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Note

Selective hydroboration / oxidation of double bond in the presence of triple bond by sodium acetoxyborohydride leading to the synthesis of acetylenic alcohols

Jasvinder Singh*, Munisha Sharma, Goverdhan L Kad & Jasamrit Kaur

Department of Chemistry & Centre of Advanced Studies in Chemistry,

Panjab University, Chandigarh 160 014, India

E-mail: jsbrar_pu@yahoo.com

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Selective hydroboration of carbon-carbon double bond has been achieved in the presence of carbon-carbon triple bond using *in situ* generation of sodium acetoxyborohydride from sodium borohydride and acetic acid in dry THF at 0°C followed by oxidation with alkaline hydrogen peroxide.

Keywords: Selective hydroboration, sodium acetoxyborohydride, acetic acid, enynes and acetylenic alcohols

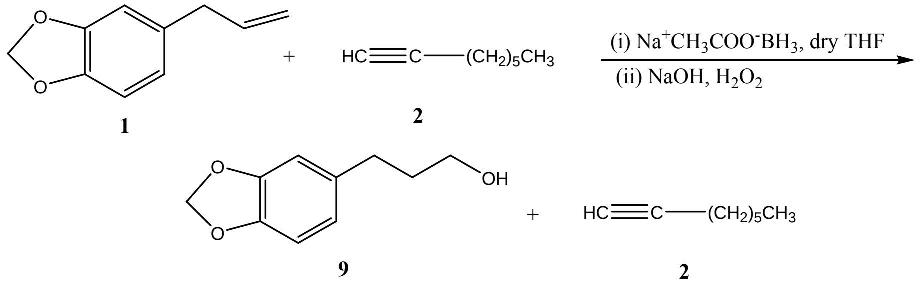
Organoboranes form a very useful class of synthetic intermediates in organic synthesis, which can be obtained conveniently by the hydroboration of carbon-carbon unsaturated bonds. Of great interest and utility is the selective hydroboration of carbon-carbon double bond in the presence of carbon-carbon triple bond and vice-versa.

Disiamylborane or bis-(3-methyl-2-butyl)borane is a highly selective reagent and acetylenes such as 1-hexyne and 3-hexyne are more reactive than the most reactive of the olefins studied[1]. On the other hand 9-borabicyclo[3.3.1]nonane (9-BBN)[2] is remarkably selective for the hydroboration of carbon-carbon double bond in the skipped enynes. Another reagent namely sodium acetoxyborohydride[3] (prepared *in situ* from sodium borohydride and acetic acid or sodium borohydride and mercuric acetate) is found to be effective for the hydroboration oxidation of olefins.

Thus, in continuation of our work with sodium acetoxyborohydride, which is also found to be selective reagent for dienes[4] and is tolerant to a number of functionalities[5], we have now studied the selective hydroboration of carbon-carbon double bond in the presence of carbon-carbon triple bond.

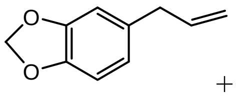
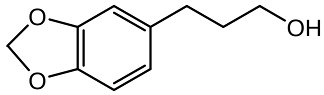
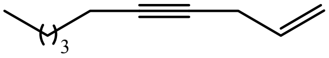
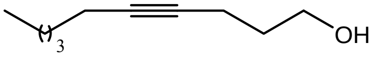
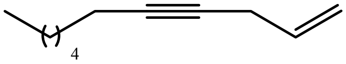
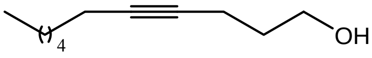
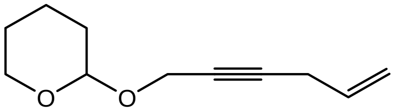
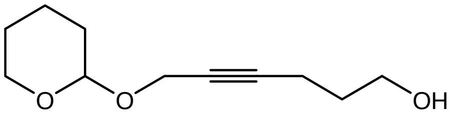
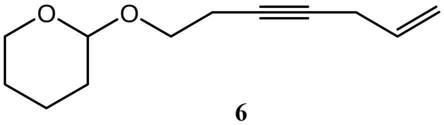
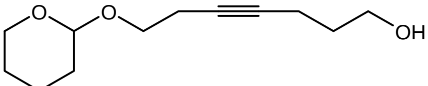
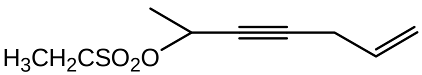
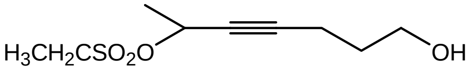
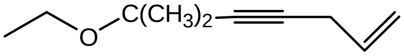
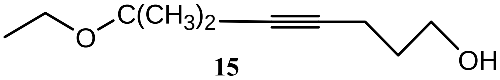
A mixture of saffrole **1** and 1-octyne **2** (1:1, **Scheme I)** was subjected to hydroboration with sodium acetoxyborohydride, followed by oxidation with alkaline H_2O_2 to yield the corresponding alcohol of the alkene and unreacted alkyne in 82% and 95% yields respectively, after column chromatography. The characteristic ^{1}H NMR signals for compound **9** were recorded at δ 1.3 (m,2H,-$CH_2CH_2CH_2OH$), 2.5 (bs,1H, O*H*, D_2O exchangeable), 3.3 (t,*J*=6Hz, 2H, -CH_2CH_2OH) with the absence of signals at δ 5.1 (m,2H,H_2C=CH-) and 6.1 (m,1H,H_2C=C*H*CH_2-). The results were also supported by the IR data which shows main absorption peaks at 3510 and 1500 with absence of peaks at 1640 cm^{-1}. These results encouraged to synthesise few enynes (**Table I** entries **3-8)** which were prepared via coupling[6] of allyl bromide with different alkynes using catalytic amount of CuCl in anhydrous THF at 0°C.

