A Convenient Synthesis of 1,4-Pentenynes (Allylacetylenes) via Allylboranes

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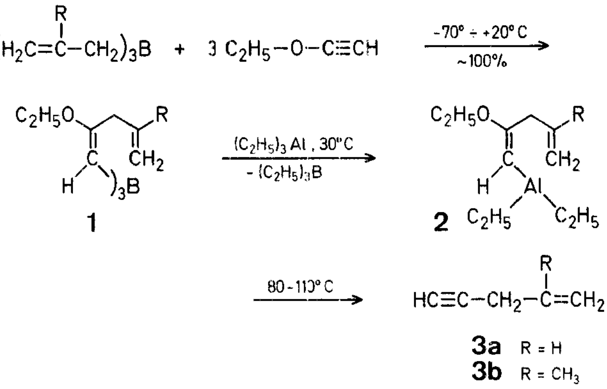
1,4-Pentenyne (allylacetylene) and its homologs having terminal double and triple bonds each are difficult to prepare. Methods for their synthesis generally involve several steps[1-6] and the products usually contain considerable amounts of isomers and other impurities which cannot be easily removed.

We present here a new convenient two-step (one-pot) method for the synthesis of 1,4-pentenynes consisting of the reaction of allylboranes with alkoxyacetylenes at −50 °C followed by heating with trialkylaluminum at 80–110 °C. The yields of pure 1,4-pentenynes thus obtained are 75–80% based on the starting allylborane.

Triallylborane and tris[2-methylallyl]-borane undergo an exothermic reaction with alkoxyacetylenes when the components are mixed at −70 to +20 °C to give thermally stable tris[(*E*)-2-alkoxy-1,4-pentadien-1-yl]-boranes (**1**) in nearly quantitative yields[7,8]. In the 1,4-pentadienylboranes **1**, the vicinal C-atoms of the 1,2 double bond carry an electron-donating (alkoxy) and an electron-withdrawing (boryl) group. These compounds should be expected to undergo β-elimination to give the corresponding 1-alkynes. However, all attempts to realize such an elimination by heating boranes **1** with various amines (triethylamine, pyridine, quinoline, aniline), acetic anhydride, or Lewis acids ($ZnCl_2$, $AlCl_3$, $AlBr_3$) failed. The desired formation of the 1,4-pentenynes (**3**) may be achieved, however, by treatment of boranes **1** with triethylalane. The reaction is carried out by heating a 1:3 mixture of boranes **1** and triethylalane in decane or without solvent at 80–110 °C at a pressure of 100–120 torr; the 1,4-pentenynes **3** and triethylborane (which is also formed in the reaction) are continuously distilled from the mixture.



Compounds **3a, b** are easily isolated from the distillate by adding pyridine [to form the high-boiling complex $(C_2H_5)_3B\cdot NC_5H_5$] and distilling off the lower-boiling products **3a, b**. The yields decrease markedly with decreasing ratio **1**: triethylalane; thus, with a 1:1 ratio only 20–30% yields of **3** are obtained.

The reaction proceeds by the replacement of the *B*-(1,4-pentadienyl) groups by ethyl groups with simultaneous replacement of one *Al*-ethyl group by the 1,4-pentadienyl group to give the diethyl-[(*E*)-2-ethoxy-1,4-pentadien-1-yl]-alane **2**. I.R. spectra of the reaction mixture recorded immediately after mixing the reagents (1:3) reveal an intense absorption band at 1525 cm^{-1} (RO—C=CH—Al) and do not contain a band at 1585 cm^{-1} (RO—C=CH—B). Unlike boranes **1**, alanes **2** are thermally unstable and eliminate the corresponding 1,4-pentenyne when heated. The elimination seems to be an intermolecular process.

In the preparative-scale performance of the reaction, isolation of the borane **1** is not necessary. Instead, the product of the reaction of triallylborane or tris[2-methylallyl]-borane with ethoxyacetylene (crude **1**) is allowed to react with triethylalane, i.e., the whole reaction is carried out as a one-pot process.

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Table. 1,4-Pentenynes (**3**) prepared

3	Yield[a] [%]	b.p. [°C]/760 torr		n_D^{20}		^{1}H-N.M.R. (neat) δ [ppm]				
		found	reported	found	reported	≡CH	≡C–CH₂–	=CH₂	=CH–	CH₃
a	75	41.5–42°	42°[1,c] 42–43°[3]	1.4076	1.4150[1] 1.4125 (16 °C)[3]	2.01 (t)	2.89 (m)	4.85–5.49	5.50–6.15	—
b	80	72–74°	67–68°[2] (762 torr)	1.4204	1.4198[2,b]	2.00 (t)	2.83 (m)	4.75 (m), 4.95 (m)		1.75 (s)
c	81	62–63°	62°[1,c]	1.4092	1.4170[1]	2.05 (d)	3.07 (m)	4.92–5.30	5.52–6.07	1.21 (d)
d	82	67–68°	67.5°[6]	1.4030	1.4050[6]	2.15 (s)	—	4.75–5.50	5.80–6.15	1.27 (s)

