

Butyl-lithium-induced Dimerization of Pent-3-en-1-yne and Some Derivatives

Lambert Brandsma,* Hermann D. Verkrüysee, and Hendrik Hommes

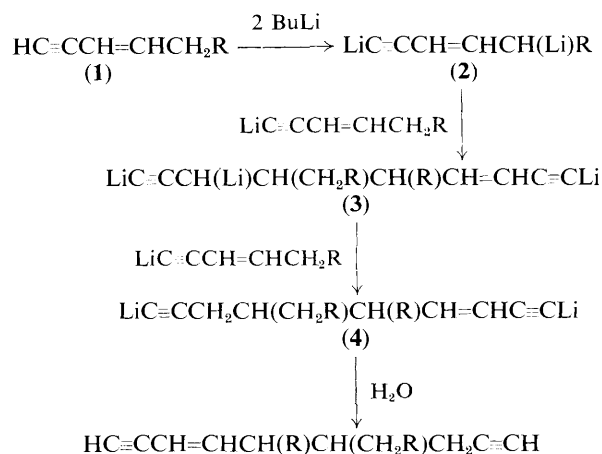
Department of Organic Chemistry of the University, Croesestraat 79, Utrecht, The Netherlands

The enynes $\text{HC}\equiv\text{CCH}=\text{CHCH}_2\text{R}$ ($\text{R} = \text{H}, \text{OMe}, \text{NMe}_2, \text{SMe}$) are converted into dimers $\text{HC}\equiv\text{CCH}=\text{CHCH}(\text{R})\text{CH}(\text{CH}_2\text{R})\text{CH}_2\text{C}\equiv\text{CH}$ by treatment with butyl-lithium in a mixture of tetrahydrofuran and hexane.

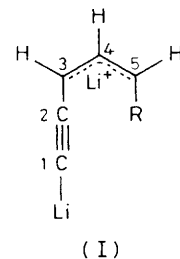
In the course of our studies on dimetalation¹ of unsaturated compounds we are investigating the reactions of butyl-

lithium with 'skipped' and conjugated enyne and di-yne systems. During an attempt to convert pent-3-en-1-yne (**1**)

(R = H) into the dilithio-derivative (2), by adding an excess of butyl-lithium to a solution of the enyne in tetrahydrofuran (THF) at 0–20 °C, extensive polymerization occurred. These polymers could be the result of a series of consecutive additions to the enyne system, starting with the addition of dilithiopentenyne (2) (R = H) to the double bond in the acetylide $\text{LiC}\equiv\text{CCH}=\text{CHR}$. To stop this polymerization at the dimer stage, we carried out a number of experiments under more carefully controlled conditions. Addition at 0 °C of a slight (5–10 mol%) excess of a hexane solution of butyl-lithium to a mixture of (1) (R = H) and THF gave, after aqueous work-up, the dimer (5) in ca. 70% yield. Comparable results were obtained with the heterosubstituted derivatives (1) (R = OMe, NMe₂, SMe). Addition of exactly one equivalent of butyl-lithium (or less) followed by hydrolysis resulted in complete recovery of the starting compounds (in the cases R = OMe, NMe₂, SMe). Alkali amides in liquid ammonia, even when used in an excess, did not cause any dimerisation or polymerization, and neither did an excess of potassium t-butoxide in THF. We assume that this dimerization reaction, which to our knowledge has no precedent in the context of unsaturated hydrocarbons and derivatives,⁴ is initiated by the formation of the dilithiated enynes (2). This species subsequently adds to the (mono) lithiated enyne $\text{LiC}\equiv\text{CH}=\text{CHR}$ to give an organotrimetallic species (3), which in turn is protonated by the excess of the mono-lithiated enyne to give a mixture of (2) and (4). The latter derivative may again undergo addition of (2) to the enyne system, but if the reaction mixture is quenched in time (after 2 h) with water, (5) results in good yields. If, instead of water D₂O is added, both terminal acetylene groups in the dimer bear a deuterium atom.



This dimerization has two interesting features: (i), it is completely *regiospecific* with respect to the sites of attachment of the two enyne units, and (ii), it is *stereospecific* in all cases: starting with mixtures of *E*- and *Z*-isomers of (1) or even with pure *E*-(1), pure *Z*-(5) is obtained.† This remarkable result may be explained by assuming that both *Z*- and *E*-(1) are converted into (2) with the stereostructure I [in the case



of *E*-(1) this involves a rotation at the C-3–C-4 bond]. The stereochemical course of this di-metalation resembles that of the metalation of allyl and prop-1-enyl ethers leading to the thermodynamically more stable *Z*-allylic anion, the $\text{LiC}\equiv\text{C}$ moiety being comparable with the OR group² (compare also ref. 3).

We further showed that it is possible to add pent-3-en-1-yne or pent-4-en-1-yne to vinylacetylene by adding, at –20 °C, a 10% (molar) excess of butyl-lithium to a 1 : 1 mixture of the enynes, dissolved in THF. The product *Z*- $\text{HC}\equiv\text{CCH}=\text{CH}[\text{CH}_2]_3\text{C}\equiv\text{CH}$ was obtained in 65% yield.

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- For a review on alkyl-lithium-induced polymerizations of alkenes and 1,3-dienes see B. J. Wakefield, 'The Chemistry of Organolithium Compounds,' Pergamon, Oxford, 1974, p. 96.

† The structures and purities of the products were checked by i.r., ¹H n.m.r., ¹³C n.m.r., and mass spectroscopic analysis and by g.l.c.