Pergamon

Tetrahedron Letters, Vol. 38, No. 51, pp. 8863-8866, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)10394-X

Lithium *Bis*-(diisopropylamino)boracetylide [$LiC{\equiv}C\text{-}B(N\textit{i}\text{-}Pr_2)_2$]. A New Reagent for the Preparation of Terminal Alkynes

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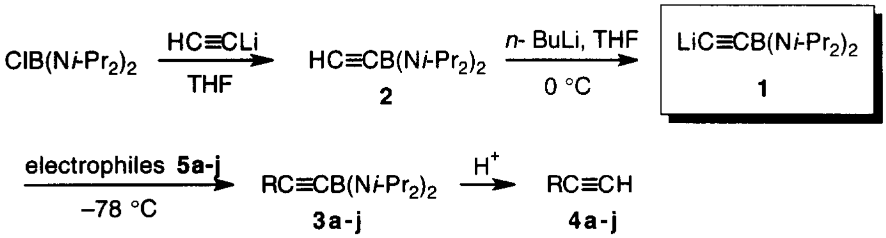
Abstract: Terminal alkynes $RC{\equiv}CH$ [R = PhCO, $PhCH_2OCO$, $(CH_3)_2CHCH_2OCO$, Et_2NCO, $(EtO)_2P(O)$, $PhCH_2$, $H_2C{=}CH\text{-}CH_2$, and Ph-CH(OH)-] may be prepared in satisfactory yield in a one-pot process by reaction in THF at −78 °C of the titled reagent with electrophiles followed by acidic workup with dilute HCl. © 1997 Elsevier Science Ltd.

We have recently reported an efficient synthesis of alkynylboronates based on refunctionalization of alkynyldiaminoboranes.[1] We now relate the excellent utility of lithium *bis*-(diisopropylamino)boracetylide **1** as a synthetic equivalent of lithium acetylide and we described its reaction with electrophiles. The method is summarized in Scheme 1 and is illustrated with the electrophiles **5a-j**, which were chosen to document generality. The terminal alkynes **4** produced in this manner are listed in Table 1.

Scheme 1



Bis-(diisopropylamino)boracetylene **2** was prepared from chloro *bis*-(diisopropylamino)borane and monolithium acetylide (86%).[1] Compound **2** is air-sensitive but appears to be indefinitely stable when kept under an inert atmosphere at ambiant temperature. Treatment of **2** in THF at 0 °C with *n*-butyllithium afforded a solution containing the stable lithium *bis*-(diisopropylamino)boracetylide **1** which was reacted smoothly

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with benzoylchloride **5a** and chloroformates **5b-d** at –78 °C (entries 1-4). The reaction completed within 30 min affording the α,β-unsaturated ketone **3a**, esters **3b,c** and amide **3d**. Clearly, **1** is not reactive enough to overadd to these reactive electrophilic substrates.[2] Lithium boracetylides could also exist in the mesomeric vinylidene carbene form, though to our knowledge there is no literature evidence for such B-C π bonding.

Expectedly, **3a-d** were ultimately converted to the propiolic acid derivatives **4a-d** through acidic workup with dilute HCl. It proved possible to carry through the synthesis without the isolation of the intermediates **3**. Consequently, the synthesis of the terminal alkynes may be carried out in an essentially one-pot process, as outlined in Scheme 1. Since lithium (trimethylsilyl)acetylide [$Me_3SiC{\equiv}CLi$] overadds to chloroformates and requires the use of *N*-alkyl-*N*-alkoxyamides[3] to produce trimethylsilylalkynyl ketones,[4] our procedure should constitute an improved route to terminal α,β-acetylenic carbonyl compounds.

There appears to be no difficulty to extend this procedure for the preparation of 1-alkynylphosphonates. Reaction of chlorodiethylphosphonate **5e** gave the corresponding 1-alkynylphosphonate **4e** in good yield (72%, entry 5). The ^{13}C-NMR spectrum of **4e** which is particularly diagnostic of the alkyne-phosphorus linkage exhibits doublets for the alkynyl carbons at δ 74.0 (C_α, J_{CP} = 288 Hz) and δ 88.2 (C_β, J_{CP} = 50 Hz). Our synthetic approach is complementary to a limited number of the existing syntheses[5] of alkynylphosphonates which are useful reagents in organic synthesis.[6]

Entry 6 demonstrates that the reaction can be performed conveniently with aldehydes. Benzylbromide **5g** gave 3-phenyl-1-propyne **4g** in good yield after acidic workup (88%, entry 7). However, allyl bromide reacted in lower yield (entry 8) and alkyl halides did not react at all (entries 9 and 10).

The ready availability of lithium *bis*-(diisopropylamino)boracetylide **1**, its good reactivity with a wide range of electrophiles and the simplicity and efficiency of its transformation into terminal alkynes should make **1** widely attractive as a lithium acetylide equivalent. The utility of lithium *bis*-(diisopropylamino)boracetylide should be particularly useful in reactions of complex electrophiles. Further chemistry and uses of this novel synthon will be the subject of future reports.

Table 1. Reaction of Lithium *Bis*-(diisopropylamino)boracetylide 1 with Electrophiles[a]

Entry	Electrophile	R		Yield (%)[b-d]	
				3	4[e]
1	PhCOCl (**5a**)	PhCO	**a**	–[f]	60
2	PhCH$_2$OCOCl (**5b**)	PhCH$_2$OCO	**b**	79	80
3	(CH$_3$)$_2$CHCH$_2$OCOCl (**5c**)	(CH$_3$)$_2$CHCH$_2$OCO	**c**	80	44
4	Et$_2$NCOCl (**5d**)	Et$_2$NCO	**d**	67	82
5	(EtO)$_2$P(O)Cl (**5e**)	(EtO)$_2$P(O)	**e**	–[f]	72
6	PhCHO (**5f**)	Ph-CH(OH)-	**f**	–[f]	76
7	PhCH$_2$Br (**5g**)	PhCH$_2$	**g**	77	88
8	H$_2$C=CH-CH$_2$Br (**5h**)	H$_2$C=CH-CH$_2$	**h**	56	61
9	*n*-BuBr (**5i**)	*n*-Bu	**i**	0	0
10	EtI (**5j**)	Et	**j**	0	0

[a] The following procedure for the synthesis of **4a** is representative. To a solution of 2.53 g (10.7 mmol) of *bis*-(diisopropylamino)boracetylene **2** in THF (20 mL) at 0 °C was added 6.70 mL (10.7 mmol) of 1.6 M *n*-butyllithium in hexane dropwise over a 30-min period. The mixture was then cooled at –78 °C. Benzoyl chloride (1.24 mL, 10.7 mmol) in THF was added, and the reaction mixture was stirred for an additional 15 min before being allowed to warm to room temperature. The solution was poured into 3N HCl, and extracted with ether (3 x 15 mL). The extracts were combined and washed with saturated ammonium chloride, and dried. The volatiles were evaporated under vacuum to afford the crude terminal alkyne, which was purified by recristallization (pentane). [b] Yields of isolated products. [c] In all cases, IR, ^{1}H, ^{13}C and^{11}B-NMR and mass spectral data were consistent with the assigned structures. [d] The chemical purity was in all the cases ≥ 99%. [e] Calculated from **2**, one-pot procedure. [f] Not isolated.

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(*Received in France* 19 *September* 1997; *accepted* 15 *October* 1997)