The Interaction of Pyridine, n-Butyl-lithium, and Carbonyl Compounds

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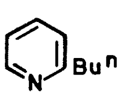
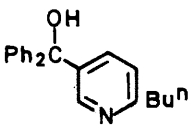
Summary 1-Lithio-2-n-butyl-1,2-dihydropyridine (V) prepared from pyridine and n-butyl-lithium in the presence or absence of TMEDA, reacts with benzophenone to give a number of products: (I), (II), (III), and of particular interest, the reduction product, (IV).

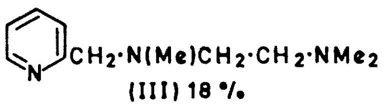
THE formation of phenyl-lithium and benzyl-lithium by the nuclear metallation of benzene and toluene using the n-butyl-lithium–tetramethylethylenediamine (TMEDA) complex as the metallating agent has been reported.[1] It occurred to us that it might similarly be possible to metallate pyridine at position-2 rather than by the indirect route involving 2-bromopyridine.



(I) 22%



(II) 22%

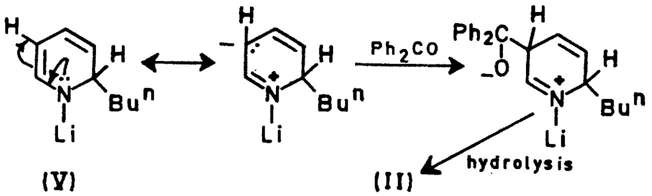


(III) 18%

Ph_2CHOH

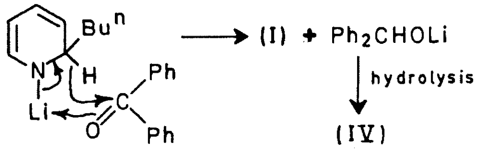
(IV) 66%

We report on the reaction of pyridine with n-butyl-lithium (in the presence and absence of TMEDA) followed by the addition of benzophenone to trap any 2-pyridyl-lithium which might be present. Depending on reaction conditions, a number of products were obtained. The pyridine ring was not metallated.



Compound (I) is the normally expected azomethine addition product, while the formation of compound (II) is analogous to that[2] of 5-alkyl-2-phenylpyridines from pyridine, phenyl-lithium, and alkyl halides. The formation of (II) can be rationalized as the reaction of benzophenone with the initially formed 1-lithio-2-n-butyl-1,2-dihydropyridine, (V). Metallation of TMEDA at one of its methyl groups followed by azomethine addition to pyridine gives (III).

The most interesting product arises from the reduction of benzophenone to benzhdyrol (IV). Its formation may be envisaged as follows.



The structures of all the products were established by n.m.r. spectroscopy and elemental analysis.

It has also been possible to reduce acetophenone in about 35% yield to 1-phenylethanol using the butyl-lithium–pyridine reagent. To our knowledge these are the first observed reductions of carbonyl compounds with a reagent such as (V).

We thank Dr. O. F. Beumel of Foote Mineral Company for samples of n-butyl-lithium.

(*Received, May* 12*th*, 1970; *Com.* 737.)

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[1] G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, 1964, **29**, 2928.

[2] C. S. Giam and J. L. Stout, *Chem. Comm.*, 1970, 478.