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Synthesis and Lithiation of Monosilylated 1,3,5,7-Octatetrayne

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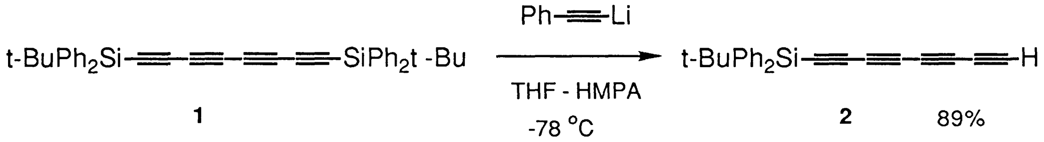
Unstable monosilylated 1,3,5,7-octatetrayne was synthesized and lithiated with butyllithium. The resulted lithium acetylide added to aldehydes and a ketone giving tetraynols in high yields.

Conjugated polyynes are an interesting group of substances for their biological activities1) and polymerization abilities.2) Although mono-protected polyynes can be convenient building blocks for the preparation of various polyyne derivatives, their instability has limited the use in organic synthesis.3) The synthesis of monosilylated 1,3,5,7-octatetrayne and its lithiation4) are noted here.

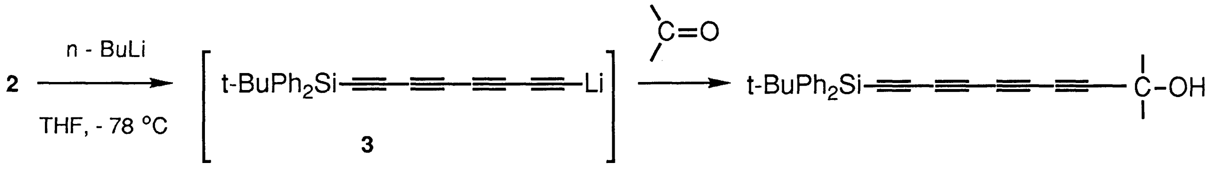
Bis-1,8-(*t*-butyldiphenylsilyl)-1,3,5,7-octatetrayne (**1**), prepared by dimerization of 1-(*t*-butyldiphenylsilyl)-1,3-butadiyne,5) was treated with lithiated phenylacetylene in THF-HMPA at -78 °C, and selective mono-desilylation was conducted (Scheme 1). The use of the acetylide is essential in this reaction, and nucleophilic MeLi6) resulted in decomposition. Since 1-*t*-butyldiphenylsilyl-1,3,5,7-octatetrayne (**2**) obtained was extremely unstable at concentrated state, it was handled as a solution. A typical procedure for the preparation of a THF-hexane solution of **2** is as follows: Under a nitrogen atmosphere, a THF-hexane solution (10 and 4.3 mL) of lithium phenylacetylide was prepared from phenylacetylene (780 mg, 7.7 mmol) and butyllithium (6.6 mmol) at -78 °C. HMPA (2 mL) and a THF (10 mL) solution of **1** (2.0 g, 3.5 mmol) was added, and the mixture was stirred at the temperature for 1 h.7) The reaction was quenched by adding water, and organic materials were extracted twice with ether. Combined extracts were washed with water and brine, and dried over Na_2SO_4. After most of the solvents were removed under reduced pressure, the residue was flush chromatographed with hexane as the eluent. Fractions containing **2** were collected and concentrated to a small volume. *Attention must be paid that the solvents are not removed completely, otherwise* **2** *polymerizes instantaneously*. The volume of the solution was adjusted to 8 mL by adding THF, and the resulted THF-hexane solution of **2** was stored at -30 °C over molecular sieves 4A. UV (hexane) λ_{max} (log ε) 264 (5.54), 251 (5.53), 240 (5.27) nm. The yield (1.04 g, 89%) was estimated by concentrating a part of the solution and weighing the polymer.

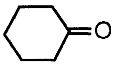


Scheme 1.

Lithiation of **2** proceeded smoothly with n-butyllithium in THF at -78 °C for 30 min, and the acetylide **3** added at the temperature to aldehydes and a ketone in high yields (Table 1). The adducts were stable enough for usual workup.

Table 1. Addition Reactions of Lithiated Octatetrayne **3** to Aldehydes and a Ketone



Carbonyl compound[a)]	Yield/%[b)]
t-BuCHO	83
n-C_4H_9CHO	80
n-$C_6H_{13}CHO$	86
n-$C_3H_7CH{=}CHCHO$	88
PhCHO	75
	87

a) Acetylide was used in 1.5–2 molar excess. b) All the products gave satisfactory H-NMR, C-NMR, IR, and elemental analysis by HRMS.

Removal of *t*-butyldiphenylsilyl group from the adduct was carried out by an alkaline treatment in THF-water as shown in Scheme 2. H-NMR spectra of unstable polyyne **4** was obtained after careful silica gel chromatography with hexane-ethyl acetate and solvent exchange to $CDCl_3$-CCl_4. H-NMR ($CDCl_3$-CCl_4) δ 1.0-2.0 (11H,m), 2.12 (1H,s). UV (hexane) λ_{max} (log ε) 236 (4.81), 224 (4.71) nm.

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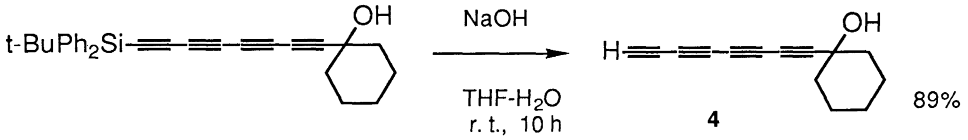

Scheme 2.

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