PERKIN 1 COMMUNICATION

New simple syntheses of (*E*)-1-azido- (or thiocyanato)-alk-1-enes from alk-1-ynes by hydroboration

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Stereochemically pure (*E*)-1-azido- (or thiocyanato)-alk-1-enes have been synthesized *in situ* and in reasonable yields from alk-1-ynes upon hydroboration with disiamylborane followed by reactions with simple reagents; sodium azide (or potassium thiocyanate) and copper(II) nitrate trihydrate, in the presence of copper(II) acetate and a small amount of water, in polar aprotic solvents.

Although many useful synthetic reactions using organoboranes have been reported,[1] these do not include a procedure for syntheses of alkenyl azides (or thiocyanates).† Previously we reported a synthesis of (*E*)-1-chloro- (or bromo)-alk-1-enes by treatment of (*E*)-alk-1-enyldialkylboranes [derived from alk-1-ynes by hydroboration with dialkylborane in tetrahydrofuran (THF)] with copper(II) chloride [or copper(II) bromide–copper(II) acetate] in the presence of a small amount of water, in a polar aprotic co-solvent.[5] We here offer an application of the above procedure to the synthesis of alkenyl azides (or thiocyanates), potentially useful intermediates in organic synthesis, from alkynes *via* alkenyldisiamylboranes.

Thus, although a subsequent reaction of (*E*)-hex-1-enyldisiamylborane[6] [prepared by hydroboration of hex-1-yne with bis(1,2-dimethylpropyl)borane in THF] with copper(II) thiocyanate[7] in the presence of hexamethylphosphorous triamide (HMPT) and a small amount of water gave no alkenyl thiocyanate but a small amount of 1,2-dimethylpropyl thiocyanate,[4] the additional introduction of copper(II) acetate[5] to the reaction mixtures provided (*E*)-1-thiocyanatohex-1-ene in 80% yield (GC),‡ accompanied by 1,2-dimethylpropyl thiocyanate (20%). Following this, several improvements of the reaction procedure were attempted. Consequently the use of pyridine in place of HMPT depressed the formation of the above by-product into trace amounts keeping the product yield high, and a mixture of potassium thiocyanate and copper(II) nitrate trihydrate (2:1) [which should form $Cu(NCS)_2$ *in situ*] could be employed favourably in place of isolated copper(II) thiocyanate. The thiocyanatoalkenes thus produced were isolated from the worked-up[8] reaction mixtures by simple column chromatography. For example, (*E*)-1-thiocyanatohex-1-ene was afforded in 75% isolated yield from hex-1-yne. Some representative results obtained by reactions depicted in Scheme 1 are shown in Table 1.

Following successful thiocyanation, this led us to attempt a synthetic approach for azidoalkenes, highly interesting and useful synthetic intermediates (for the construction of azacyclopropane systems *etc.*).[9] Thus, a subsequent reaction of (*E*)-hex-1-enyldisiamylborane in THF with copper(II) acetate, copper(II) nitrate trihydrate and sodium azide in the presence of *N*,*N*-dimethylacetamide (DMA) and a small amount of water readily provided the expected (*E*)-1-azidohex-1-ene in reasonable yield [93% (GC) and 85% (isolated)]. HMPT was also usable as solvent, but the employment of pyridine was not appropriate (product yields, 85 and 25% respectively). Some representative results by reactions depicted in Scheme 2 are shown in Table 2.

Table 1 Synthesis of thiocyanatoalkenes from alkynes *via* hydroboration by disiamylborane

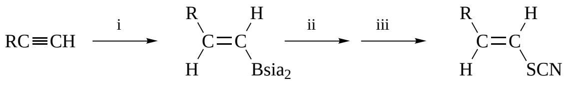
Alkyne	Product[b]	% Yield[a] GC	% Yield[a] Isolated[c]
Hex-1-yne	(*E*)-$BuCH=CHSCN$	88	75
tert-Butylacetylene	(*E*)-$Bu^tCH=CHSCN$	81	72
Phenylacetylene	(*E*)-$PhCH=CHSCN$	74	65

[a] All yields are for the overall process, and are based on starting alkynes. [b] Neither Z-isomer nor isothiocyanato-isomer was detected by GC. [c] After flash column chromatography (silica gel; pentane–dichloromethane). GC purity is 95–99%.

