Tetrahedron Vol. 49, No 39, pp 8877-8886, 1993
Printed in Great Britain

0040-4020/93 $6 00+.00

Reaction of I_2 with α-Boraalkylmagnesium bromide : A New Synthesis of Mixed Alkyl Secondary Alcohols

Ch.Kishan Reddy and Mariappan Periasamy*
School of Chemistry, University of Hyderabad, Central University P.O,
Hyderabad-500 134, India.

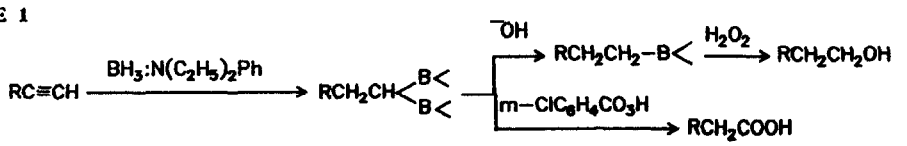
(*Received in UK* 7 *April* 1993; *accepted* 23 *July* 1993)

Abstract: 1,1-Diborylalkanes, prepared through hydroboration of 1-alkynes using BH_3:$N(C_2H_5)_2Ph$ complex, on reaction with Grignard reagent followed by I_2/NaOH treatment and H_2O_2/OH^- oxidation give the corresponding mixed alkyl secondary alcohols.

1,1-Diborylalkanes can be readily prepared by hydroboration of 1-alkynes with BH_3:LB complexes.[1-3] These compounds can be also prepared using two equivalents of dicyclohexylborane, 2,3-dimethyl-2-butylborane and 9-BBN for the hydroboration of 1-alkynes.[4-7] Although, the latter methods give well-defined 1,1-diborylalkanes, there will be always side products derived from the alkyl groups in applications utilizing these derivatives. In this laboratory, we have developed a convenient method for the generation of B_2H_6 using $NaBH_4/I_2$ through modification of a reported procedure.[8,9] In continuation of our efforts towards the applications of the N,N-diethylaniline-borane complex prepared in this way,[10-12] we became interested in the preparation and utilization of 1,1-diborylalkanes through hydroboration of 1-alkynes with the BH_3:$N(C_2H_5)_2Ph$ complex. We describe here the results of these studies.

In order to ascertain the formation of 1,1-dibora derivatives, we have first carried out the hydroboration of 1-decyne (7.5mM) using BH_3:$N(C_2H_5)_2Ph$ complex (5mM) in benzene. Oxidation of the intermediate boron compound with H_2O_2/OH^- gives 1-decanol in 82% yield and oxidation with m-chloroperbenzoic acid gives 1-decanoic acid in 80% yield, indicating the formation of the 1,1-dibora compound in good yields in the hydroboration step.[2]

SCHEME 1



We have also observed that the reaction of n-butyllithium with 1,1-diborylalkane prepared in this way affords boron-stabilized carbanions which upon treatment with certain alkyl bromides and esters followed by oxidation give secondary alcohols and carbonyl compounds, respectively. These results are summarized in Table 1. The yields are comparable to the yields reported with methods utilizing BH_3:THF for hydroboration.[7]

SCHEME 2

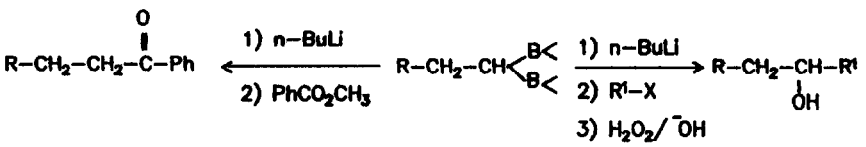


Table 1:Synthesis of secondary alcohols and carbonyl compounds through reaction of boron stabilized carbanion:

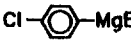
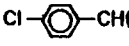
Entry [a]	Substrate	Product [b]		Yield(%) [c]
1	$PhCH_2Br$	$PhCH_2CH(OH)(CH_2)_8CH_3$	[1]	62
2	$H_2C{=}CHCH_2Br$	$H_2C{=}CHCH_2CH(OH)(CH_2)_8CH_3$	[2]	60
3	$H_3C(CH_2)_2CH_2Br$	$H_3C(CH_2)_3CH(OH)(CH_2)_8CH_3$	[3]	59
4	$PhCOOCH_3$	$PhCOCH_2(CH_2)_8CH_3$	[4]	61

a) For entries 1-3, alkyl bromides(10mM), 1,1-diboryldecane (7.5mM) and n-Buli (8ml,1.2M) were utilized. The organoborane was oxidized using OH^-/H_2O_2. For entry 4, methyl benzoate (10mM), 1,1-diboryldecane (7.5mM) and n-BuLi (8ml,1.2M) were utilized.

