Journal of Organometallic Chemistry, 359 (1989) 151–158
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preparation of 1-substituted 1-vinylcycloalkanes from 3,3-tetra- and 3,3-penta-methyleneallylboranes

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(Received May 25th, 1988)

Abstract

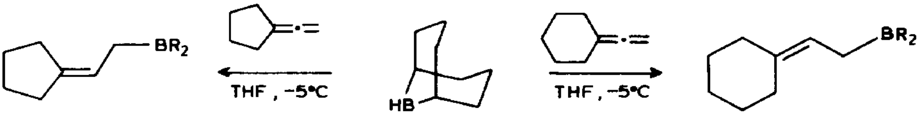
The boranes I and II, obtained by hydroboration of 1,1-tetra- and 1,1-pentamethyleneallenes with 9-BBN, were used as key reactants in the synthesis of a series of unsaturated *gem*-substituted carbinols (VIIa–VIIg, Xa–Xc, and XII), as well as 1,1-divinylcyclopentane and 1,1-divinylcyclohexane (XV and XVIII). The addition reactions of the boranes I and II to the carbonyl compounds and ethoxyacetylene studied, and the protolytic cleavage of II occur with total rearrangement of the allylic moiety.

The β,γ-unsaturated (allylic) boron compounds are useful and unique tools for the construction of new C–C bonds as well as for the cyclization and functionalization of different organic substances [1,2].

Here we report on the synthesis of two new β,γ-unsaturated boron derivatives, I and II, containing an exocyclic double bond, and we discuss some aspects of their use for the synthesis of 1-substituted 1-vinylcyclopentanes and 1-vinylcyclohexanes. The results presented here have been briefly described previously [3].

One of the approaches to allylic boranes involves the hydroboration of allenic hydrocarbons [1–8]. Unfortunately, the reaction often proceeds without specificity and results in the formation of a mixture of vinylic and allylic boranes, i.e. the products of a boron addition to the central (C_{sp}), or to one of the terminal allene atoms (C_{sp^2}), respectively. Allylboranes can only be smoothly prepared starting with 1,1-disubstituted allenes and $(R_2BH)_2$ [4,5], the best hydroborating agent being 9-borabicyclo[3.3.1]nonane (9-BBN) [7,8].

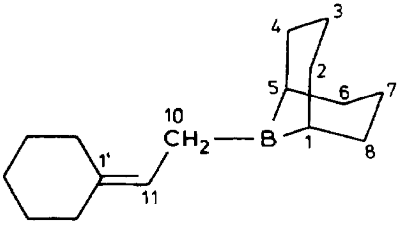
We used the hydroboration of 1,1-tetra- and 1,1-penta-methyleneallenes with 9-BBN in tetrahydrofuran at −5°C to synthesize boron-containing ethylidenecyclopentane (I) and ethylidenecyclohexane (II).



(I,76%)   (9-BBN)   (II, 83%)

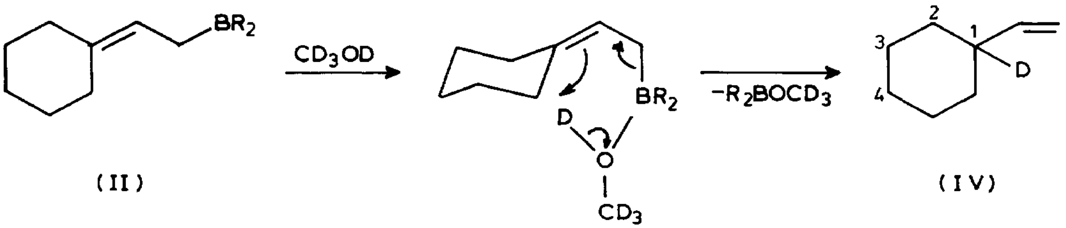
0022-328X/89/$03.50

Compounds I and II, which are monomeric, colourless mobile liquids, which are stable in inert atmospheres show chemical shifts of 84.00 and 83.74 ppm, respectively relative to $Et_2O \cdot BF_3$ in the ^{11}B NMR spectra. The IR spectra contain weak bands of the trisubstituted double bond (1665–1670 cm^{-1}). The ^1H NMR spectrum of I reveals signals (ppm) at 2.27 m ($B-CH_2$) and 5.43 t.q (C=CH, ^3J 7.6 Hz, ^4J 2.2 Hz); the spectrum of II contains signals at 2.22 d ($B-CH_2$, ^3J 8.0 Hz) and 5.25 t (C=CH, ^3J 8.0 Hz). Mean values of the $CH_2-C=$ proton chemical shifts in the cycles are 2.18 (I) and 2.15 (II).



