

A New Facile Route to Primary Alkanenitriles from Terminal Alkenes *via* a Hydroboration–Cyanation Sequence

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Terminal alkenes are converted into one-carbon homologated primary alkanenitriles in high yields *via* hydroboration followed by a reaction with copper(I) cyanide, copper(II) acetate, and copper(II) acetylacetonate.

Although some methods for the synthesis of alkanenitriles by two- or more-carbon homologation of organoborane have been reported,¹ a synthesis of secondary alkanenitrile from trialkylcyanoborate,² reported previously by us, seemed to be a potentially useful method for the conversion of internal alkenes to the corresponding one-carbon homologated secondary alkanenitriles.³ However, an attempt to obtain primary alkanenitriles from terminal alkenes by similar procedures (Scheme 1) failed to give satisfactory results because of the sluggishness of the reaction.

We now report a high yield synthesis of primary alkane-

nitriles from terminal alkenes employing a modified procedure. Thus, a successive treatment of hexyldicyclohexylborane, prepared by hydroboration of hex-1-ene with dicyclohexylborane in tetrahydrofuran (THF), with excess amounts of copper(I) cyanide and copper(II) acetate in the presence of a small amount of copper(II) acetylacetonate gave heptanonitrile in 98% yield (estimated by g.l.p.c.), accompanied by very small amounts of cyclohexanecarbonitrile and undefined by-products (Scheme 2). Thus, the hexyl group was cyanated in preference to the cyclohexyl group.

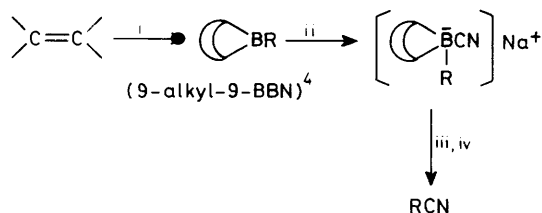
The above result is in marked contrast to our previous work,

Table 1. Synthesis of alkanenitriles from terminal alkenes *via* hydroboration by dicyclohexylborane.^a

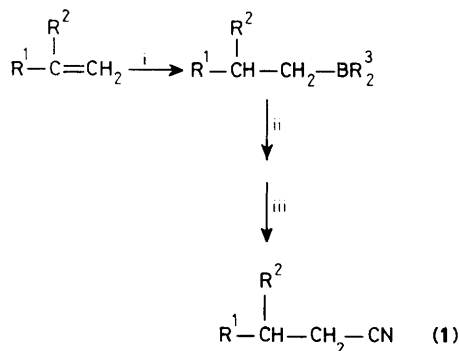
Alkene	Product	% Yield ^b	B.p./°C (Torr) [lit.]
Hex-1-ene	C ₆ H ₁₃ ⁿ CN	98 (92) ^c 68 ^d	81 (24) [70–72 (10)] ⁵
Oct-1-ene	C ₈ H ₁₇ ⁿ CN	97 (91) ^c	100 (13) [102 (11)] ⁷
4-Methylpent-1-ene	Me ₂ CH(CH ₂) ₃ CN	97 (90) ^c	75 (24)
3,3-Dimethylbut-1-ene	Me ₃ C(CH ₂) ₂ CN	95 (87) ^c	84 (39)
2-Methylpent-1-ene	C ₃ H ₇ ⁿ CH(Me)CH ₂ CN	72 (63) ^c 14 ^d	91 (52)
Methylenecyclopentane	c-C ₅ H ₉ CH ₂ CN	86 (80) ^c	78 (18) [76–78 (15)] ⁸
Methylenecyclohexane	c-C ₆ H ₁₁ CH ₂ CN	78 (71) ^c	89 (14) [82 (11)] ⁷

^a The reactions were carried out using dicyclohexylborane (50 mmol), alkene (50 mmol), Cu₂(CN)₂ (100 mmol), Cu(OAc)₂·H₂O (300 mmol), Cu(MeCOCHCOMe)₂ (12.5 mmol), and THF (200 ml) under argon atmosphere. ^b By g.l.p.c. method based on terminal alkenes employed.

^c Isolated by distillation. After filtration of the contents under argon atmosphere, the crude product was distilled out, washed with aqueous K₂CO₃, and dried over anhydrous Na₂SO₄. Then the pure product was obtained by distillation. ^d In the absence of Cu(II) acetylacetonate.



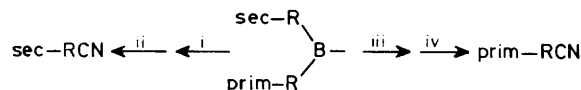
Scheme 1. Reagents: i, 9-borabicyclo[3.3.1]nonane [9-BBN]; ii, NaCN; iii, NaCN; iv, Pb(OAc)₄.



Scheme 2. Reagents and conditions: i, R₃BH, 0 °C, 2 h; ii, CuCN, 0 °C for 0.5 h then 20 °C for 2 h; iii, Cu(OAc)₂·H₂O/Cu(acac)₂, -15 °C for 0.5 h then 20 °C for 15 h. R¹ = alkyl, R² = H or alkyl, R³ = cyclohexyl.

where the secondary alkyl group in mixed trialkylboranes was cyanated in preference to the primary one.[†]

In the reactions using several types of terminal alkenes as starting materials, similar results were obtained giving high yields of corresponding primary alkanenitriles (Scheme 3). The presence of copper(II) acetylacetonate promoted markedly the reaction. Thus, 2-methyl-pent-1-ene was converted to 3-methylhexanenitrile in 72% yield in the presence of copper(II) acetylacetonate (acac), whereas only 14% yield was obtained in the absence of this reagent. In all cases, the amount of cyclohexanecarbonitrile (<1%) and other by-



Scheme 3. Reagents: i, NaCN; ii, Pb(OAc)₄; iii, CuCN; iv, Cu(OAc)₂/Cu(acac)₂.

products were negligible. The primary alkanenitriles thus obtained were isolated from the worked-up reaction mixture by such simple procedures as distillation or column chromatography. These experimental results are shown in Table 1.

The features, *i.e.*, the anti-Markownikoff hydrocyanation of terminal alkenes, the mild reaction conditions, and the high yields which are comparable to those reported in the reaction of haloalkanes with alkali cyanide,^{5,6} widely employed for the synthesis of alkanenitrile, make the present reaction practically and generally applicable to the synthesis of primary alkanenitriles.

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[†] Unpublished result: for example, in the reaction of sodium hexyldicyclohexylcyanoborate with sodium cyanide and lead(IV) acetate, cyclohexanecarbonitrile was afforded in preference to heptanenitrile.