enolates in solution were required in order to obtain satisfactory natural abundance ^{13}C NMR spectra in a reasonable period of time (1–3 h), we were gratified to find that interference between ^{13}C NMR signals for the metal enolates and the solvents was much less of a problem than had been encountered in measurements of ^{1}H NMR spectra of metal enolates.[2] Consequently, where solubility permitted, satisfactory ^{13}C NMR spectra of various metal enolates could be obtained in most common solvents used in preparative work including Et$_2$O, THF, DME, DMF, and HMP. The data obtained from these measurements are summarized in Tables I and II. In one case (enolate **5a** in DME, Table I) we demonstrated that the chemical shift values were essentially the same for 1.0 and 0.2 M solutions of the enolate. Because of the time required to obtain satisfactory ^{13}C NMR spectra of dilute solutions, it was not practical to collect data for enolate solutions less concentrated than 0.2 M.

In order to compare the ^{13}C NMR data for various metal enolates, we elected to relate the enolate chemical shift

Table I. ^{13}C NMR Data for Phenylacetone Derivatives



Compd (solvent)	Position of ^{13}C NMR signals, ppm relative to Me_4Si					
	p	o and m positions		q	α (Δδ)[a]	C=O	CH_3 and other C atoms
$PhCH_2COCH_3$ **11** (DME)	127.2	129.5	129.5	135.7	50.9	204.3	28.8
$PhCH{=}C(CH_3)OCOCH_3$ **17** (DME)	127.5	128.9	128.9	135.4	116.6[c]	147.0	168.0, 20.6[b]
$PhCH{=}C(CH_3)OSi(CH_3)_3$ **23** (DME)	125.1	127.7	127.7	137.1	108.7 (7.9)	148.8	23.8, 0.8
$PhCH{=}C(CH_3)OK$ **5c** (DME)	118.6	123.3	128.4	145.6	91.8 (24.8)	170.7	29.5
$PhCH{=}C(CH_3)ONa$ **5b** (DME)	119.2	124.1	128.2	145.1	93.4 (23.2)	169.3	29.4
5b (DME + 1.0 equiv of crown ether **35**)[d]	116.4	123.1	126.7	146.0	90.7[e] (25.9)	170.3	29.7
$PhCH{=}C(CH_3)OLi$[f] **5a** (DME)	120.0	125.0	127.2	143.2	95.3 (21.3)	164.7	28.6
5a (DME + 4.1 equiv of HMP)	117.7	124.1	126.6	144.8	93.1 (23.5)	167.4	28.9
5a (THF)	120.9	125.5	127.5	141.8	97.1 (19.5)	162.5	28.6
5a (THF + 3.9 equiv of HMP)	118.9	124.7	127.6	144.0	94.4 (22.2)	166.0	28.7
5a (Et_2O)	122.3	125.8	128.4	142.1	97.8[g] (18.8)	160.6	27.1
5a (Et_2O + 5.1 equiv of HMP)	118.5	124.6	127.0	144.3	94.1 (22.5)	166.4	28.6
5a (THF + 0.9 equiv of crown ether **36**)	120.5	125.1	127.5	142.5	96.4 (20.2)	163.7	28.7
5a (THF + 1.1 equiv of crown ether **37**)	120.5	125.1	127.6	142.5	96.5 (20.1)	163.9	28.8

[a] Δδ is the difference in chemical shift between the α-carbon atom of the enol acetate and the α-carbon atom of the enolate or trimethylsilyl enol ether. [b] The signals for both CH_3 groups are superimposed. [c] The $^1J_{CH}$ value was 154 ± 3 Hz. [d] Within experimental error, the same ^{13}C chemical shift values were obtained with a solution containing 2 molar equiv of the crown ether **35**. [e] The $^1J_{CH}$ value was 146 ± 3 Hz. [f] The values listed were obtained with a 1.0 M solution of the enolate **5a**. For a 0.2 M solution of the same enolate, the values follow: 120.0, 125.0, 127.4, 143.3, 95.3, 164.8, and 28.6 ppm. [g] The $^1J_{CH}$ value was 154 ± 3 Hz.