The assignment of signals in ^{13}C NMR spectra of II was carried out, bearing in mind the data from ref. 10. The downfield signals of double bond carbon atoms are observed at 139.7 s ($C(1^1)$) and 115.8 d (C(11)) ppm; signals of carbon atoms bonded to the boron are broadened and have chemical shifts of 33.7 (C(10)) and 31.4 ppm (C(1) and C(5)). In addition, some "off-resonance" triplets are observed in the spectrum: 33.3 (C(2), C(4), C(6), C(8)), 23.3 (C(3) and C(7)), 27.2, 27.9, 28.8 and 29.0 ppm (cyclohexane ring carbon atoms).

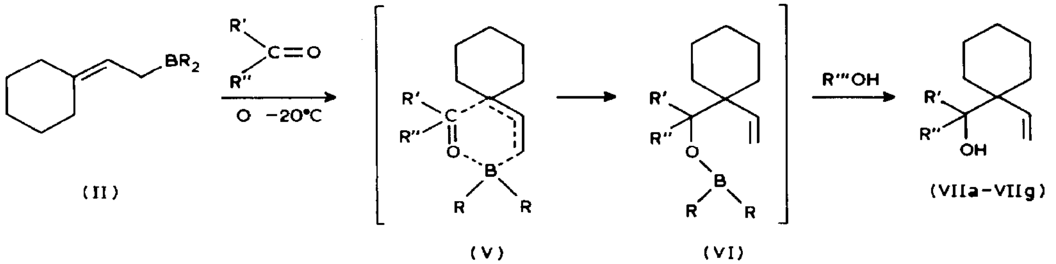
Compounds I and II possess high reactivities characteristic of this type of compound because they are specific allyl derivatives of boron. Their reactions with water or alcohols for example, produce vinylcyclopentane or vinylcyclohexane, respectively. Reaction of I with deuteromethanol led to 1-vinyl-1-deuterocyclohexane (IV):



(II) (III) (IV)

Hence the alcoholysis (hydrolysis) takes place with allylic rearrangement via the six-membered transition state III. The structure of compound IV was confirmed from its IR, ^1H and ^{13}C NMR spectra. Under full proton decoupling condition, six signals are observed in ^{13}C NMR spectrum (δ, ppm): 145.7 s (CH=), 112.3 s ($CH_2=$), 42.6 (C(1), a triplet with equal intensities of components, J(C–D) 15.2 Hz), 33.6 s (C(2)), 27.3 s (C(4)), 26.9 s (C(3)). The J(C–D) value serves as a direct evidence for the location of the deuterium atom in the position 1.

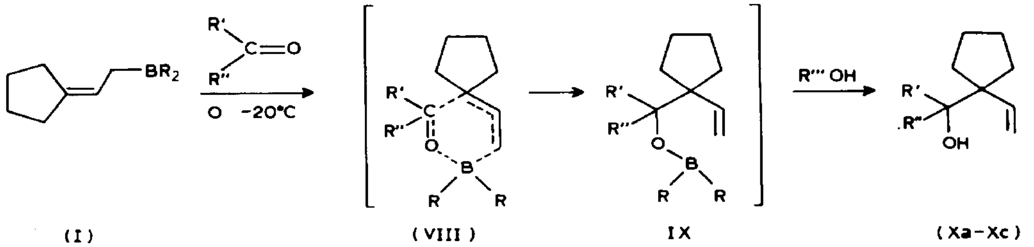
Like the other β,γ-unsaturated boron derivatives [1,2], boranes I and II can easily add to carbonyl compounds. Reactions of II with aldehydes and ketones proceed exothermally at 0–20 °C to give the esters VI; subsequent reesterification of these, gave the carbinols VII (vinylcyclohexane derivatives) (Table 1).



