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Synthesis of Z-Alkenes from Alkenylcatecholboranes Through Reaction with RMgX and I_2 Induced Rearrangement [1]

Mariappan Periasamy*, A.S.Bhanu Prasad and Yantrapragada Suseela

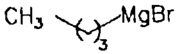
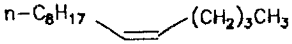
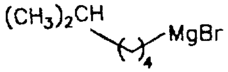
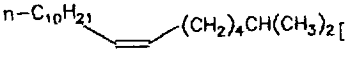
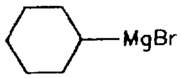
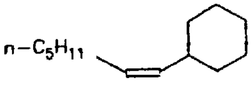
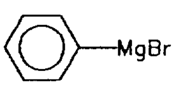
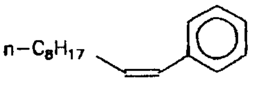
School of Chemistry, University of Hyderabad,
Central University P.O.,Hyderabad - 500134, India

ABSTRACT: Addition of RMgX and $BrMg(CH_2)_nMgBr$ reagents to alkenylcatecholborane followed by iodine induced rearrangement and oxidation provided Z-olefins and Z-olefinic alcohols in moderate to good yields. This procedure is advantageous over the previous methods of synthesis of Z-olefins from alkenylboranes since the alkyl groups which are not available through hydroborations can be also utilized.

It has been known for sometime that the reaction of E-alkenylalkyl boranes ($RCH=CH-BR_2$) with I_2/NaOH yields the corresponding stereochemically pure Z-olefins. The starting borane is generally prepared through stepwise hydroboration of alkynes and alkenes using $HBBr_2:SMe_2$ complex.[2] We wish to report the syntheses of Z-alkenes starting from the readily accessible alkenylcatecholboranes through reaction with RMgBr and I_2/NaOH treatment. We also describe here new syntheses of Z-olefinic alcohols, including certain naturally occurring compounds using diorganomagnesium derivatives.

Matteson and co-workers briefly reported that 1-propenylboronic esters prepared from tris[ethylenedioxyboryl]methane on reaction with 2 equivalents of n-butyllithium followed by I_2/NaOH treatment gives Z-2-heptene.[3] This transformation has not been studied in detail. The advantage in this method is that alkyl groups which are not available through hydroboration can be also utilized. We have employed catecholborane to get the required 1-alkenylboronic esters directly by hydroboration of 1-alkynes following a method developed in this laboratory.[4] Reaction of these alkenylboronic esters with freshly prepared Grignard reagent (2 eq.) followed by iodine induced rearrangement (Scheme 1) affords the corresponding Z-alkenes in 59-89% yields (Table 1).

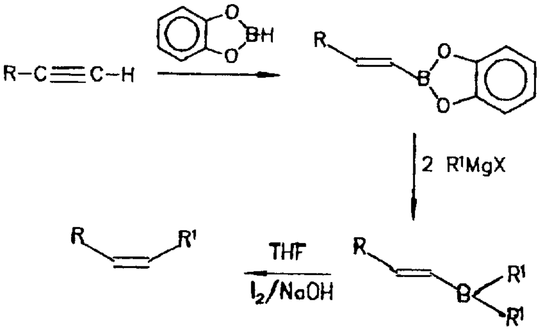
Table 1. Synthesis of cis-olefins using various Grignard reagent

Entry no.	Alkyne[a]	Grignard reagent[b]	Product[c]	Yield (%)[d]
1	$n\text{-}C_8H_{17}\text{-}C{\equiv}C\text{-}H$		 [1]	60
2	$n\text{-}C_{10}H_{21}\text{-}C{\equiv}C\text{-}H$		 [2]	59
3	$n\text{-}C_5H_{11}\text{-}C{\equiv}C\text{-}H$		 [3]	62
4	$n\text{-}C_8H_{17}\text{-}C{\equiv}C\text{-}H$		 [4]	89

a) All the reactions were carried out using 5.2 mmol of catecholborane, 5 mmol of 1-alkyne. b) RMgBr prepared using RBr (10 mmol) and Mg (15 mmol) were utilized. c) All the products were identified by IR, ^1H NMR and ^{13}C NMR data. ^{13}C-NMR data of products in entries no.2[5], 4[6] are in accordance with the reported data. d) Yields are of isolated and purified products.