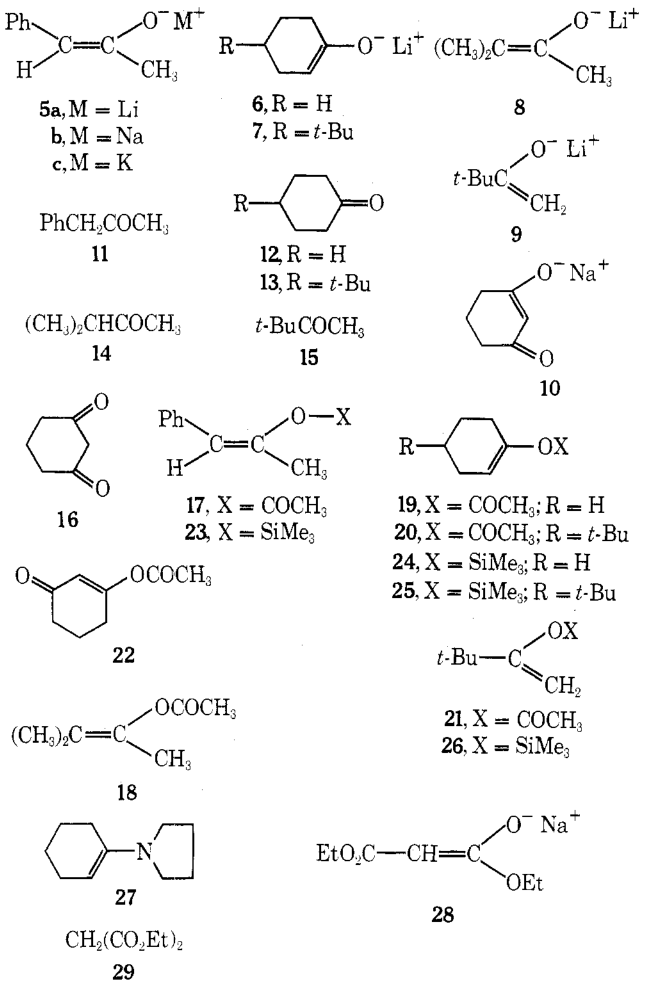
data to the analogous data for the corresponding enol acetates,[4] which can serve as neutral model compounds with geometries and substituent patterns similar to those of the metal enolates. This comparison utilizes the ^{13}C NMR shift difference ($\Delta\delta = \delta_{\text{enol acetate}} - \delta_{\text{enolate}}$) between the α-carbon atom in a metal enolate and the corresponding carbon atom in the related enol acetate. It will be seen from Tables I and II that Δδ values for the α-carbon atom of monoketone enolates are in the range +19 to +25 ppm. This upfield shift of signal for the α-carbon atom in the metal enolate is accompanied by a downfield shift of −13 to −23 ppm for the "carbonyl carbon atom" of the metal enolate. In general, the largest upfield shifts of α-carbon atoms are accompanied by the largest downfield shifts of the enolate "carbonyl carbon atoms".

One of the factors responsible for an upfield shift of the ^{13}C NMR signal for an sp^2 carbon atom[2] (or a hydrogen atom bound to this carbon[5]) is an increase in the π-electron density at carbon. From studies of various hydrocarbons and the related ions, it has been suggested that an increase by one unit of negative charge in the p orbital of such a carbon atom should result in an upfield shift of 150–160 ppm for the ^{13}C NMR signal[6] and an upfield shift of ca. 10 ppm for the ^{1}H NMR signal of a proton bound to such a carbon atom.[5a,7] As examples of this upfield shift in hydrocarbons, the α-carbon atoms and the C-4 carbon atoms of the phenyl groups in DME solutions of the organolithium reagents **30** and **31** (Scheme II) exhibit ^{13}C NMR signals at 14–71 ppm higher field than the analogous neutral olefin **32**[8,9] and the ^{13}C NMR signal for the cyclopentadienide anion **33** (in THF) is at 25 ppm higher field than the corresponding signal for benzene (**34**).

