

The Tetralithium Derivative of Penta-1,3-diyne

By ROBERT WEST* and T. LING CHWANG

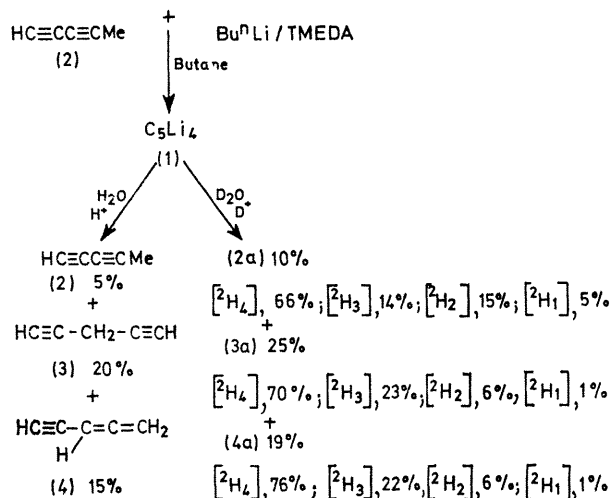
(Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706)

Summary Penta-1,3-diyne reacts with n-butyl-lithium in the presence of *NNN'*-tetramethylethylenediamine to give C_5Li_4 which upon treatment with water yields a mixture of penta-1,3-diyne, penta-1,4-diyne, and penta-1,2-dien-4-yne.

PREVIOUSLY we have shown that propyne reacts with n-butyl-lithium in hexane to form the tetralithium compound, C_3Li_4 .^{1,2} We report here the preparation of a second known perlithium compound, C_5Li_4 (1), obtained by lithiation of penta-1,3-diyne (2) in butane solution with n-butyl-lithium complexed with *NNN'*-tetramethylethylenediamine (TMEDA). Treatment of this polyolithiated species with excess of water under acidic conditions leads to a mixture of three isomers, penta-1,3-diyne (2), penta-1,4-diyne (3), and penta-1,2-dien-4-yne (4).

In a typical reaction, TMEDA (2.8 ml, 0.02 mol) was added to a stirred solution of Bu^nl (0.08 mol) in butane (60 ml). The mixture was stirred for 1 h at 2–3°, then penta-1,3-diyne (2)³ (0.8%; 153 ml, 13 mmol) in butane at –80° was added during 2.5 h. The mixture was then stirred at 2–3° for 43 h. Conc. HCl (10 ml, 0.12 mol) in H_2O (20 ml, 1.1 mol) was then added rapidly to the mixture at –25°. The organic layer was dried ($MgSO_4$) and distilled (0.1 Torr; distillate collected in –80° trap). The distillate was then separated by preparative gas chromatography yielding (2), (3), and (4) as shown in the Scheme. Product (2) was identified by comparing its retention time, and i.r., n.m.r., and mass spectra with those of an authentic

sample. Compound (4) has the same characteristic i.r. bands as previously reported.⁴ (3)⁵ was characterized by its spectral data.



Quenching of the polyolithiated species, C_5Li_4 (1), with excess of D_2O in the presence of DCl yields three deuteriated isomers† (2a), (3a), and (4a) of (2), (3), and (4). Each deuteriated product was characterized by its i.r. and mass

† Isomers were separated and yields were estimated by preparative gas chromatography. The relative deuterium content of each isomer was calculated by comparing its low-voltage mass spectrum with that of undeuteriated species. It was found that penta-1,3-diyne (2) does not rearrange or exchange with deuterium under the conditions of the acid work-up.

spectra, which were fully consistent with the assigned structures, as well as by comparing its retention time with that of the corresponding undeuteriated compounds.⁶ For each pair of compounds, the deuteriated and undeuteriated substances showed identical retention times. (2a), (3a), and (4a) each consisted of about 70% tetradeuteriated material, indicating that (1) is mainly a tetralithium species.

Polyolithiation appears to be a general reaction for 1-alkynes bearing α -hydrogen atoms. Propyne,^{1,2} but-1-yne,¹

oct-1-yne,² hex-1-yne,² and hexa-1,5-diyne, as well as 1-phenylpropyne,^{7,8} have all been observed to form polyolithium derivatives. So far only propyne and penta-1,3-diyne, a conjugated diyne, have been converted into perlithiated species. The perlithiated 1,3-diyne and its use in the synthesis of other organometallic and organic derivatives are now under investigation.

We acknowledge support by the Air Force Office of Scientific Research.

(Received, December 15th, 1970; Com. 2171.)

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