

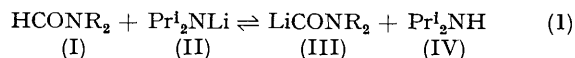
Direct Formation, and Reactions of a Carbonyl Anion free from Competitive Nucleophiles

By KEITH SMITH* and KALYANARAMAN SWAMINATHAN

(Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP, U.K.)

Summary At low temperature, in tetrahydrofuran (THF)-ether-pentane, Bu^tLi abstracts a proton from bis(isopropyl)formamide to give LiCONPr_2 , which reacts with carbonyl compounds to give high yields of α -hydroxyamides.

THERE has been much recent interest in the application of carbonyl anion equivalents as synthetic reagents, because they enable a reversal ('umpolung') of normal carbonyl group reactivity.¹ Carbonyl anions derived from *NN*-dialkylformamides have even been synthesised directly, either by reaction of a bis(dialkylcarbamoyl)mercury with Bu^nLi^2 (a method which is 'troublesome and not without danger'³), or, more conveniently, by deprotonation of dialkylformamides with LiNPr_2 at low temperature [reaction (1), $\text{R} = \text{Me}, \text{Pr}^i$].^{3,4}



Despite the encouraging results obtained by the latter method, yields of products derived by further reactions of

(III) were somewhat variable, which led Fraser and Hubert to conclude that reaction (1) was a mobile equilibrium (K_{eq} ca. 2 for $\text{R} = \text{Pr}^i$).⁴ Our interest in an anion of type (III) stems from our attempts to synthesise acylboron compounds,⁵ and for our purposes the presence of other

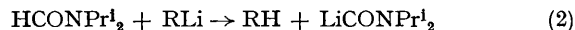
TABLE

Yields of products from reaction of LiCOPr_2 with electrophiles.^a

Electrophile	Product ^b	Yield (%) ^c
PhCOPh	$\text{Ph}_2\text{C}(\text{OH})\text{CONPr}_2$	85
PhCHO	$\text{PhCH}(\text{OH})\text{CONPr}_2$	80
MeCOMe	$\text{Me}_2\text{C}(\text{OH})\text{CONPr}_2$	81
EtCHO	$\text{EtCH}(\text{OH})\text{CONPr}_2$	62
PhCO_2Et	PhCOCONPr_2	70
$\text{PhCH}=\text{CHCHO}$	$\text{PhCH}=\text{CHCH}(\text{OH})\text{CONPr}_2$	68
D_2O	DCONPr_2 ^d	70

^a Ratio $\text{HCONPr}_2:\text{Bu}^t\text{Li}:\text{electrophile} = 1:1:0.8$. ^b All products were characterised by their spectral properties and gave satisfactory analyses. ^c Yield of product purified by chromatography, based on the electrophile. ^d Ratio $\text{HCONPr}_2:\text{Bu}^t\text{Li}:\text{electrophile} = 1:1:1$; n.m.r. spectroscopy showed no undeuterated material.

nucleophiles, such as (II) and (IV), could not be tolerated. Thus, notwithstanding discouraging reports in the literature,³ we have investigated the reaction of (I) with organolithium compounds, which, if successful, would be unlikely to produce a mobile equilibrium and would give rise only to a hydrocarbon by-product [reaction (2)].



We have found that Bu^tLi reacts with (I) at -95°C in a solvent composed of THF, diethyl ether, and pentane (4:4:1, Trapp's mixture)⁶ to give (III) in high yield. The

Table records the results of reactions of this product, prepared in this way, with a number of electrophiles. The yields are good, comparable with yields obtained in the most favourable cases when it was prepared according to reaction (1).^{3,4}

For the first time a carbonyl anion can be produced conveniently in the absence of other, potentially problematical nucleophiles.

K. Swaminathan thanks the S.R.C. for a fellowship.

(Received, 1st April 1976; Com. 336.)

¹ D. Seebach and M. Kolb, *Chem. and Ind.*, 1974, 687.

² U. Schöllkopf and F. Gerhart, *Angew. Chem. Internat. Edn.*, 1967, 6, 805.

³ B. Bánhidai and U. Schöllkopf, *Angew. Chem. Internat. Edn.*, 1973, 12, 836.

⁴ R. R. Fraser and P. R. Hubert, *Canad. J. Chem.*, 1974, 52, 185.

⁵ K. Smith and K. Swaminathan, *J.C.S. Chem Comm.*, 1975, 719; *J.C.S. Dalton*, submitted for publication.

⁶ B. J. Wakefield, 'Chemistry of Organolithium Compounds,' Pergamon, Oxford, 1974, p. 34.