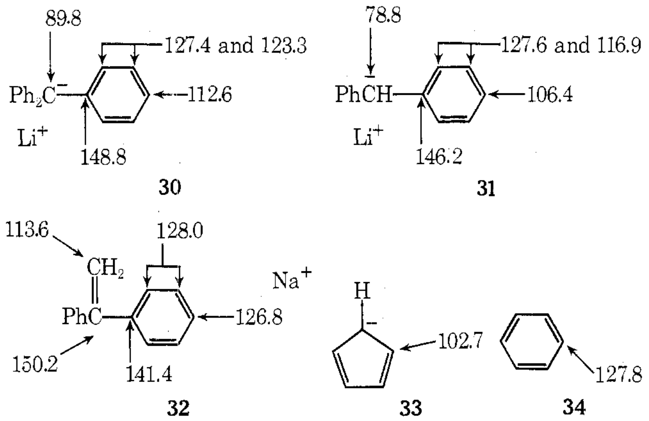
The aforementioned upfield shift differences (0.7–1.0 ppm for α-H atoms and 19–25 ppm for α-C atoms) observed when metal enolates are compared with the analogous enol acetates would suggest that the π-electron density at the α-C atom is greater in the metal enolates than in enol acetates by approximately 12–17% of a unit negative charge. Since there is question as to the quantitative relationship between ^{13}C chemical shift differences and calculated charge densities, especially in ionic molecules and in molecules containing heteroatoms,[3,10] it appears prudent to discuss the properties of various metal enolates in terms of the measured chemical shift difference parameter Δδ rather than calculated charge densities. However, it is appropriate to note that this parameter Δδ does appear to be largest in those circumstances where the enolate anions **1** might be expected to have a significant contribution from structure **1b** with the negative charge concentrated at the α-carbon atom.

In two cases, enolates **5a** and **6**, we measured the coupling constants, $^1J_{CH}$, between the α-carbon atom and the attached proton. The J values obtained, 145–154 Hz, did not differ appreciably from the J values, 154–157 Hz, for

Scheme I



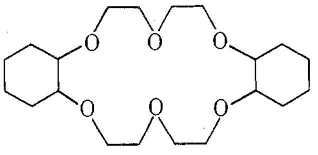
Scheme II. ^{13}C NMR Data

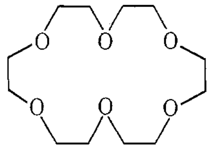


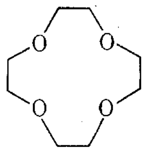
the corresponding enol acetates **11** and **19**. Consequently, these measurements suggest that the α-carbon atom of these enolates is not deformed significantly from a planar sp^2 configuration.

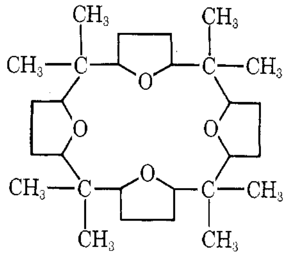
The high order of reactivity observed[11] in reactions of potassium enolates with alkyl halides is compatible with the $\Delta\delta$ values observed. In DME solution, the $\Delta\delta$ values decrease regularly in progressing from the K enolate **5c** ($\Delta\delta$ 24.8) to the Na enolate **5b** ($\Delta\delta$ 23.2) to the Li enolate **5a** ($\Delta\delta$ 21.3). The enhanced rate of alkylation of lithium enolates obtained by use of DME rather than Et$_2$O as a reaction solvent[12] is also consistent with the $\Delta\delta$ values observed. For the Li enolate **5a**, the $\Delta\delta$ values change with solvent as follows: DME ($\Delta\delta$ 21.3), THF ($\Delta\delta$ 19.5), Et$_2$O ($\Delta\delta$ 18.8). The addition of 4 equiv [sufficient to form the tetracoordinate solvated cation, Li(HMP)$_4^+$] of HMP, a solvent believed to be one of the most effective for solvation of metal cations,[13] to solutions of the lithium enolate **5a** in Et$_2$O, THF, or DME increased the values of $\Delta\delta$ to 22.5, 22.2, and 23.5 ppm, respectively. The largest effect (increasing $\Delta\delta$ by 3.7 ppm) was observed in adding 4 equiv of HMP to an Et$_2$O solution of the Li enolate. This observation is consistent with the practice of adding HMP to an Et$_2$O solution of a lithium enolate in order to increase its rate of reaction with an alkyl halide.[14]

Interestingly, the most effective additive for increasing the $\Delta\delta$ value at the α carbon of the enolate **5** (to $\Delta\delta$ 25.9) was the addition of 1 molar equiv of the crown ether **35** to a solution of the Na enolate **5b** in DME. Since no further change in the chemical shift values of enolate **5b** was observed when a second molar equivalent of the crown ether **35** was added, the formation of a 1:1 Na$^+$ cation–crown ether **35** complex is evidently very favorable. Unfortunately, we were unable to obtain sufficiently concentrated solutions of the K enolate **5c** in the presence of 1 molar equiv of either of the crown ethers **35** or **36** to permit NMR measurements.


