of a "cyclopropylmethylene" diradical[16] of the general formula **17** as an intermediate.

17

We are continuing to investigate both the synthetic and mechanistic aspects of 2,3-diazabicyclo[3.1.0]hex-2-ene photochemistry.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

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[16] R. Srinivasan, *J. Amer. Chem. Soc.*, **90**, 4498 (1968); J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **92**, 3227 (1970).

[17] National Science Foundation Undergraduate Research Participant, summer 1971.

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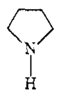
The Remarkable Fast Reaction of Potassium Hydride with Amines and Other Feeble Organic Acids. A Convenient Rapid Route to Elusive New Superbases[1]

Sir:

Potassium hydride exhibits remarkable activity toward weak organic acids such as amines, sulfoxides, and hindered tertiary carbinols. At 25–50°, this insoluble saline hydride reacts smoothly to form mono- and dialkylamides, a previously unknown class of extremely vigorous "superbases" soluble in organic solvents. Other important strong bases such as "dimsyl" anion and hindered tertiary alkoxides are also formed with unprecedented ease.

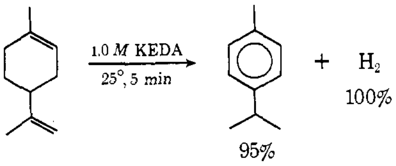
Pyrrolidine is inert toward fine (<0.5 mm) potassium sand at 50° for 24 hr; in refluxing amine, 20% of the potassium reacts in 8 hr with considerable darkening of the reaction mixture and decomposition of the amine. In contrast, KH (50.0 mmol, 2.0 g) in 50 ml of dry pyrrolidine at 25° reacts completely in 2 hr. The yield of amide is 93% by titration (triphenylmethane indicator). Sodium hydride is far more sluggish, as shown in Figure 1. Kaliation of some representative amines is summarized in Table I.

Table I. Kaliation of Amines with KH in Excess Amine[a]

Amine	Temp, °C	Time	Yield, %	
			H_2[b]	Amide[c]
	25	2 hr	95	93
$H_2NCH_2CH_2NH_2$[d]	25	5 min	100	95
$(CH_3)_2CHCH_2NH_2$[d]	50	1 hr	105	92

[a] 50.0 ml of amine, 50.0 mmol of KH. [b] ±5%. [c] Minimum values from titration with triphenylmethane indicator, compared to titration of total base after quenching with water. [d] Monometalation.

Potassium mono- and dialkylamides appear unknown in the literature. These elusive materials—now readily available *via* kaliation with KH—are bases of exceptional reactivity for prototropic reactions. Thus, 1.0 *M* *N*-kaliopyrrolidine in excess amine isomerizes 2-methyl-1-pentene with $k_{isom} > 10^{-2}$ sec^{-1}, much faster than KO-*t*-Bu–DMSO.[2] *N*-Kalioethylenediamine (1.0 *M* in excess amine) aromatizes limonene in 5 min at 25°. The lithium analog[3a] fails to aromatize limonene in 1 hr under comparable conditions.[3b] Investigations of these base systems for isomerization, elimination, and aromatization reactions are in progress.



Other useful bases such as "dimsyl" anion[4a] and hindered tertiary alkoxides[5] are also readily formed.

Dry dimethyl sulfoxide (DMSO) reacts vigorously at 25° with KH[6] to yield a clear, pale yellow solution of "dimsyl" potassium; hydrogen evolution is quantitative in 8 min. In contrast, NaH is much more sluggish.[6b,7]

The solutions of "dimsyl" potassium react analogously to "dimsyl" sodium.[4,8] Kaliation with KH provides the only rapid direct route to "dimsyl" solutions with a completely inert, noncondensable, and insoluble by-product.[9]

Hindered tertiary alcohols also react vigorously with quantitative liberation of hydrogen. Thus, 50 ml of 3-ethyl-3-pentanol reacts with 50.0 mmol of KH upon contact to yield a clear, colorless solution of potassium triethyl carboxide. Potassium metal sand is more sluggish and fails to react completely unless heated vigorously; moreover, highly colored solutions occur unless the potassium is carefully freed of superoxide coating.[5a,10] Sodium hydride is nearly inert to hindered alcohols (Figure 2).

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[1] Kaliation. I.

[2] S. Bank (*J. Org. Chem.*, **37**, 114 (1972)) reports $k_{isom} \approx 2 \times 10^{-4}$ at 55°.

[3] (a) L. Reggel, S. Friedmen, and I. Wonder, *J. Org. Chem.*, **23**, 1136 (1958); (b) at 90°, over 2 hr is required for aromatization of limonene by excess $LiNHCH_2CH_2NH_2$.

