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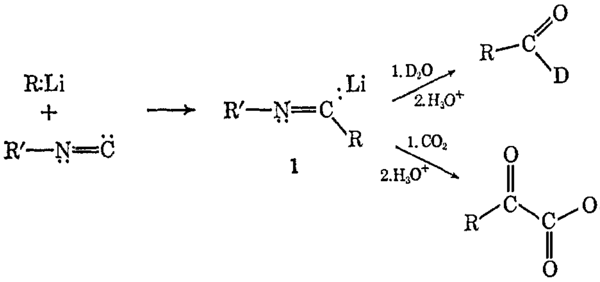
Lithium Aldimines. A New Synthetic Intermediate[1]

Sir:

The recent reports by Meyers[2] on his elegant syntheses of aldehydes and ketones prompts us to report our findings on the simple synthesis of lithium aldimines (1), which we have used as precursors for the preparation of aldehydes, 1-deuterio aldehydes, and α-keto acids.[3]



The lithium aldimine (1) reagent is prepared by the addition of an organolithium reagent to the appropriate isonitrile, which in this case is 1,1,3,3-tetramethylbutylisonitrile[4] (TMBI). For example, when 1 equiv of *sec*-butyllithium and TMBI were combined, treated with D_2O, and then hydrolyzed, 1-deuterio-2-methylbutanal was isolated in 92% yield.[5] This is, in our opinion, the cheapest and most convenient synthesis of C-1 labeled aldehydes yet reported.[2,6] Moreover, carbonation of the intermediate lithium aldimine (1) yields, after hydrolysis, the corresponding α-keto acid in 80% yield.

Various types of α additions to isonitriles have been observed originally by Ugi and coworkers[7] and later by Saegusa and coworkers,[8] but our work represents the first successful 1:1 addition by an organometallic to an isonitrile.[9] Table I lists the reactions carried out to date and the isolated yields of pure products.

Table I. Aldehydes and α-Keto Acids from Organolithium and 1,1,3,3-Tetramethylbutylisonitrile (TMBI)

		—% overall yield—	
RiLi	% crude 1	Aldehyde[b]	α-Keto acid[b]
sec-Butyl	100[a]	96	80
	100[c]	92[c]	
n-Butyl	100[a]	93	56
Phenyl	67	55	52

[a] Reaction solvent was pentane. [b] All aldehydes and α-keto acids gave 2,4-dinitrophenylhydrazones which compared with the literature values. [c] Represents yield of 1-deuterio derivative.

The following is an experimental procedure which shows the simplicity of the synthesis. To a stirred solution of 3.76 g (0.027 mol) of TMBI[10] dissolved in 27 ml of ether at 0° under a nitrogen atmosphere is added rapidly 0.027 mol of *sec*-butyllithium in hexane to yield a solution of **1**.

(a) After 10 min, 1.6 ml (0.08 mol) of D_2O was added and stirring continued for an additional 10 min. The reaction mixture was filtered and the solvent evaporated to yield 5.45 g (quantitative crude yield) of aldimine. Steam distillation of the crude aldimine from 0.027 mol of oxalic acid yielded 2.16 g (0.025 mol 92%) of 1-deuterio-2-methylbutanal, bp 92°. Nmr analysis showed >97% deuterium incorporated.

(b) After 10 min, the solution of **1** was added dropwise to an ether slurry of Dry Ice. The solvent was evaporated and the carbonated imine was refluxed in an oxalic acid solution (7.5 g of oxalic acid in 60 ml of water) for 15 min. Extraction with methylene chloride, followed by evaporation of solvent, gave 2.8 g (80% yield) of 2-oxo-3-methylpentanoic acid which gave a 2,4-DNP derivative, mp 169–170°.

The scope and limitations of this[11] and related reactions are under current investigation.

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(1) The support of this work by grants from the National Science Foundation and Public Service Research Grant No. 04065 from the National Cancer Institute is gratefully acknowledged.

(2) A. I. Meyers, A. Nabeya, H. W. Adickes, and I. R. Politzes, *J. Amer. Chem. Soc.*, **91**, 763 (1969); A. I. Meyers, *et al.*, *ibid.*, **91**, 764, 765 (1969); A. I. Meyers and A. C. Kovelesky, *ibid.*, **91**, 5887 (1969).

(3) It should be recognized that lithium aldimines (1) have the potential use as intermediates for the preparations of ketones, α-amino acids, and acyloins, just to name a few. We are in the process of exploring this potential.

(4) The reason for the choice of this particular isonitrile will be discussed in our full paper.

(5) Isotopic purity is greater than 97% by nmr analysis.

(6) E. J. Corey and D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 1075, 1077 (1966); D. Seebach, B. Erickson, and G. R. Singh, *J. Org. Chem.*, 31, 4303 (1966); J. C. Craig, *ibid.*, 33, 781 (1968); R. A. Olafson and P. M. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 5058 (1967); D. J. Bennett, *Chem. Commun.*, 218 (1967).

(7) (a) I. Ugi, *Angew. Chem. Intern. Ed. Engl.*, **1**, 8 (1962); (b) I. Ugi, K. Rosendahl, and F. Bodesheim, *Ann.*, **666**, 54 (1963); (c) I. Ugi and E. Boettner, *ibid.*, **670**, 74 (1963); (d) I. Ugi and K. Offermann, *Ber.*, **97**, 2276 (1964); (e) I. Ugi, W. Betz, and K. Offermann, *ibid.*, **97**, 3008 (1964).

(8) (a) T. Saegusa, Y. Ito, S. Hobayashi, and K. Hirota, *Tetrahedron Lett.*, 521 (1967); (b) T. Saegusa, Y. Ito, S. Kobayaski, N. Takeda, and K. Hirota, *ibid.*, 1273 (1967); (c) T. Saegusa, Y. Ito, S. Kobayashi, and K. Hirota, *J. Amer. Chem. Soc.*, **89**, 2240 (1967); (d) T. Saegusa, S. Kobayashi, K. Hirota, Y. Okumura, and Y. Ito, *Bull. Chem. Soc. Jap.*, **41**, 1638 (1968); T. Saegusa, Y. Ito, S. Hobayashi, K. Hirota, and N. Takeda, *Can. J. Chem.*, **47**, 1271 (1969).

(9) I. Ugi and U. Fetzer, *Ber.*, **94**, 2239 (1961), found that phenylmagnesium bromide did not undergo a simple addition to cyclohexylisonitrile, but rather several dimeric forms were isolated from the complex reaction mixture.

(10) Prepared in 93% yield from commercially available 1,1,3,3-tetramethylbutylamine by converting the amine to the formamide with formic acid and dehydrating the amide with thionyl chloride in N,N-dimethylformamide. The experimental procedure will be provided upon request. Available from Columbia Organic Chemicals.

(11) The use of different isonitriles and organometallics is now being investigated.

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Photodetachment Energies of Negative Ions by Ion Cyclotron Resonance Spectroscopy. Electron Affinities of Neutral Radicals

Sir:

The electron affinities of free radicals remain some of the most elusive quantities of chemical interest. Because of the great difficulty in obtaining gas-phase electron affinities and consequent lack of available data,