35


36


37



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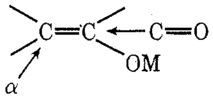
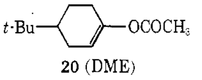
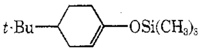
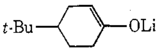
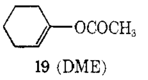
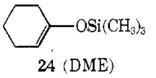
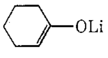
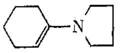
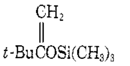
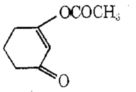
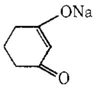
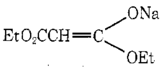
In contrast to the results obtained with the sodium enolate **5b**, the addition of 1 molar equiv of either of the crown ethers **36** or **37** to THF solutions of the lithium enolate **5a** had relatively little effect on the chemical shift values. Consequently, it appears that neither of the crown ethers **36** or **37** forms a sufficiently stable complex with Li$^+$ cation to enhance significantly the reactivity of lithium enolates. Since the common synthetically useful methods for the regiospecific generation of metal enolates produce lithium enolates, it is clearly desirable to find a crown ether of proper geometry to form a very stable complex with Li$^+$ cation, and we plan to continue our search for a suitable additive. Unfortunately, the low solubility of the crown ether **37** in ethereal solvents prevented us from obtaining useful ^{13}C NMR data in the presence of this material. It should be noted that the type of ^{13}C NMR measurements described in this paper do offer a rather simple experimental method for evaluating efficacy of various polydentate ligands as additives to enhance the reactivity of metal enolates.

It was also of interest to compare the $\Delta\delta$ values for the terminal lithium enolate **9** with the corresponding values for enolates **6–8** in which alkyl substituents are present at the α-carbon atom. Earlier work[15] had suggested that metal enolates with no alkyl substituents at the α-carbon atom are *less reactive* than analogous metal enolates with α-alkyl substituents. The $\Delta\delta$ values for DME solutions of

Table II. ^{13}C NMR Data for Saturated Carbonyl Derivatives



Compd (solvent)	Position of ^{13}C NMR signals, ppm relative to Me_4Si		
	α (Δδ)[a]	C=O	Other C atoms[b]
$(CH_3)_2CHCOCH_3$ **14** (DME)	41.7	210.0	18.3 (2 CH_3), 27.1 (acetyl CH_3)
$(CH_3)_2C{=}C(CH_3)OCOCH_3$ **18** (DME)	117.8	139.8	16.0 (CH_3), 17.3 (CH_3), 18.6 (CH_3), 20.3 (acetyl CH_3), 168.4 (ester C=O)
$(CH_3)_2C{=}C(CH_3)OLi$ **8** (DME)	92.3 (25.5)	150.6	18.7 (CH_3), 20.4 (CH_3), 21.5 (CH_3)
 **20** (DME)	113.0	148.4	20.5 (acetyl CH_3), 27.4 (3 CH_3 of *t*-Bu group), 24.5 (CH_2), 25.4 (CH_2), 28.3 (CH_2), 44.0 (CH at C–4), 32.3 (C of *t*-Bu group), 167.6 (ester C=O)
 **25** (DME)	102.5 (10.5)	149.7	0.0 (3 CH_3 of Me_3Si group), 27.0 (3 CH_3 of *t*-Bu group), 24.4 (CH_2), 25.0 (CH_2), 30.9 (CH_2), 44.0 (CH at C–4), 31.9 (C of *t*-Bu group)
 **7** (DME)	91.5 (21.5)	158.4	27.7 (3 CH_3 of *t*-Bu group), 25.9 (CH_2), 26.5 (CH_2), 34.5 (CH_2), 45.7 (CH at C–4), and 32.5 (C of *t*-Bu group)
 **19** (DME)	113.2[c]	148.5	20.5 (acetyl CH_3), 22.3 (CH_2), 23.2 (CH_2), 24.0 (CH_2), 27.3 (CH_2), 167.8 (ester C=O)
 **24** (DME)	102.8 (10.4)	149.9	0.3 (3 CH_3 of Me_3Si group), 22.6 (CH_2), 23.3 (CH_2), 23.8 (CH_2), 30.0 (CH_2).
 **6** (DME)	91.7[d] (21.5)	158.6	24.5 (CH_2), 25.0 (CH_2), 25.5 (CH_2), 33.7 (CH_2)
6 (THF)	89.6 (23.6)	159.0	25.0 (CH_2), 25.6 (CH_2), 26.1 (CH_2), 33.9 (CH_2)
 **27** (DME)	93.0 (20.2)	142.5	23.7 (CH_2), 24.0 (CH_2), 24.9 (3 CH_2, cyclohexenyl CH_2 and 2 CH_2 at β position of pyrrolidine), 47.4 (2 CH_2 at α position of pyrrolidine)
t-$BuCOCH_3$ **15** (DME)	24.1	210.3	26.4 (3 CH_3 of *t*-Bu group), 44.0 (C of *t*-Bu group)
t-$BuC(OCOCH_3){=}CH_2$ **21** (DME)	98.4	162.2	20.6 (acetyl CH_3), 27.9 (3 CH_3 of *t*-Bu group), 36.3 (C of *t*-Bu group) 167.3 (ester C=O)
 $t\text{-}Bu\overset{\overset{CH_2}{\Vert}}{C}OSi(CH_3)_3$ **26** (DME)	85.5 (12.9)	166.5	0.1 (3 CH_3 of Me_3Si group), 28.2 (3 CH_3 of *t*-Bu group) 36.6 (C of *t*-Bu group)
t-$BuC(OLi){=}CH_2$ **9** (DME)	73.5 (24.9)	176.8	29.7 (3 CH_3 of *t*-Bu group), 37.5 (C of *t*-Bu group)
 **22** (DME)	117.1	169.1	20.7 (acetyl CH_3), 21.7 (CH_2), 28.3 (CH_2), 36.9 (CH_2), 166.8 (ester C=O), 197.1 (ketone C=O)
22 (DMF)	116.7	169.6	20.9 (acetyl CH_3), 21.5 (CH_2), 28.5 (CH_2), 36.8 (CH_2), 167.7 (ester C=O), 197.7 (ketone C=O)
 **10** (DMF)	102.3 (14.4)	193.5	22.9 (CH_2 at C–5), 36.6 (2 CH_2 at C–4 and C–6)
$CH_2(CO_2Et)_2$ **29** (DMF)	41.6	166.1	14.1 (2 CH_3 of ethoxyl groups), 61.0 (2 CH_2 of ethoxyl groups)
 **28** (DMF)	62.1[e]	171.4	15.3 (2 CH_3 of ethoxyl groups) 56.1 (2 CH_2 of ethoxyl groups)