[4] (a) E. J. Corey and M. Chaykowski, *J. Amer. Chem. Soc.*, **84**, 866 (1962); *ibid.*, **87**, 1345 (1965), and references therein; (b) L. F. Fieser and M. F. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 310; Vol. II, 1969, p 166; Vol. III, 1972, p 123.

[5] For example, see: (a) S. P. Acharya and H. C. Brown, *Chem. Commun.* 305 (1968); (b) H. C. Brown and I. Moritani, *J. Amer. Chem. Soc.*, **75**, 4112 (1953); (c) H. C. Brown, J. H. Kawakami, and S. Misumi, *J. Org. Chem.*, **35**, 1360 (1970); (d) H. C. Brown and B. Carlson, private communication (reactions of organoboranes with halo compounds).

[6] (a) Optimum temperature for preparation of "dimsyl" sodium is reported[4a] to be 70–75°; decomposition occurs over 80°.[4a,6b] Sjöberg reports that solutions prepared at the recommended temperature are unstable; stable "dimsyl" Na solutions are obtained only by reaction of NaH with DMSO under prolonged ultrasonic aggitation at 25°.[6c] (b) C. C. Price and T. Yukuta, *J. Org. Chem.*, **34**, 2503 (1969); (c) K. Sjöberg, *Tetrahedron Lett.*, 6383 (1966).

[7] Corey and Chaykowsky[4a] report heating at 70–75° for 45 min. We find that at 25°, less than 5% of the hydrogen is evolved in 20 min. At temperatures above 75°, the reaction is faster but decomposition occurs.[4a,7b] Even at 70° some decomposition occurs, rendering the "dimsyl" solutions unstable with time.[6c]

[8] However, some differences as titrating agents have been reported; see ref 9a.

[9] Past preparations of "dimsyl" potassium: (a) DMSO + KNH_2, E. C. Steiner and M. C. Gilbert, *J. Amer. Chem. Soc.*, **85**, 3054 (1963); (b) DMSO + KO-*t*-Bu, G. J. Mikol and G. A. Russell, *Org. Syn.*, **48**, 109 (1968); (c) DMSO + K, A. Ledwith and N. McFarlane, *Proc. Chem. Soc.*, 108 (1964). This latter procedure yields $CH_3S^-K^+$ and K^+OH^- along with the dimsyl anion.

[10] D. E. Pearson and O. D. Keaton, *J. Org. Chem.*, **28**, 1557 (1963).

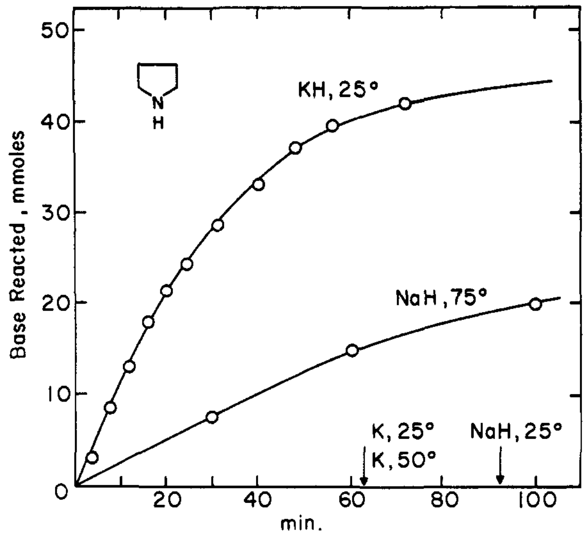

Figure 1. Reaction of strong metalating agents with pyrrolidine.

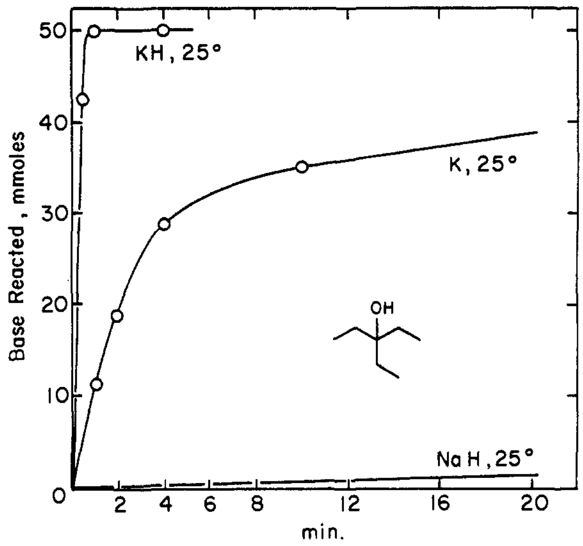

Figure 2. Reaction of strong metalating agents with triethylcarbinol.