(VIIa: $R' = H$, $R'' = Me$; VIIb: $R' = R'' = Me$; VIIc: $R' + R'' = (CH_2)_4$;
VIId: $R' + R'' = (CH_2)_5$; VIIe: $R' = H$, $R'' = CH{=}CHMe$;
VIIf: $R' = Me$, $R'' = CH_2CH_2CH{=}CH_2$;
VIIg: $R' = Me$, $R'' = CH{=}CH_2$; $R'''OH$ = monoethanolamine, triethanolamine)

Esters VI were deboronated with mono- or tri-ethanolamine. The latter should be used if the carbinol to be formed has a relatively low boiling point. This method was used for the synthesis of carbinols (VIIa,b,e–g). The esters VI prepared from higher ketones, were reesterified with monoethanolamine (1/1) in hydrocarbon solvents (pentane or hexane). The intracomplex 9-(2-aminoethoxy)-9-borabicyclo[3.3.1]nonane thus formed precipitates while the carbinol remains in the solution. After decanting the solution and washing the residue with the same solvent, the carbinol (VIIc or VIId) is isolated by vacuum distillation in 50–70% yield (Table 1).

In an analogous way, borane (I) was used to make the cyclopentane carbinols (X):



(Xa: $R' = R'' = Me$; Xb: $R' + R'' = (CH_2)_4$; Xc: $R' = Me$, $R'' = CH{=}CH_2$;
$R'''OH$ = monoethanolamine, triethanolamine)

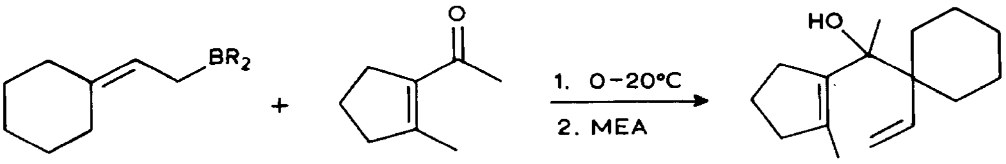
The formation of the esters VI and IX containing the vinyl group in position 1 indicates that the addition of the boranes I and II proceeds by allylic rearrangement via a six-membered transition state (V or VIII) which is apparently a concerted process ($2\pi + 2\pi + 2\sigma$).

Table 1

Compound	Yield (%)	B.p. (°C/mmHg)	n_D^{20}	(Found (calcd.) (%)) C	H	IR ν(C=C) (cm^{-1})
I	76	117–118/1	1.5173	82.93 (83.33)	11.59 (11.58)	1665
II	83	115–116/0.08	1.5180	83.06 (83.48)	11.83 (11.74)	1645 1670
VIIa	52	54– 55/2	1.4824	77.79 (77.92)	11.81 (11.69)	1642
VIIb	71	53– 55/2	1.4872	78.11 (78.57)	11.93 (11.91)	1640
VIIc	68	96– 96.5/1	1.5059	80.82 (80.41)	11.45 (11.34)	1635
VIId	50	100–101/1 m.p. 47– 49	–	80.74 (80.77)	11.53 (11.54)	1635
VIIe	68	77– 78/1	1.4932	79.85 (80.00)	11.24 (11.11)	1635 1675
VIIf	64	87– 89/1	1.4945	80.98 (80.77)	11.75 (11.54)	1640
VIIg	65	77– 78/1	1.4961	79.95 (80.00)	10.96 (11.11)	1642
Xa	65	45– 47/1	1.4780	77.51 (77.92)	11.67 (11.69)	1635
Xb	65	63– 66/1	1.4982	80.20 (80.00)	11.20 (11.11)	1640
Xc	50	78– 79/6	1.4829	79.48 (79.52)	10.99 (10.84)	1638
XII	55	105–106/2	1.5206	81.81 (82.05)	11.23 (11.11)	1635
XV	67	62– 63/6	1.4640	79.58 (79.52)	10.95 (10.84)	1600 1645
XVIII	73	85– 87/9	1.4719	79.74 (80.00)	11.16 (11.11)	1600 1645

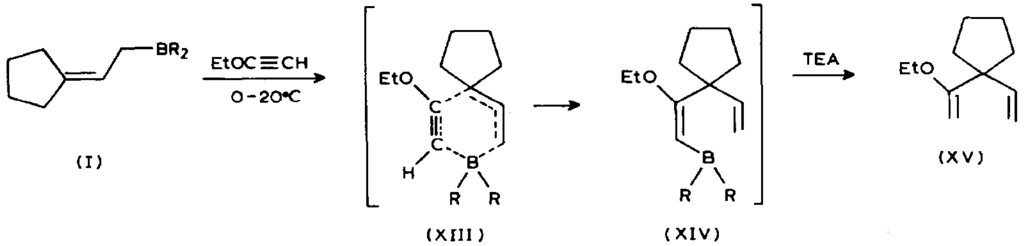
As with the other allyl(dialkyl)boranes [1,2], reactions of I and II with the α,β-unsaturated carbonyl compounds, crotonaldehyde and methyl vinyl ketone, take place only at the C=O group. In no case were 1,4-addition products observed.