[a] Δδ is the chemical shift difference between the α-carbon atom of the enol acetate and the α-carbon atom of the enolate or related derivative. [b] Unless otherwise noted, each ^{13}C signal corresponds to a single carbon atom. [c] The $^1J_{CH}$ value was 157 ± 3 Hz. [d] The $^1J_{CH}$ value was 145 ± 3 Hz. [e] Since we lacked a suitable model, no measure of Δδ was made.

the unsubstituted enolate **9** ($\Delta\delta$ 24.9) and the enolate **8** ($\Delta\delta$ 25.5) with two methyl substituents are practically the same and both are greater than the values observed for the cyclohexanone enolates **6** ($\Delta\delta$ 21.5) and **7** ($\Delta\delta$ 21.5). Even in the case of a DME solution of the Li enolate **5a**, where some delocalization of negative charge into the para position of the phenyl ring was evident, the $\Delta\delta$ value (21.3) was comparable to the values observed with the cyclohexanone enolates **6** and **7**. Only in the case of the β-diketone enolate **10**, where delocalization of the negative charge to two equivalent carbonyl groups was possible, did the $\Delta\delta$ value (14.4) decrease. The decreased value of $\Delta\delta$ (presumably corresponding to diminished charge density at the enolate α-carbon atom) is compatible with the general observation that enolates of β-diketones tend to give significant amounts of O-alkyl products upon reaction with alkylating agents.

The several trimethylsilyl enol ethers **23, 25, 24,** and **26** examined had $\Delta\delta$ values (7.9–12.9) approximately half as large as the values observed for the metal enolates, an observation consistent with the fact that these materials are significantly poorer nucleophiles than metal enolates. Interestingly, the $\Delta\delta$ value (20.2) for the one enamine **27** examined was practically the same as the value for the corresponding metal enolate.

In conclusion, the $\Delta\delta$ values observed with a particular enolate system do appear to vary in a systematic way with changes in the metal cation, the solvent, and added ligands that can coordinate with the metal cation. In general, those combinations of cation, solvent, and added ligands that give the largest value of $\Delta\delta$ are also the combinations that result in the highest reactivity of the enolate with alkyl halides and in the greatest proportion of O- to C-acylation in reaction with Ac_2O. However, comparison of $\Delta\delta$ values for structurally different enolates derived from monoketones has not revealed any obvious relationship between the substitution pattern of the enolate anion, its reactivity, and its $\Delta\delta$ value.