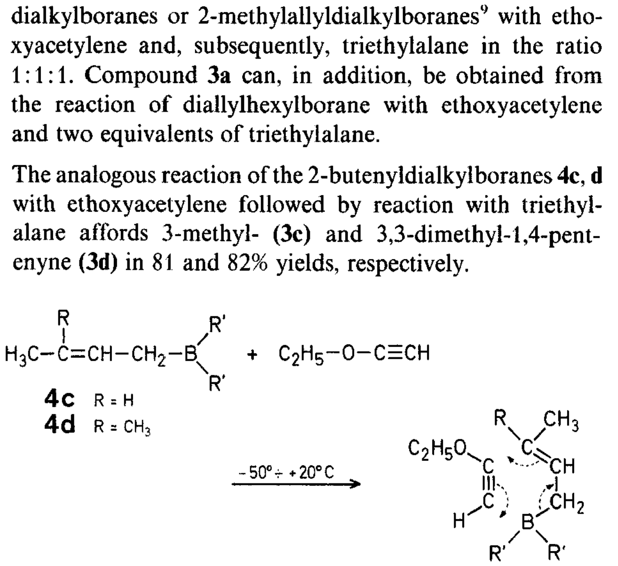
[a] Yield of isolated product. All compounds **3** gave satisfactory microanalyses.

[b] The product of Ref.[2] contained 16% 2-methylallyl chloride.

[c] The ^{1}H-N.M.R. spectrum is described in Ref. 1.

Compounds **3a** and **3b** may also be prepared in 82 and 78% yields, respectively, by reaction of (unsymmetrical) allyldialkylboranes or 2-methylallyldialkylboranes[9] with ethoxyacetylene and, subsequently, triethylalane in the ratio 1:1:1. Compound **3a** can, in addition, be obtained from the reaction of diallylhexylborane with ethoxyacetylene and two equivalents of triethylalane.

The analogous reaction of the 2-butenyldialkylboranes **4c, d** with ethoxyacetylene followed by reaction with triethylalane affords 3-methyl- (**3c**) and 3,3-dimethyl-1,4-pentenyne (**3d**) in 81 and 82% yields, respectively.



R' = C_2H_5, n-C_3H_7, n-C_4H_9, $-CH_2-CH=CH-CH_3$

1,4-Pentadienylboranes (**5**) are intermediates in these reactions.

The structures of the 1,4-pentenynes **3** were confirmed by microanalyses and spectral data. The I.R. spectra show bands at ν = 2130, 3315 (C≡CH), 1643, and 3087 cm^{-1} (C=CH₂). According to ^{1}H-N.M.R. spectrometry and G.L.C. analysis, the 1,4-pentenynes **3** obtained by our method do not contain any isomers as impurities (1,2,4-pentatrienes, 1,3-pentenynes, 2,4-pentenynes).

The reaction of borane **1a** (R = H) with butyllithium affords 1,4-pentenyne (**3a**) contaminated with 1,2,4-pentatriene (1–10%). When borane **1a** (R = H) is heated with sodium hydride, the main product is 1,2,4-pentatriene contaminated with a small amount of 1,4-pentenyne.

All reactions are carried out under nitrogen in a 50-ml three necked round-bottom flask equipped with a dropping funnel, thermometer, magnetic stirrer, Claisen adapter with a condenser for downward distillation, and a receiver.

1,4-Pentenyne (3a):

Ethoxyacetylene (11 ml, 125 mmol) is added dropwise, over a 30 min period, to a stirred solution of triallylborane (4.9 g, 37 mmol) in decane (15 ml) at −70 to −50 °C. An exothermic reaction takes place immediately. The mixture is allowed to warm to room temperature and stirring is continued for 2 h. Then, triethylalane (14.3 g, 125 mmol) is slowly added and the receiver is cooled to −78 °C (Dry Ice/acetone). The system is evacuated to ~120 torr and the reaction mixture is heated at 80–110 °C. The distillate (9.5 g, consisting of **3a** with an admixture of triethylborane) is thoroughly mixed with pyridine (5 ml) and distilled at ambient pressure to give pure **3a**; yield: 5.07 g (75%); b.p. 41.5–42 °C.

2-Methyl-1,4-pentenyne (3b):

This compound is prepared as above from ethoxyacetylene (10.5 g, 147 mmol), tris[2-methylallyl]-borane (7.5 g, 43 mmol), and triethylalane (15.1 g, 132 mmol); yield: 8.5 g (80%); b.p. 72–74 °C.

3-Methyl-1,4-pentenyne (3c):

Ethoxyacetylene (4.5 g, 64 mmol) is added dropwise to a stirred solution of dibutyl-(2-butenyl)-borane[9] (11.8 g, 65 mmol) in isopentane (25 ml) at −50 °C. The mixture is allowed to warm to 20 °C and stirring is continued for 2 h. The solvent is then removed under reduced pressure and triethylalane (7.5 g, 65 mmol) is slowly added to the residue. The receiver is cooled to −78 °C (Dry Ice/acetone), the system is evacuated to ~100 torr, and the mixture is heated at 80–110 °C. The distillate (6.3 g) is thoroughly mixed with pyridine (5 ml) and distilled at ambient pressure to give pure **3c**; yield: 4.2 g (81%); b.p. 62–64 °C.

3,3-Dimethyl-1,4-pentenyne (3d):

This compound is prepared as above from ethoxyacetylene (5.5 ml, 63 mmol; in 20 ml isopentane), dipropyl-(3-methyl-2-butenyl)-borane[9] (**4d**; 5.3 g, 32 mmol), and triethylalane (6 ml, 43 mmol); yield: 2.47 g (82%); b.p. 67–68 °C.

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