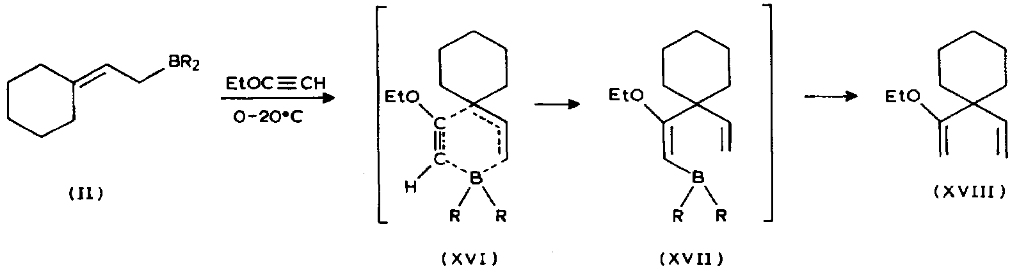
Cyclic unsaturated carbonyl compounds react similarly. For example, the diene alcohol XII was prepared starting from the ketone XI and borane II:



(II) (XI) (XII)

We have further used boranes I and II for the preparation of 1,1-divinyl derivatives of cyclopentane XV and cyclohexane XVIII. The key stage of this two-step one-pot procedure is the *cis*-allylboration of the alkoxyacetylene. Reac-





tions of boranes I and II with EtOC≡CH proceed at 0–20 °C to give the adducts, XIV and XVII, all with *trans*-located boryl and ethoxy groups.

We did not isolate the adducts XIV and XVII, but, their formation was indicated by IR spectral data. The spectra of the reaction products of I and II with ethoxyacetylene contain very intense absorption bands in the region of 1590 cm^{-1}, attributable to the B–CH=C–O fragment. The B–C_{sp^2} bond in XIV and XVII is polarized [9] and is thus readily cleaved by alcohols to give the dienes XV and XVIII.

The structure of the carbinols VII, X, XII and dienes XV, XVIII is supported by elemental analyse and spectral data (Tables 1 and 2). The IR spectra of all of the compounds contain absorption bands of the terminal double bond at 910–920, 1635–1645, and 3080–3085 cm^{-1}, in addition to bands of the OH groups (3200–3600 cm^{-1}) in the spectra of VII, X, XII. The IR spectra of 1-vinyl-1-(1-ethoxyvinyl)cycloalkanes XV and XVIII also show an intense band at 1600 cm^{-1}, which is attributable to CH_2=COEt. The ^1H NMR data listed in Table 2 indicate that the protons at the double bond show the usual chemical shifts and coupling constants. Thus, the signals from the vinyl protons (CH=C) are in the region 5.6–6.1 ppm whereas those of the terminal protons (CH_2=C) are between 5.0–5.4 ppm.

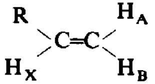
Experimental

All manipulations of the organoboron compounds were carried out under dry argon.

^1H NMR spectra were recorded on a BRUKER WM-250 spectrometer, ^{13}C and ^{11}B NMR spectra were recorded on a BRUKER AM-300 instrument using a pulse rate and full or partial proton decoupling.