Experimental Section[16]

Reagents and Starting Materials. All ethereal solvents were distilled from $LiAlH_4$ immediately before use. Previously described purification procedures[17] were used for Me_2NCHO (DMF) and $(Me_2N)_3PO$ (HMP). Oil dispersions (Alfa Inorganics) of NaH and KH were washed free of oil with purified pentane immediately before use. Ethereal solutions of halide-free MeLi (Foote Mineral Co.) were standardized by previously described procedures.[18] Samples of the trans enol acetate **17** and the trans silyl enol ether **23** were obtained by the previously described[2,19] reactions of the trans enolate **5b** with Ac_2O or Me_3SiCl. Previously described procedures were also used to obtain the silyl enol ethers **24**,[19a] **25**,[19a] and **26**[19a] and the enol acetates **19**,[2] **20**,[19b] and **21**.[19c] Reaction of dihydroresorcinol with excess boiling Ac_2O as previously described[20] produced the enol acetate **22** in 80% yield as a colorless liquid: bp 96 °C (0.8 mm); $n^{25}{}_D$ 1.4916 [lit.[20] bp 117 °C (6 mm)]; ir (CCl_4) 1773 (enol ester C=O), 1680 (conjugated C=O), and 1642 cm^{-1} (C=C); NMR (CCl_4) δ 5.6–5.7 (1 H, m, vinyl CH) and 1.7–2.7 (9 H, m, aliphatic CH including a CH_3CO singlet at 2.15); mass spectrum m/e (rel intensity), 154 (M^+, 12), 112 (15), 84 (56), 69 (12), and 43 (100).

Preparation of the Enol Acetate 18. To a solution of 200 g (2.0 mol) of Ac_2O and 34.4 g (0.40 mol) of i-PrCOMe in 450 ml of CCl_4 was added 0.28 ml of aqueous 70% $HClO_4$. After the resulting solution had been allowed to stand overnight, it was partitioned between 300 ml of pentane and 320 ml of saturated aqueous $NaHCO_3$. The organic layer was stirred over cold (0–8 °C) saturated aqueous $NaHCO_3$ to which was added portionwise 300 g of solid $NaHCO_3$ to complete the hydrolysis of Ac_2O. The combined organic layer and pentane extract of the aqueous phase were washed successively with H_2O, aqueous $NaHCO_3$, and aqueous NaCl and then dried (Na_2SO_4) and concentrated by fractional distillation. Fractional distillation of the residual liquid separated 9.0 g of material, bp 110–115 °C $n^{25}{}_D$ 1.4370, containing (GLC, TCEP on Chromosorb P) ca. 80% of the enol acetate **18** (retention time 5.3 min) accompanied by CCl_4 (1.3 min) and the starting ketone (2.7 min) and 16.54 g of material, bp 116–125 °C, $n^{25}{}_D$ 1.4230 [lit.[21] bp 121 °C (763 mm), $n^{20}{}_D$ 1.4222], containing (GLC) >98% of the enol acetate **18**: ir (CCl_4) 1755 (enol ester C=O) and 1701 cm^{-1} (enol C=C); NMR (CCl_4) δ 2.03 (3 H, s, $COCH_3$) with three partially resolved multiplets at 1.81, 1.70, and 1.51 (each 3 H, allylic CH_3); mass spectrum m/e (rel intensity) 128 (M^+, 66), 87 (17), 86 (79), 85 (18), 71 (100), 58 (22), 43 (89), 41 (46), and 39 (27).

