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Communications

Facile Reaction of Potassium Hydride with Ketones. Rapid Quantitative Formation of Potassium Enolates from Ketones *via* Kaliation[1]

Summary: In contrast to lighter saline hydrides, KH in tetrahydrofuran vigorously metalates a wide range of ketones with little or no self-condensation or reduction; solutions of highly reactive potassium enolates are formed quantitatively in minutes at 20°.

Sir: Potassium hydride in ethereal solvents exhibits exceptional reactivity toward weak carbon acids such as fluorene (pK_A = 23), methyl *tert*-butyl ketone (pK_A = 20.8), and indene (pK_A = 19), in marked contrast to the sluggishness or inertness of lighter saline hydrides (NaH and LiH). Of particular interest is the metalation of ketones; quantitative formation of highly reactive potassium enolates requires only minutes at room temperature even with relatively hindered structures. Pure solutions of the enolates—free of ketone by ir—are obtained by decantation.

Ketone enolates are versatile reactive intermediates of interest as probes of cation solvation and ion pairing in ambient ions,[2] in formation of carbon–carbon bonds in synthesis,[3] and as ligands of transition metals.[4] Formation of enolates from ketones has been accomplished recently by a variety of methods[5-12] with lithium as the cation in the great majority of cases. Only occasionally have saline hydrides been employed[13,14] despite their attractive simplicity: they are insoluble in nonreacting organic solvents and are readily separated; the sole by-product of metalation is hydrogen gas; and hydrides are both readily available and indefinitely stable. Unfortunately, reaction of LiH and NaH with unactivated ketones has proven exceptionally sluggish. Even a relatively acidic ketone—butyrophenone—has been reported to require several days at 35° (ether solvent) for complete metalation by NaH.[13a] Metalation by NaH is also complicated by considerable self-condensation of the ketone.[14]

KH[16a] is far more reactive than LiH[16a] or NaH[16a] toward ketones in tetrahydrofuran (THF), as illustrated in Figure 1 in metalation of methyl *tert*-butyl ketone (pinacolone). This enhanced reactivity is *not* an artifact of the degree of dispersion of solid KH; even particularly finely divided NaH (sedimentation rate in pentane <0.1 times that of KH) reacts much more sluggishly.

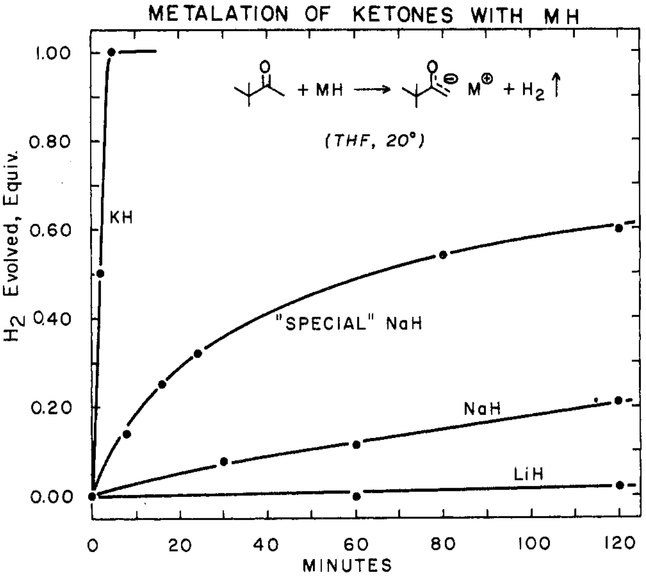

Figure 1. Metalation of pinacolone in tetrahydrofuran (0.5 *M*) with excess saline hydrides. "Special NaH" was a sample of particularly finely divided NaH obtained from Ventron Corp.[16b] Other hydrides are standard commercial products of Alfa Products Div. of Ventron Corp.

Metalation is readily accomplished by addition of the ketone to a vigorously stirred suspension of KH in anhydrous THF at 20°; hydrogen evolution commences immediately and is very vigorous. In a typical example 25 mmol of pinacolone was metalated in 5 min by 28 mmol of KH suspended in 40 ml of THF, the bulk of the hydrogen being evolved in <2 min. The clear supernatant solution showed 0-1% ketone in several runs by ir analysis.[17] The 1710-cm^{-1} absorption (C=O stretch) disappears upon metalation and is replaced by a strong absorption at 1568 cm^{-1}. Glpc analysis of a sample quenched in a mixture of ether and 1.0 *M* HCl showed 100% recovery of ketone. Addition of excess triethylamine and trimethylchlorosilane[5] to the reaction mixture at −78° yielded >98% trimethylsilyl enol ether.

Similar results were obtained with a variety of ketones including those labile toward self-condensation, as shown in Table I. No reduction of the carbonyl group by KH was observed.[18] Unsymmetrically substituted ketones yield directly equilibrium mixtures of enolates.