Table 2

^{1}H NMR spectra of the carbinols VII, X, XII, and the dienes XV and XVIII



No	A	B	X	CH_3	AB	AX	BX	Signals of remaining protons (δ, ppm; *J*, Hz)
VIIa	5.08	5.34	5.62	1.08	1.8	17.3	10.7	3.44 qr (1H, OCH); *J* 6.5; 1.1–1.9 m (11H; CH [c] protons)
VIIb [a]	5.05	5.37	5.63	1.12	1.7	15.6	9.7	1.2–1.77 m (12H; CH and OH protons)
VIIc [a]	5.07	5.33	5.61	–	2.0	18.0	11.0	1.0–1.9 m (19H; CH, CP [c], and OH protons)
VIId	5.02	5.35	5.60	–	1.85	18.1	11.25	0.90–1.85 m (21H; CH and OH protons)
VIIe	5.08	5.32	5.63	1.7	1.7	18.5	11.3	5.45 d.d.qr (1H, $CH_3CH{=}C\mathit{H}{-}C$); 5.60 d.d.qr (1H, $CH_3C\mathit{H}{=}CH{-}C$); J_{trans} 16.1; *J* 7.2, *J* 1.6; 3.68 m (1H, OCH); 1.1–1.7 m (11H; CH and OH protons)
VIIf	5.05	5.37	5.62	1.08	1.9	18.6	11.4	5.01 d.qr ($1H_{trans}$, $CH_2{=}C$); 4.92 d.qr ($1H_{cis}$, $CH_2{=}C$); J_{gem} 1.8; J_{trans} 16.5; J_{cis} 9.8; 2.13 m (2H, $CH_2{-}C{=}C$); 1.2–1.77 m (11H; CH and OH protons)
VIIg	5.07	5.38	5.58	1.18	1.8	18.0	11.1	5.17 d.d ($1H_{trans}$, $CH_2{=}C$); 5.07 d.d ($1H_{css}$, $CH_2{=}C$); 6.01 d.d (1H, $CH{=}C$); J_{gem} 1.8; J_{trans} 17.5; J_{cis} 11.0; 1.0–1.9 m (11H; CH and OH protons)
Xa	5.03	5.05	5.83	1.13	1.6	17.8	11.0	1.3–1.9 m (9H; CP and OH protons)
Xb	5.10	5.15	5.89	–	1.7	17.7	10.7	1.4–1.9 m (17H; CP and OH protons)
Xc [b]	4.98	5.07	5.85	1.17	1.5	17.5	11.0	5.27 d.d ($1H_{trans}$, $CH_2{=}C$); 5.04 d.d ($1H_{cis}$, $CH_2{=}C$); 5.98 d.d (1H, $CH{=}C$); $J_{gem} = 1.9$; $J_{trans} = 17.3$; J_{cis} 10.9; 1.3–1.95 m (9H; CP and OH protons)
XII	5.08	5.37	5.62	1.28	1.8	17.5	10.7	1.88 s (3H, $CH_3{-}C{=}C$); 2.33 m (4H, $C{=}C{-}CH_2$); 0.95–1.8 m (13H; CH, OH, and CCH_2C protons)
XV	5.04	5.02	5.90	–	1.8	16.7	10.4	3.88 d (1H, $C{=}CH_2$); 3.98 d (1H, $C{=}CH_2$); J_{gem} 2.0; 3.7 qr (2H, OCH_2); *J* 6.7; 1.28 t (3H, CH_3); 1.5–2.0 m (8H; CP protons)
XVIII	5.0	4.80	5.80	–	1.5	18.0	10.0	3.9 d (1H, $C{=}CH_2$); 4.0 d (1H, $C{=}CH_2$); J_{gem} 2.0; 3.70 qr (2H, OCH_2); *J* 7.0; 1.3 t (3H, CH_3); 1.5–2.0 m (10H; CH protons)

[a] Details of the ^{13}C NMR spectra are given in experimental. [b] In a solution of C_6D_6. [c] CH = cyclohexane ring, CP = cyclopentane ring.

1,1-Tetra- and 1,1-penta-methyleneallenes were prepared as described in ref. 11 by reaction of the corresponding 1-chloro-1-ethynylcycloalkanes with a zinc–copper couple.

9-(3,3-Pentamethyleneallyl)-9-borabicyclo[3.3.1]nonane (II)

A 200 ml three-necked round-bottomed flask equipped with a magnetic stirrer, condenser, thermometer and a pressure-equalizing dropping funnel was charged with 8.25 g of 9-BBN and 120 ml of dry THF. During 40 min, 7.3 g of 1,1-pentamethyleneallene in 20 ml of THF, at −5° C was added to the mixture. After stirring for 4 h, the mixture was left to stand overnight, then the solvent was removed and the residue distilled to give 12.85 g (83%) of compound II, b.p. 115–116° C/0.8 mmHg, n_D^{20} 1.5180.

9-(3,3-Tetramethyleneallyl)-9-borabicyclo[3.3.1]nonane (I)

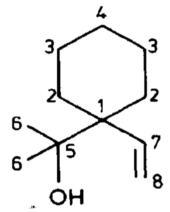
As above, starting from 4.3 g of 9-BBN in 70 ml of THF and 3.3 g of 1,1-tetramethyleneallene in 20 ml of THF, 5.77 g (76%) of borane I was obtained, b.p. 117–118° C/1 mmHg, n_D^{20} 1.5173.

