1,3-Disubstitution Reactions of 1,3-Dilithiopropyne. 'One-pot' Linear Chain Extensions at Both Termini of Propyne

By Subramaniam Bhanu and Feodor Scheinmann*

(*The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford* M5 4WT)

Summary Controlled 1,3-disubstitution of 1,3-dilithiopropyne with various electrophiles leads to the formation of terminal and non-terminal acetylenes without allenic by-products.

1,3-Dilithio acetylides obtained by treating terminal acetylenes or their halogeno derivatives with butyl-lithium in hexane, provide intermediates for the synthesis of 3-alkylalk-1-ynes.[1] Propyne itself has been shown to react with an excess of butyl-lithium to give a tetralithio derivative which yields tetrakis(trimethylsilyl)allene as the major product, upon derivatisation with trimethylsilylchloride.[2]

TABLE

Products, $BuCH_2–C{\equiv}C–R$, from 1,3-disubstitution reactions of propyne

R	H	I	Bu^n	CH_2OH	$PhCHCH_2COPh$[4]
Isolated yield/%	35	30	30	80	60

We now report that the reaction of propyne with two equivalents of butyl-lithium gives rise selectively to the 1,3-dilithio derivative (**1**). The latter underwent smooth reactions with various electrophiles to give fair to good yields of the corresponding 1,3-disubstitution products (Scheme). In a typical reaction a slow stream of propyne was bubbled through a cooled (−60 °C), stirred solution containing two equivalents of butyl-lithium in hexane–ether in the presence of one equivalent of tetramethylethylenediamine (TMEDA) or 1,4-diazobicyclo[2,2,2]octane (DABCO). In the absence of TMEDA or DABCO only variable yields of reaction products are obtained since butyl-lithium alone is not sufficiently basic readily to form the dilithio-derivative of propyne. The rate of propyne addition should be controlled so that the white, insoluble, monolithio derivative initially formed immediately reacts further to give the yellow-brown dilithio propyne. The latter reacted regiospecifically with various electrophiles first at the propargylic carbon, then at the terminal acetylide site to give the substituted acetylenes. Thus alkylation at the propargylic site with butyl bromide followed by the addition of various electrophiles, *e.g.* iodine, butyl bromide and paraformaldehyde gave substituted acetylenes by a 'one-pot' 1,3-disubstitution reaction (Scheme). Alkylation of the propargylic carbon can also be followed by conversion of the resulting lithium acetylide into the diethyl alkynylalane with diethylaluminium chloride. This allows 1,4-conjugate addition of the acetylide to benzalacetophenone.[3] Typical one-pot reactions and isolated yields are given in the Table.

$$MeC{\equiv}CH \xrightarrow{(i)} \underset{(\mathbf{1})}{LiCH_2C{\equiv}CLi} \xrightarrow{(ii)}$$

$$BuCH_2C{\equiv}CLi \xrightarrow{(iii)} BuCH_2C{\equiv}CR$$

(i) BuLi–TMEDA; (ii) BuBr in hexane; (iii) electrophiles H^+,I_2,BuBr–HMPT, CH_2O, PhCH=CHCOPh (*via* alane).

SCHEME

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