Potassium enolates are highly reactive. Thus the enolate of 2,4-dimethyl-3-pentanone reacts with excess methyl iodide in 5 min at −78°; a 50:1 ratio of mono to dialkylated products is formed.[19]

In the absence of excess ketone, potassium enolates do not equilibrate; however, the highly reactive enolates may be equilibrated readily in the presence of small amounts of free ketone even at −78° to yield enolate mixtures enriched in the more stable component. Thus 3-methyl-2-butanone is metalated to yield an equilibrium mixture of enolates containing 88% *less* substituted isomer at 20°; no

Table I: Kaliation of Ketones at 20° [a]

Compd	Time (min)		Enolate yield, %[c]	Enolate (less:more substd)[d]
	50%[b]	100%[b]		
Acetone	0.5	1.5	90	
2-Heptanone	0.5	1.5	100	46:54
3-Me-2-butanone	0.5	1	101	88:12
3,3-DiMe-2-butanone	2.0	5	97	
2,4-DiMe-3 pentanone	2.5	10	100	
Isobutyrophenone	3.5	12	93	
Cyclohexanone	0.5	1.5	88	
2-Methylcyclohexanone	2.0	6	95	33:67

[a] 25.0 mmol of ketone, 28–32 mmol of KH in ~50 ml of THF. Glyme solvents are also satisfactory. No evidence of reduction was observed. [b] Per cent reaction was determined by gas evolution. [c] Determined by quenching samples containing hydrocarbon standards in water followed by glpc analysis. Ketone was absent in enolate solutions by ir. [d] By silylation at −78°. Silyl ethers isolated had spectra consistent with structures.

change in the composition is observed in 1 hr at −78°. However, if the enolate solution (0.4 *M*) is stirred at −78° for 0.75–1.0 hr with 0.08 equiv of free ketone, the enolates are reequilibrated to a mixture containing >98.5% less substituted isomer.

Alkylation and silylation may be carried out without difficulties *in situ* in the presence of excess KH.

The solutions of potassium enolates may be transformed into lithium enolates by metathesis with lithium bromide in THF; KBr precipitates immediately upon mixing. In the case of pinacolone, the cation exchange was accompanied by a shift in the enolate ir absorption from 1568 to 1604 cm^{-1}, consistent with tighter association of the lithium ion with the more electronegative end of the anion. The preparation of enolates of di- and trivalent cations is in progress.

Current preparations of enolates are often based upon lithium amides.[10,11] However, varying amounts of addition to the carbonyl group appear to occur even with the highly hindered lithium diisopropylamide. Moreover, lithium enolates are far less reactive (10^{-3}–10^{-4}) than potassium enolates,[13a] and lithium halides do not precipitate from ethereal solvents to assist metathesis reactions.

The exceptionally high reactivity of KH toward ketones provides a novel direct route to highly reactive potassium enolates. The facile formation of these intermediates provides new possibilities for investigation of enolate chemistry.

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(17) Infrared spectra was determined using a Perkin-Elmer Model 521 spectrometer in scale change scan mode, relative to the 1944-cm^{-1} absorption of polystyrene, in ~0.50 *M* THF solution.

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Photochemical Transformation of Truxones to C-Nor-D-homo Steroid Systems

Summary: Photodecarbonylation of truxones leads to benzobicyclohexene systems which undergo a rearrangement to products with a C-nor-D-homo steroid skeleton.

Sir: In the synthesis of 6-methoxyindenones **2** through the AlCl$_3$-catalyzed internal ketovinylation of the corresponding β-chlorovinyl ketones **1**,[1] we observed the formation of small to large amounts of truxones, which were identified as endo head-to-tail dimers **3**.[2] The ability of the 6-methoxy group to stabilize a positive charge on the C$_3$ is probably responsible for this easy AlCl$_3$-catalyzed dimerization, which does not occur with 2-ethyl-5-methoxyindenone, even at much higher temperatures.[3] In an attempt to obtain the indenone **2a** through a photocycloreversion from the dimer **3a**, a new product was obtained, which, according to the mass spectral analysis, should correspond to a decarbonylated dimer. A 16-hr irradiation of the endo dimer **3a** with a high pressure mercury lamp afforded 54% of the decarbonylated product and 46% indenone **2a**. This decarbonylated product was identified as **5a**, a product with a C-nor-D-homo steroid skeleton. An alternative structure **4a** was rejected as the product showed no long-wavelength absorption (400 nm) as is observed in comparable *o*-quinodimethanes.[4] The decarbonylated product did not show any Diels–Alder activity with tetracyanoethylene, as was expected for **4a**.

The nmr spectrum of the decarbonylated product shows a coupling constant of 1.5 Hz between one of the methyl groups and the vinylic proton. This is in good agreement with structure **5a**, but not with structure **4a**, where a coupling across six bonds is required. In C$_6$D$_6$ 1-H undergoes a large downfield shift (0.54 ppm) which is expected for structure **5a** but not for the corresponding proton in structure **4a**. The dimer **3b** gives analogous results. According to the mass spectral data of the rearranged product **5b**, the most important fragmentation is loss of CH$_3$COOEt from the molecular ion (M − 88). This indicates that the 8-H and the 9-CH$_2$COOEt are located at