It is of interest to note that the phenyl substituted Z-olefin (entry no.4, Table 1) can be also prepared in this way. Also, the precursor olefin used in the synthesis of the epoxy natural product *Disparlure* is obtained in 59% yield (entry no. 2, Table 1).

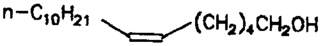
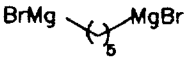
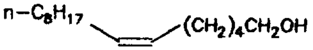
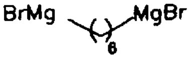
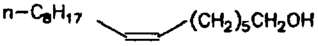
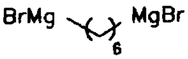
Scheme 1



The Z-1-phenyl-1-decene has been isomerized to E-1-phenyl-1-decene in 81% yield using $CoCl_2/NaBH_4/Ph_3P$ reagent system following a procedure reported from this laboratory.[7]

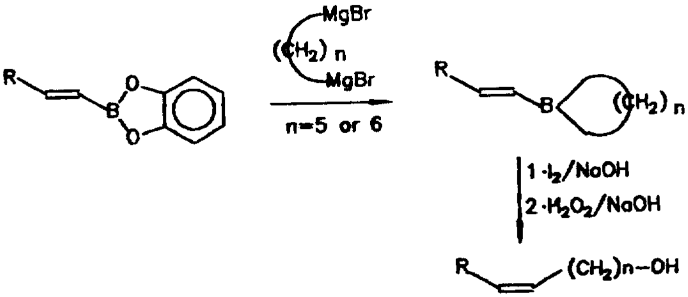
The reaction of the alkenylcatecholboranes with Grignard reagents, prepared from 1,5- and 1,6-dibromides, followed by I_2/NaOH treatment and oxidation resulted in the corresponding Z-olefinic alcohols (Scheme 2), however, in relatively lower yields, 30-47% (Table 2).

Table 2. Synthesis of cis-olefinic alcohols using various Grignard reagent

Entry no.	Alkyne[a]	Grignard reagent[b]	Product[c]	Yield (%)[d]
1	$n-C_{10}H_{21}-C\equiv C-H$		 [5]	47
2	$n-C_8H_{17}-C\equiv C-H$		 [6]	44
3	$n-C_4H_9-C\equiv C-H$		 [7]	40
4	$n-C_8H_{17}-C\equiv C-H$		 [8]	40
5	$n-C_4H_9-C\equiv C-H$		 [9]	30

a) All the reactions were carried out using 5.2 mmol of catecholborane, 5 mmol of 1-alkyne. b) $BrMg(CH_2)_nMgBr$ prepared using $Br(CH_2)_nBr$ (7.5 mmol) and Mg (20 mmol) were utilized. c) All the products were identified by IR, ^1H NMR and ^{13}C NMR data. All the products have been previously reported but spectral data have not been reported in several cases. d) Yields are of isolated and purified products.

Scheme 2



In these cases, the major side product is the aldehyde (13-19%) derived from the oxidation of alkenylcatecholboranes. However, the desired olefinic alcohols can be readily separated by column chromatography on silica gel. Again, it is of interest to note that the product in entry 4 (Table 2) is the precursor of the naturally occurring aldehydic insect pheromone *Iridomyrmex humilis*[8] and the product in entry 5 (Table 2) is insect pheromone *Raphia frater Grt.*[9]

Brown and co-workers have reported the synthesis of some of these olefinic alcohols through hydroboration of n-alkyn-1-ols followed by protonolysis[8] or hydroboration of excess (12 fold) of 1-alkynes using borinane and borepane at -78°C.[9] The chemical yields are somewhat lower in the present method, but this procedure should be more flexible since alkyl groups not available through hydroboration could be also employed.

EXPERIMENTAL SECTION

Benzene and THF were freshly distilled over sodium benzophenone. All bromides supplied by Sisco-Chem, India and Aldrich, USA were freshly distilled and utilized. 1-Alkynes were prepared following a reported procedure[10]. ^{1}H NMR spectra were recorded at 100 or 200 MHz and ^{13}C NMR spectra at 25 or 50 MHz, respectively. All boiling points are uncorrected.