Preparation of Solutions for NMR Study. A. Ph_3CLi and Ph_2CHLi. Solutions of ca. 23 mmol of MeLi in 8 ml of DME were prepared by a previously described procedure[18b] in which Et_2O solutions of MeLi were concentrated under reduced pressure and the residual solid MeLi (still containing some Et_2O) was redissolved in DME. These solutions were treated with 2–3 ml of a DME solution containing either 2.44 g (10 mmol) of Ph_3CH or 1.67 g (10 mmol) of Ph_2CH_2 and the resulting solutions were stirred for 30–90 min at 25 °C at which time ^1H NMR analysis indicated that conversion of the hydrocarbons to their lithio derivatives was complete and some excess MeLi remained in the solutions. Aliquots (3.0 ml) of these red (Ph_3CLi) or orange (Ph_2CHLi) solutions were mixed with 0.3 ml of C_6D_6 (to provide a "lock" signal) and 0.3 ml of Me_4Si (internal reference signal). The ^{13}C NMR spectra of these solutions and all subsequently described solutions were determined both with complete proton decoupling and with partial (off-resonance) proton decoupling. The "extraneous" ^{13}C NMR signals (from solvents and reagents) found in these and subsequently described solutions were found at the following locations (in parts per million relative to internal Me_4Si): C_6D_6, 126.9, 127.8, and 128.8; DME, 58.5 and 72.1; Et_2O, 15.5 and 65.8; THF, 26.1 and 67.8; MeLi, −14.0; DMF, 30.8, 35.8, and 161.9; $CDCl_3$, 75.3, 76.6, and 77.8; t-BuOLi (in DME), 35.6 and 66.4; t-BuOH (in DME), 31.4 and 67.8. In certain cases involving subsequently described solutions of enol acetates and metal enolates, the ^{13}C NMR spectra were measured without proton decoupling to obtain the coupling constant, $^1J_{CH}$, for the α carbon of the enol acetate or metal enolate. These $^1J_{CH}$ values are indicated in Tables I and II.

B. Olefins, Ketones, Enol Acetates, and Trimethylsilyl Enol Ethers. Solutions of these materials were prepared by dissolving 200–500 mg of each purified material in 2.5–3.0 ml of the solvent indicated in the tables and then adding 0.3 ml of C_6D_6 and 0.3 ml of Me_4Si.

C. Sodium and Potassium Enolates. A slurry of excess prewashed KH or NaH (1–2 mmol/ml of solvent) in the solvent stated in the tables was treated with one of the active methylene compounds **11**, **16**, or **29** and the mixture was stirred at 15–25 °C until H_2 evolution ceased (typically 20–30 min). Aliquots of these solutions were mixed with 10% (by volume) of C_6D_6 and 10% (by volume) of Me_4Si for ^{13}C NMR measurements. The ^1H NMR spectra of the phenylacetone enolates **5** were described previously.[2] A 1 M solution of the Na enolate **10** in DMF exhibited NMR signals at δ 4.49 (s, vinyl CH) and 1.1–2.5 (m, aliphatic CH).

D. Lithium Enolates. A 1.1 M solution of the Li enolate **8** (accompanied by t-BuOLi) in DME was obtained by reaction of the enol acetate **18** with a DME solution of MeLi in the usual manner.[18b] Solutions containing about 1 M Li enolate **5a** in Et_2O, THF, and DME were obtained by reaction of the trimethylsilyl enol ether **23** with excess MeLi in the appropriate solvent at 25 °C for 60 min. Aliquots of these solutions containing 2 mmol of the enolate **5a** in 2 ml of solvent were also either diluted with DME or treated with 1.4 ml (8 mmol) of freshly purified HMP before measurement of the ^{13}C spectra. Solutions containing 1 M Li enolate **6** or **9** in THF or DME were obtained by reaction of the corresponding trimethylsilyl enol ether **24** or **26** with MeLi. The Li enolate **6** was not sufficiently soluble in Et_2O to permit satisfactory NMR study. A 1 M solution of the Li enolate **7** in DME was similarly prepared by reaction of the trimethylsilyl enol ether **25** with MeLi.

E. $Na^+C_5H_5^-$. Freshly prepared cyclopentadiene (124 ml, 1.65 mol) was added dropwise and with stirring at 25 °C during 1.5 h to a suspension of 69.0 g (1.5 g-atom) of Na dispersion (50% in mineral oil) in 600 ml of DME.[22] After the addition was complete the white slurry was heated to reflux with stirring and then allowed to cool. The white to pale-pink crystalline $C_5H_5^-Na(DME)^+$ was separated from the red supernatant liquid, washed with hexane, and dissolved in THF to give a solution containing[18a] 0.80 M $C_5H_5^-Na^+$ as well as the DME present in the original complex. This solution (with added Me_4Si) exhibited a ^1H NMR singlet at δ 5.59; after addition of C_6D_6 and Me_4Si, the ^{13}C NMR spectrum exhibited a signal attributable to the $C_5H_5^-$ anion at 102.7 ppm.