The KH and NaH[11,12] employed in this study are prepared by hydrogenation of the molten metal dispersed in mineral oil at 200°. No current data are available regarding surface area or aggregation; however, the particle size appeared to be similar. Both hydrides appear to be totally insoluble in the common ethereal solvents; no H^- activity appears in the centrifuged supernatant liquid after prolonged stirring. KH appears to be a very poor reducing agent, although methyl iodide is attacked slowly at 50° in tetrahydrofuran (THF). In THF, alcohols react vigorously with KH to yield the alkoxide; however, pretreatment of the KH with trimethylchlorosilane inhibits or poisons the surface, possible through formation of insoluble KCl.

At present, insufficient data are available to explain the high reactivity of KH; however, it is interesting to note that reactivity increases (LiH[13] $<$ NaH $<$ KH) while lattice energies[14] of the saline hydrides fall (LiH $>$ NaH $>$ KH).[15]

In the few cases where comparisons exist, the reactivity of bases varies with the cation in the order K $\gg$ Na $>$ Li.[2,16a,b] This order is also observed for dissociation of "dimsyl" salts.[16c] Nonetheless, lithium salts of very weak acids are far more generally used[17] due to ease of formation *via* available organolithium compounds; no comparable route to potassium analogs has existed. Kaliation with KH[18] now provides strong potassium bases with unprecedented ease. The new mono- and dialkylamides of potassium appear to be the most reactive bases both soluble in and stable toward moderately polar organic solvents. Preliminary results indicate that they will open new avenues in synthetic chemistry and proton transfer studies.

Further studies on the reactions of KH with organic, organometallic, and inorganic compounds as well as exploitations of the new amide "superbases" are in progress. It is also hoped that the high observed reactivity of KH will stimulate investigations of KH surface reactions beyond the scope of our laboratory.

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(11) Obtained from Alfa Products, Division of Ventron Corp.

(12) (a) Highly reactive NaH has been prepared by hydrogenation of sodium naphthalene.[12b,c] The potassium naphthalene complex fails to hydrogenate under similar circumstances; however, other more reactive radical anions of potassium may be suitable. (b) S. Bank and T. A. Lois, *J. Amer. Chem Soc.*, **90**, 4505 (1968); (c) E. E. van Tamelen and R. B. Fechter, *ibid.*, **90**, 6854 (1968).

(13) (a) LiH has been reported less reactive than NaH toward DMSO,[4a] weak Lewis acids,[12b] and amides;[12c] (b) H. C. Brown, private communication; (c) R. Schlessinger, private communication.

(14) (a) S. R. Gunn and L. G. Green, *J. Amer. Chem. Soc.*, **80**, 4782 (1958); (b) L. Dass and S. C. Saxena, *J. Chem. Phys.*, **43**, 1747 (1965).

(15) (a) The ionic radius of H^-, calculated from lattice constants and alkali metal Pauling radii, increases substantially from LiH to KH. After KH, the calculated H^- radius is constant. Possibly this reflects either some covalency of M–H or compression of H^- in LiH and NaH, which might be expected to hinder the $H^- H^+$ reaction. (b) The reactions of weak acids with KH should present a useful entry into reactions at crystal faces; unlike common metathetical reactions, the reaction liberating H_2 is essentially irreversible.

(16) (a) S. Bank, A. Schriesheim, and C. A. Rowe, Jr., *J. Amer. Chem. Soc.*, 87, 3244 (1965); (b) A. Schriesheim, address to the New York Academy of Sciences, Oct 10, 1968; (c) E. C. Steiner, R. O. Trucks, J. D. Starkey, and J. G. Exner, *Amer. Chem. Soc. Polym. Prepr.*, **9**, 1135 (1968).

(17) (a) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, New York, N. Y., 1972, Chapters 9 and 10; (b) see ref 17a, p 547, and references therein.

(18) Potassium hydride in oil reacts slowly with moist air and is best handled under nitrogen or argon. It reacts very vigorously with water, smoking and sputtering in a manner similar to sodium metal. We normally handle the oil dispersion with a wide mouth (*ca.* 2 mm) medicine dropper. Droppers and stirrers are washed with kerosine; the kerosine–KH residue should be disposed of in a manner analogous to $LiAlH_4$, Na metal, etc. If desired, the oil may be removed by washing the dispersion with *dry* pentane, benzene, ether, etc. KH which has been separated from the oil by washing should *never* be allowed to contact air.

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Photoionization of Pyrene in Polar Solvents. The Role of the Triplet State

Sir:

Pyrene, when excited by light in the wavelength range of its visible and uv absorption spectrum, undergoes a