Preparation of Z-1-phenyl-1-decene (4): Catechol (0.57 g, 5.2 mmol) was placed in an oven dried 2-necked flask bearing a side-arm septum. Dry benzene (20 mL) was introduced through a cannula. Diborane generated by slow addition of iodine (3.2 g, 12.5 mmol) in diglyme to sodium borohydride (1.0 g, 25 mmol) in diglyme was passed slowly through the suspension during 3-4h at 25°C. The outlet was connected to an acetone trap to destroy the excess of diborane. A clear benzene solution of catecholborane was obtained[4]. 1-Decyne (0.69 g, 5 mmol) was added and the contents were refluxed for 12h and cooled to 0°C. Phenylmagnesium bromide freshly prepared using bromobenzene (1.6 g, 10 mmol) and Mg (0.36 g, 15 mmol) in THF (40 mL) was added at 0°C and stirred for 8h at 25°C. The reaction mixture was cooled to -10°C and 3N NaOH (5 mL) was added, followed by drop wise addition of iodine (1.5 g, 6 mmol) in THF (10 mL) over 30 min. The contents were further stirred for 4h. The reaction mixture was quenched with saturated sodium thiosulphate solution and filtered over celite pad. The organic layer was separated and the aqueous layer was extracted with ether (2 X 20 mL). The combined organic extract was washed with 1N NaOH (3 X 20 mL) followed by water (10 mL) and brine. It was dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column using hexane as eluent solvent. The product Z-1-phenyl-1-decene was obtained in 89% (0.96 g) yield; IR (neat) 1650, 725 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.86 (t, 3H), 1.16-1.36 (m, 12H), 2.14-2.36 (m, 2H), 5.42-5.76 (m, 1H), 6.2-6.4 (m, 1H), 7.18 (m, 5H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 14.00, 22.65, 28.60, 29.23, 29.65, 29.94, 31.80, 126.48, 128.18, 129.83, 133.36, 137.85. MS (m/e) 216 (M^+, 15%), 104 (100%). This product has been reported.[6]

This procedure has been followed for the other entries in Table 1.
(Z)-5-tetradecene (1):IR (neat): 1650, 725 cm^{-1};^{1}H NMR (100 MHz,$CDCl_3$) 0.84 (m, 6H), 0.96-2.16 (m, 20H), 5.0-5.4 (m, 2H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 14.12, 22.41, 22.77, 29.41, 29.59, 29.76, 32.00, 129.95, 130.00. This product has been reported.[11]
(Z)-2-methyl-7-octadecene (2):IR (neat): 1650, 725 cm^{-1};^{1}H NMR (100 MHz, $CDCl_3$): δ 0.76-0.94 (m, 9H), 1.21-1.38 (m, 23H), 1.96 (m, 4H), 5.4 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.21, 22.49, 22.85, 27.46, 28.85, 29.35, 29.53, 29.76, 29.86, 32.10, 36.53, 128.59, 130.74. This product has been reported.[12]
(Z)-1-cyclohexyl-1-heptene (3):IR (neat) 1650, 725 cm^{-1};^{1}H NMR (200 MHz, $CDCl_3$) δ 0.85-1.73 (m, 19H), 2.01 (m, 3H), 5.23 (m, 2H); ^{13}C NMR (25 MHz, $CDCl_3$): 14.06, 22.65, 26.12, 27.00, 29.47, 29.86, 30.30, 31.53, 31.65, 36.41, 43.60, 128.25, 136.13. This product has been reported.[13]
Analysis: Calculated C:86.57, H:13.41; Found C:86.75, H:13.48.