Table 2 Synthesis of azidoalkenes from alkynes *via* hydroboration by disiamylborane

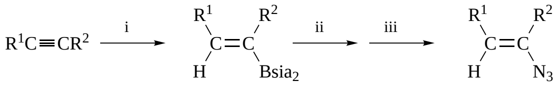
Alkyne	Product[b]	% Yield[a] GC	% Yield[a] Isolated[c]
Hex-1-yne	(*E*)-$BuCH=CHN_3$	93	85
Oct-1-yne	(*E*)-$C_6H_{13}CH=CHN_3$	91	86
tert-Butylacetylene	(*E*)-$Bu^tCH=CHN_3$	84	75
1-Ethynylcyclohexene	(*E*)-$(1\text{-}C_6H_9)CH=CHN_3$		73
Phenylacetylene	(*E*)-$PhCH=CHN_3$		70
Hex-3-yne	(*E*)-$EtCH=C(Et)N_3$	89	78

[a] All yields are for the overall process, and are based on starting alkynes. [b] The *Z*-isomers were not detected by GC. [c] After flash column chromatography (silica gel; pentane–dichloromethane). GC purity is 96–98%.



R = alkyl or phenyl

Scheme 1 *Reagents and conditions*: i, Sia_2BH, THF, −15 °C then 0–5 °C; ii, C_5H_5N, $Cu(OAc)_2$, $Cu(NO_3)_2\cdot3H_2O$, KSCN, H_2O and THF, −25 °C then −15 °C; iii, 0 °C then 20 °C



R^1 = alkyl or phenyl, R^2 = H or alkyl

Scheme 2 *Reagents and conditions*: i, Sia_2BH, THF, −15 °C then 0–5 °C; ii, Me_2NCOMe, $Cu(OAc)_2$, $Cu(NO_3)_2\cdot3H_2O$, NaN_3, H_2O and THF, −25 °C then −15 °C; iii, 0 °C then 20 °C

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† The synthesis of azidoalkanes *via* trialkylboranes has been reported.[2] We also reported the syntheses of azido[3] (or thiocyanato[4]) alkanes *via* trialkylboranes.

‡ The employment of dicyclohexylborane (a dialkylborane) (see ref. 6, p. 178) resulted in a lower product yield (55%). Besides, the hydroboration of alk-1-ynes by 9-BBN is not a particularly high yielding reaction (ref. 6, p. 41).

It should be noted that the present reaction can be accomplished without preparing and handling neat copper(II) azide (reported as being explosive when dry), furthermore, it can be carried out under wet conditions and in the presence of the relatively non-toxic solvent (DMA).

Although the reaction mechanism can hardly be clarified at present, the indispensability of copper(II) acetate (as mediator) in the reaction seems to suggest the formation of an alkenylcopper-like intermediate.

Whilst it is reported that (*E*)-alkenylpentafluorosilicates react with copper(II) thiocyanate in DMF to give (*E*)-alkenyl thiocyanates in reasonable yields.[10a] In comparison, the present reaction has some advantageous features, mainly the use of the more conveniently obtainable alkenylborane, and higher product yields *in situ*. However, for azidoalkenes, apart from the well-known 2-azidoalk-1-enes,[9a] only *Z*-isomers of 1-azidoalk-1-enes can be synthesized by the reaction between 1,2-epoxyalkylsilanes and azidotrimethylsilane,[11a] whilst the *E* isomers are only produced in poor yields by the reaction of 1,2-epoxyalkylsilanes with sodium azide.[12a] In comparison, with our present reaction, (*E*)-1-azidoalk-1-enes were easily provided using the more readily prepared alkenylboranes, and in reasonable yields too.

In conclusion, the present reactions reveal a novel and simple synthesis of (*E*)-1-azidoalk-1-enes and of (*E*)-1-thiocyanatoalk-1-enes, intriguing synthetic intermediates, in a one pot process from alkynes *via* hydroboration.