F. Metal Enolates in the Presence of Crown Ethers. The dicyclohexyl crown ether **35** (mp 41–55 °C, lit.[23] mp 38–54 °C, a mixture of the cis-syn-cis and cis-anti-cis stereoisomers) was prepared by a previously described procedure[23] as was the crown ether **38** (mp 203–206.5 °C, lit.[24] mp 208–211 °C, a mixture of stereoisomers).[24] Preparative procedures for the crown ethers **36** and **37** have been described elsewhere.[25] Solutions of the crown ethers **35**–**37** in DME (containing C_6D_6 and Me_4Si) exhibited the following ^{13}C NMR signals: **37**, 71.1 ppm; **36**, 70.9 ppm; **35**, 77.8 (CH–O), 71.2 (CH_2–O), 68.8 (CH_2–O), 28.4 (CH_2), and 22.6 ppm (CH_2). The polyether **38** was too insoluble in the ethereal solvents employed in this study to obtain useful ^{13}C NMR data.

Our efforts to study the ^{13}C NMR spectra of mixtures of the potassium enolate **5c** and a crown ether were unsuccessful because addition of 1 molar equiv of either of the crown ethers **35** or **36** to a DME solution of the potassium enolate **5c** resulted in the immediate separation of a precipitate. This precipitate from **5c** and **36** was also insoluble in Et_2O and in DMF. After a slurry of 468 mg (19.5 mmol) of NaH (prewashed with pentane) in 9 ml of DME containing 3.00 g (8.0 mmol) of crown ether **35** had been stirred at 25 °C for 15 min, 1.07 g (8.0 mmol) of ketone **11** was added, dropwise and with stirring. The mixture was stirred until H_2 evolution ceased to give a dark red solution of the enolate **5b** containing 1 molar equiv of crown ether **35**. A comparable procedure was used to obtain a DME solution of the enolate **5b** containing 2 molar equiv of crown ether **35**. Aliquots (2.00 ml) of these solutions were mixed with 0.25 ml of C_6D_6 and 0.25 ml of Me_4Si to obtain the ^{13}C NMR data listed in Table I. The ^1H NMR spectrum of this solution exhibited a singlet at δ 4.60 attributable to the enolate vinyl CH; the corresponding signal for a solution of this enolate **5b** in DME with no added crown ether is at δ 4.70.[2]

A 3-ml aliquot of a solution of the enolate **5a**, prepared from 1.265 g (6.14 mmol) of the silyl enol ether **23** and 8.8 mmol of MeLi in 6 ml of THF, was mixed with 750 mg (2.8 mol, 0.9 molar equiv) of the crown ether **36** in 1.2 ml of THF containing 0.35 ml of C_6D_6 and 0.25 ml of Me_4Si for NMR study. Similarly, a solution for NMR study was prepared from 1.0 ml of a THF solution containing 1.12 mmol of the lithium enolate **5a**, 1.2 mmol (1.1 molar equiv) of the crown ether **37** (dried over LiH), 0.25 ml of C_6D_6, and 0.15 ml of Me_4Si.

Registry No.—**5a**, 37392-64-6; **5b**, 37392-66-8; **5c**, 57918-71-5; **6**, 21300-30-1; **7**, 20826-82-8; **8**, 57918-72-6; **9**, 34865-75-3; **10**, 57910-97-1; **11**, 103-79-7; **14**, 563-80-4; **15**, 75-97-8; **17**, 19980-46-2; **18**, 3814-41-3; **19**, 1424-22-2; **20**, 7360-39-6; **21**, 3840-71-9; **22**, 57918-73-7; **23**, 19980-24-6; **24**, 6651-36-1; **25**, 19980-19-9; **26**, 17510-46-2; **27**, 1125-99-1; **28**, 57918-74-8; **29**, 105-53-3; **30**, 733-90-4; **31**, 881-42-5; *cis-syn-cis*-**35**, 15128-65-1; *cis-anti-cis*-**35**, 15128-66-2; **36**, 17455-13-9; **37**, 294-93-9; acetic anhydride, 108-24-7.

References and Notes

(1) This research has been supported by Public Health Service Grant RO1-GM-20197 from the National Institute of General Medical Science. The execution of this research was also assisted by Institution Research Grants from the National Science Foundation for the purchase of a mass spectrometer and a Fourier transform NMR spectrometer.

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(9) In a private communication, Professor Daniel H. O'Brien has suggested that the differences between the ^{13}C NMR values we observed for the lithium compounds **30** and **31** in DME solution and the values he observed (ref 6e) for the analogous potassium derivatives in THF is attributable to the existence of the Li derivatives in DME as solvent separated ions and the K derivatives in THF as contact ion pairs.

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