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

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Summary At low temperature, in tetrahydrofuran (THF)–ether–pentane, Bu^{t}Li abstracts a proton from bis(isopropyl)formamide to give LiCONPr$^i_2$, 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^{n}Li[2] (a method which is 'troublesome and not without danger'[3]), or, more conveniently, by deprotonation of dialkylformamides with LiNPr$^i_2$ at low temperature [reaction (1), R = Me, Pr^i].[3,4]

$$\begin{array}{ccccccc} \mathrm{HCONR_2} & + & \mathrm{Pr^i_2NLi} & \rightleftharpoons & \mathrm{LiCONR_2} & + & \mathrm{Pr^i_2NH} \\ \text{(I)} & & \text{(II)} & & \text{(III)} & & \text{(IV)} \end{array} \qquad (1)$$

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 R = 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$^i_2$ with electrophiles.[a]

Electrophile	Product[b]	Yield (%)[c]
PhCOPh	$Ph_2C(OH)CONPr^i_2$	85
PhCHO	$PhCH(OH)CONPr^i_2$	80
MeCOMe	$Me_2C(OH)CONPr^i_2$	81
EtCHO	$EtCH(OH)CONPr^i_2$	62
$PhCO_2Et$	$PhCOCONPr^i_2$	70
PhCH=CHCHO	$PhCH{=}CHCH(OH)CONPr^i_2$	68
D_2O	$DCONPr^i_2$[d]	70

[a] Ratio HCONPr$^i_2$: Bu^{t}Li : 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 HCONPr$^i_2$: Bu^{t}Li : electrophile = 1 : 1 : 1; n.m.r. spectroscopy showed no undeuteriated 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)].

$$\mathrm{HCONPr^i_2 + RLi \rightarrow RH + LiCONPr^i_2} \qquad (2)$$

We have found that $\mathrm{Bu^tLi}$ 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.

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