1-Vinyl-1-deuterocyclohexane (IV)

To 1.95 g of borane II was added 3 ml of deuteromethanol (CD_3OD) at −10° C. The mixture was left to warm to room temperature and then distilled to give 0.58 g (68%) of 1-vinyl-1-deuterocyclohexane, b.p. 125–126° C, n_D^{20} 1.4463. The ^{1}H NMR spectrum of the compound is similar to that described in ref. 12.

1-Vinyl-1-(1-hydroxy-1-methylethyl)cyclohexane (VIIb)

1.5 ml of acetone was added to 2.96 g of borane II at 0° C. The reaction mixture was heated to room temperature, the excess of acetone was removed in vacuo, and 5 ml of triethanolamine was added. After 1 h, 1.5 g (71%) of carbinol (VIIb) was distilled off. ^{13}C NMR spectrum (ppm): 142.6 d (C(7)), 117.0 t (C(8)), 74.1 s (C(5)), 47.6 s (C(1)), 29.1 t (C(2)), 26.3 t (C(4)), 22.4 t (C-3), 24.9 quart (C-6).



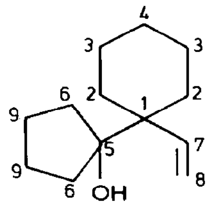
1-Vinyl-1-(1-hydroxybut-2-en-1-yl)cyclohexane (VIIe)

In a distillation vessel was placed 2.96 g of borane II and, after cooling to 0° C, was added with shaking, 0.9 of crotonaldehyde. The reaction mixture was gradually heated to room temperature and 5 ml of triethanolamine was added. After 0.5 h, from the mixture was distilled off 1.6 g of carbinol VIIe which was chromatographed on silica gel (100/160) (hexane/ether 2/1) and distilled to give 1.35 g (68%) of compound VIIe.

Carbinols VIIa, VIIf, VIIg and Xa, Xc were prepared similarly.

1-Vinyl-1-(1-hydroxycyclopent-1-yl)cyclohexane (VIIc)

Into a three-neck flask equipped with a magnetic stirrer bar, a thermometer, and a dropping funnel was placed 3.2 g of borane II in 10 ml of pentane, and then 1.18 g of cyclopentanone in 4 ml of pentane was added at 0–10 °C. The mixture was heated to 20 °C and stirred for 1 h, and 0.85 g of monoethanolamine was added. The crystalline 9-(2-aminoethoxy)-9-BBN was filtered and washed with pentane. Distillation of the pentane extract gave 1.84 g (68%) of carbinol VIIc, b.p. 95–96.5 °C/1 mmHg. ^{13}C NMR spectrum (ppm): 142.7 d (C(8)), 116.8 t (C(7)), 86.3 s (C(5)), 47.0 s (C(1)), 29.8 t (C(2)), 26.4 t (C(4)), 22.2 t (C(3)), 34.5 t (C(6)), 23.8 t (C(9)).



1-Vinyl-1-(1-ethoxyvinyl)cyclopentane (XV)

To a solution of 1.2 g of borane I in 5 ml of pentane placed in a vessel prepared for distilling was added, at 0–10 ° C, a solution of 0.55 ml of ethoxyacetylene in 2 ml of pentane. The mixture was heated to 20 °C and the pentane and the excess of ethoxyacetylene was removed. To the residue was added 3.5 ml of triethanolamine. After 0.5 h, 0.6 g (67%) of diene XV was distilled off, b.p. 62–63 °C/6 mmHg.

1-Vinyl-1-(1-ethoxyvinyl)cyclohexane (XVIII)

A three-neck flask equipped with a magnetic stirrer, thermometer and dropping funnel was charged with 3.65 g of borane II in 10 ml of pentane, and 1.12 g of ethoxyacetylene in 3 ml of pentane was added at 0–10 °C. After heating to room temperature and stirring for 0.5 h, 0.98 g of monoethanolamine was added to the mixture. Crystalline 9-(2-aminoethoxy)-9-BBN was filtered off and then washed with pentane. Removal of the solvent from washings and subsequent distillation gave 2.05 g (73%) of diene XVIII, b.p. 85–87 °C/2 mmHg.

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