Preparation of (Z)-6-pentadecene-1-ol (6): 1-Decenylcatecholborane was prepared from 1-decyne (0.69 g, 5 mmol) and catecholborane (5.2 mmol) following a reported procedure[4]. The $BrMg(CH_2)_5MgBr$ derivative prepared using $Br(CH_2)_5Br$ (1.73 g, 7.5 mmol) and Mg (0.48 g, 20 mmol) in THF (30 mL) was added at 0°C and stirred for 3h at this temperature and refluxed for 12h. This mixture was cooled to 0°C and 3N NaOH (5 mL) was added. Iodine (1.5 g, 6 mmol) in THF (10 mL) was added over 30 min. The contents were further stirred for 4h at this temperature. Saturated sodium thiosulphate solution (3 mL) was added and the mixture was filtered through celite. The filtrate was oxidized using 3N NaOH (10 mL) and 30% Hydrogen Peroxide (10 mL). The organic layer was separated and the aqueous layer was extracted with ether (2 X 15 mL). The combined organic extract was washed with aqueous sodium hydroxide solution, water, brine and dried over anhydrous $MgSO_4$. Solvent was evaporated and the residue was subjected to column chromatography on a silica gel column. The product Z-6-pentadecene-1-ol was isolated using hexane:ethyl acetate (90:10) as eluent solvent. Yield 44% (0.50 g.);IR (neat) 3300, 1650, 1050, 725 cm^{-1};^{1}H NMR (100 MHz, $CDCl_3$) δ 0.9 (t, 3H), 1.1-1.6 (m, 18H), 2.0 (m, 4H), 2.96 (br, 1H exchangeable with D_2O), 3.6 (t, 2H), 5.3 (m, 2H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 13.9, 22.59, 25.41, 25.83, 27.12, 29.29, 29.59, 31.88, 32.59, 62.29, 129.54, 130.00. This product has been reported.[8]

This procedure has been followed for other entries in Table 2.
(Z)-6-heptadecene-1-ol (5):IR (neat) 3300, 1650, 1050, 725 cm^{-1}; ^{1}H NMR (200MHz, $CDCl_3$): 0.9 (dist t, 3H), 1.2-1.7 (m, 22H), 2.05 (m, 4H), 3.64 (t, 3H, 1H exchanges with D_2O), 5.35 (m, 2H): ^{13}C NMR (50 MHz, $CDCl_3$):

14.17, 22.76, 25.48, 25.83, 27.23, 27.31, 29.42, 29.72, 31.40, 32.79, 63.08, 129.58, 130.28. This product has been reported.[14] Analysis: Calculated C:80.39, H:13.49, O:6.30 ; Found C:80.15, H:13.50, O:6.35.

(Z)-6-undecene-1-ol (7):IR (neat) 3300, 1650, 1050, 725 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 0.88 (dist. t, 3H), 1.2-1.7 (m, 10H), 2.0 (m, 4H), 3.6 (t, 3H, 1H exchangeable with D_2O), 5.35 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): 13.77, 22.24, 25.41, 26.86, 27.16, 29.53, 31.88, 32.59, 62.59, 129.60, 130.12. This product has been reported.[9]

(Z)-7-hexadecene-1-ol (8):IR (neat) 3300, 1650, 725 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 0.88 (dist.t, 3H), 1.2-1.7 (m, 20H), 2.0 (m, 4H), 3.65 (t, 3H, 1H exchanges with D_2O), 5.35 (m, 2H); ^{13}C NMR (25 MHz, $CDCl_3$): 13.88, 22.53, 25.65, 27.06, 29.24, 29.41, 31.83, 32.53, 62.34, 129.66, 129.95.

This product has been converted into the natural product aldehyde using PCC according to a procedure reported.[15]

(Z)-7-hexadeceneal: Yield 80%; IR (neat) 1726, 723 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$):δ 0.86 (t, 3H), 1.1-1.7 (m, 18H), 1.8-2.5 (m, 6H), 5.3 (m, 2H), 9.8 (s, 1H);^{13}C NMR (50 MHz, $CDCl_3$): δ 14.13, 22.10, 22.78, 27.04, 27.31, 28.86, 29.40, 29.57, 29.82, 31.96, 43.95, 129.40, 130.37, 202.75. This product has been reported.[8]

(Z)-7-dodecene-1-ol (9): IR (neat) 3300, 1650, 1050, 725 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 0.9 (dist. t, 3H), 1.2-1.7 (m, 12H), 2.0 (m, 4H), 3.65 (t, 3H, 1H exchangeable with D_2O), 5.35 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): 13.94, 22.35, 25.70, 27.00, 27.20, 29.12, 29.77, 32.06, 32.88, 63.06, 129.70, 130.30. This product has been reported.[9]

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