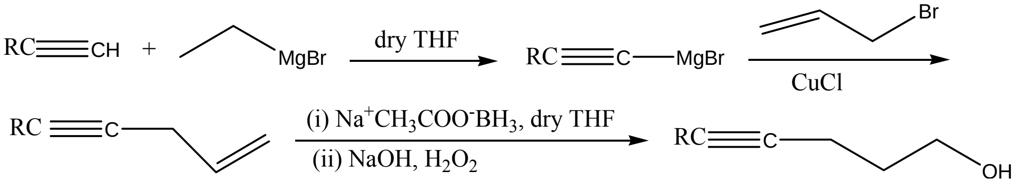
These enynes were treated with sodium acetoxyborohydride in dry THF followed by oxidation with alkaline H_2O_2 to furnish the products in good yields **(Scheme II)**. The major ^{1}H NMR signals for the acetylenic alcohols **(Table I** compounds **9-15)** were obtained at δ 1.3-2.2 (m,2H,-CH_2CH_2OH), 3.2-3.8 (t,*J*=6Hz,2H,-CH_2CH_2OH) and 3.8-4.5 (bs,1H,-O*H*, D_2O exchangeable) and the IR spectra showed a prominent peak at 3500-3400 cm^{-1}. The ^{1}H NMR spectra of compounds **9-15** did not record any signals



Scheme I

Table I — Selective hydroboration / oxidation of enynes to acetylenic alcohols

Entry	Substrate (s)	Product	Yield (%)	^{1}H NMR (δ)
1	 **1** + $HC\equiv C-(CH_2)_5CH_3$ **2**	 **9**	70	1.3 (m, 2H), 2.5 (bs, 1H), 2.7 (m, 2H), 3.6 (t, *J* = 6Hz, 2H), 5.9 (s, 2H), 6.6 (s, 3H)
2	 **3**	 **10**	68	0.85 (m, 3H), 1.4 (m, 8H), 2.2 (m, 4H), 3.8 (t, *J* 6Hz, 2H), 4.7 (bs, 1H)
3	 **4**	 **11**	75	0.9 (m, 3H), 1.3 (m, 10H), 2.2 (m, 4H), 3.6 (t, *J*=6Hz, 2H), 4.8 (bs, 1H)
4	 **5**	 **12**	77	1.1(bs, 8H), 2.2 (m, 2H), 3.5 (bs, 1H), 3.8 (m, 6H), 4.9 (bs, 1H)
5	 **6**	 **13**	77	1.2(bs, 8H), 1.9 (m, 4H), 3.8 (m, 6H), 3.9 (bs, 1H), 4.9 (s, 1H)
6	 **7**	 **14**	70	0.9 (t, *J*=6Hz, 3H), 1.2 (d, *J*=6Hz, 3H), 2.0 (m, 4H), 2.9 (bs, 1H), 3.6 (m, 2H), 4.0 (q, *J*=6Hz, 1H), 4.2 (q, *J*=6Hz, 1H)
7	 **8**	 **15**	74	1.3(bs, 11H), 2.0 (m, 2H), 3.1 (bs, 1H), 3.6 (m, 2H), 4.0 (q, *J*=6Hz, 2H)



Scheme II

at δ 5.1 (m,2H,C*H*$_2$=CH-) and 6.1 (m, 1H, CH$_2$ = C*H*CH$_2$-) and the IR spectra showed no peak at 1640 cm^{-1}, indicating addition of H_2O on the carbon-carbon double bond. The presence of carbon-carbon triple bond in the products was confirmed by ^{1}H NMR signal of the protons on the carbon adjacent to the triple bond at δ 2.2 (m,4H,-C*H*$_2$C≡CCH$_2$-) as well as by the IR peak at 2260 cm^{-1} and in some cases by ^{13}C NMR (disappearance of signals of quaternary carbons in DEPT[135°] analysis.

Experimental Section

^{1}H NMR spectra were recorded in $CDCl_3$ on a 300 MHz Bruker spectrometer with TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer 337 spectrophotometer. All the organic extracts were dried over anhydrous Na_2SO_4. silica gel (ASC, Mumbai) impregnated with $CaSO_4$ was used for TLC.

Typical procedure for hydroboration / oxidation. To an ice-cooled suspension of $NaBH_4$ (8 mmoles) in dry THF (40 mL) was added AcOH (8 mmoles) and the contents were stirred for 15 min. followed by addition of enyne (8 mmoles). The reaction-mixture was brought to room temperature and stirring was continued for 12 hr. To the organoborane thus prepared was added aq. NaOH (3M, 8 mL) and water (8 mL) at 0°C. The reaction- mixture was cooled, filtered and saturated with NaCl followed by extraction of organic layer with diethyl ether (3 × 20 mL). The organic extracts were washed with water, brine and dried over Na_2SO_4. Evaporation of solvent *in vacuo* followed by purification via column chromatography over silica gel furnished the alcohol in 68-77% yields **(Table I** entries **9-15)**.

Acknowledgements

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