Experimental

Typical experimental procedure: preparation of (*E*)-1-thiocyanatohex-1-ene

In an argon-flushed flask, (*E*)-hex-1-enyldisiamylborane (20 mmol) in THF was prepared by the successive reactions of borane (20 mmol) in THF (15 cm^3) with 2-methylbut-2-ene (2.81 g, 40 mmol) in THF (10 cm^3) at -15 °C for 30 min and then at 0–5 °C for 2 h and then with hex-1-yne (1.65 g, 20 mmol) in THF (5 cm^3) at -15 °C for 30 min, then at 0–5 °C for 3 h.[6] To the solution, pyridine (30 cm^3), copper(II) acetate (3.65 g, 20 mmol), copper(II) nitrate trihydrate (9.70 g, 40 mmol), potassium thiocyanate (7.80 g, 80 mmol), water (0.36 cm^3) and THF (30 cm^3) were added successively at -25 °C under argon, after which the mixture was stirred at -15 °C for 1 h, then at 0–5 °C for 2 h and then at 20 °C for 20 h. The color of the reaction mixture changed from dark brown to light green. After filtration of the contents of the flask, the filtrate was washed with brine and extracted with diethyl ether. The extract was evaporated and the residue oxidized with sodium perborate (10 g, 65 mmol) in water (20 cm^3) and THF (20 cm^3) with stirring at 0–20 °C for 4 h.[8] The mixture was washed with brine, extracted with diethyl ether, and the extract dried (Na_2SO_4), filtered and evaporated. Chromatography of the organic residue (consisting of the thiocyanatoalkene and an almost quantitative amount of 3-methylbutan-2-ol derived from the residual disiamylboryl group by the above oxidative treatment) on a flash column (silica gel; pentane–dichloromethane) gave pure (*E*)-1-thiocyanatohex-1-ene (2.12 g, 75%); ν_{max}(neat)/cm^{-1} 3046 (C=CH), 2158 (sh, SC≡N), 1624 (C=C) and 954 (*trans*-CH=CH); δ_H(90 MHz; $CDCl_3$) 0.90 (3H, deformed t, Me), 1.1–1.6 [4H, m, $(CH_2)_2$], 2.18 (2H, q, *J* 6.4, $CH_2C{=}C$), 5.85 (1H, d, *J* 14.5) and 6.16 (1H, dt, *J* 14.5 and 6.4); δ_C(22.4 MHz; $CDCl_3$) 13.21 (Me), 21.54, 29.93, 32.04, 109.10 (=CH), 110.43 (SCN) and 142.34 (=CH); *m*/*z* 141 (M^+).

Preparation of (*E*)-1-azidooct-1-ene

To the solution of (*E*)-oct-1-enyldisiamylborane (20 mmol) in THF prepared as described above, DMA (30 cm^3), copper(II) acetate (3.65 g, 20 mmol), copper(II) nitrate trihydrate (9.70 g, 40 mmol), sodium azide (5.20 g, 80 mmol), water (0.36 cm^3) and THF (30 cm^3) were added successively at -25 °C under argon, followed by stirring at -15 °C for 1 h, then at 0–5 °C for 2 h and then at 20 °C for 10 h. The color of the reaction mixture changed from dark green to light green. After the same operations as above, the residue was oxidized with 3 mol dm^{-3} aq. sodium hydroxide (7.5 cm^3), 30% hydrogen peroxide (7.5 cm^3) and THF (10 cm^3) with stirring at 0–20 °C for 4 h. After the same work-up as above, chromatography of the organic residue (consisting of the azidoalkene and an almost quantitative amount of 3-methylbutan-2-ol) gave (*E*)-1-azidooct-1-ene (2.63 g, 86%) in a similar manner to that described above; ν_{max}(neat)/cm^{-1} 2105 (N_3), 1653 (C=C) and 931 (*trans*-CH=CH); δ_H(90 MHz; $CDCl_3$) 0.89 (3H, deformed t, Me), 1.1–1.6 [8H, m, $(CH_2)_4$], 2.03 (2H, q, *J* 6.8, $CH_2C{=}C$), 5.40 (1H, dt, *J* 13.4 and 6.8) and 5.86 (1H, d, *J* 13.4); δ_C(22.4 MHz; $CDCl_3$) 13.92 (Me), 22.52, 28.67, 29.32, 29.44, 31.60, 120.65 (=CH) and 126.1 (=CH); *m*/*z* 153.1245 (M^+) ($C_8H_{15}N_3$ requires *M*, 153.1266).

(*E*)-1-Azido-3,3-dimethylbut-1-ene. The GC retention time and satisfactory spectral data (IR, ^{1}H NMR, ^{13}C NMR, HRMS) were completely consistent with those of the prepared authentic sample.[9a]

Acknowledgements

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