b) Products were isolated by column chromatography [silica gel/hexane:ethyl acetate (95:5)] and identified by spectral data (IR, ^1H & ^{13}C NMR). Products (1-4), have been reported in the literature.[13-16] Satisfactory elemental analysis data have been obtained for products 1 and 4 (C±0.1% and H±0.2%). The ^{13}C-NMR data (δppm/$CDCl_3$) are as follows:[1] 14.0, 22.6, 25.7, 29.3, 31.8, 36.8, 44.0, 72.7, 126.5, 128.6, 129.6, 138.9. [2] 13.7, 22.4, 25.4, 29.3, 31.7, 36.6, 41.7, 70.6, 117.7, 135.1. [3] 14.0, 22.6, 25.6, 29.4, 29.6, 31.9, 37.5, 72.0. [4] 14.0, 22.6, 24.3, 29.3, 29.5, 31.8, 38.5, 128.0, 128.6, 132.8, 137.2, 200.5.

c) Yield based on 1-alkyne utilized.

Table 2 :Synthesis of secondary alcohols through reaction of 1,1-diboryldecane with RMgX/I_2 followed by oxidation.

Entry [a]	Grignard reagent	Product [b]		Yield(%) [c]
1			[5]	60
2			[6]	59
3			[7]	57
4	$H_3C(CH_2)_2CH_2MgBr$	$H_3C(CH_2)_3CH(OH)(CH_2)_8CH_3$	[8]	59
5	$(H_3C)_2CHMgBr$	$(H_3C)_2CHCH(OH)(CH_2)_8CH_3$	[9]	52
6	$H_2C{=}CHCH_2MgBr$	$H_2C{=}CHCH_2CH(OH)(CH_2)_8CH_3$	[10]	50
7	$H_3C(CH_2)_4C{\equiv}CMgBr$	$H_3C(CH_2)_4C{=}CCH(OH)(CH_2)_8CH_3$	[11]	32

a) For entries 1-7, 1,1-diboryldecane (7.5mM) and Grignard reagent prepared using RBr (30mM), Mg (35mM) in THF (30ml) and BF_3:OEt_2 (2.5mM) were utilized.

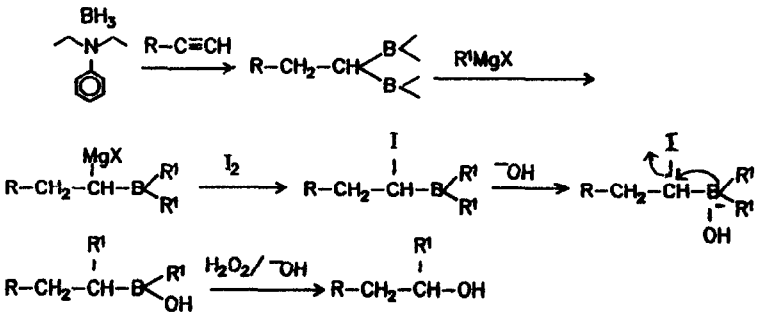
b) Products were isolated by column chromatography [silica gel/hexane:ethyl acetate (95:5)] and identified by spectral data (IR, ^1H & ^{13}C NMR). The products 5,8 and 10 have been reported.[14,15,17] Elemental analysis data (C±0.07% and H±0.02%) have been also obtained for compounds 7,10 and 11. Mass spectral data (EI,M^+-1) have been obtained for product 9. ^{13}C-NMR data (δppm/$CDCl_3$) are as follows. [5] 13.9, 22.5, 25.6, 29.2, 29.5, 31.8, 32.2, 62.8, 115.5, 120.2, 129.6, 156.0. [6] 14.0, 22.6, 25.6, 29.3, 29.5, 31.8, 32.4, 63.0, 116.8, 125.0, 129.4, 154.9. [7] 14.1, 22.7, 25.6, 27.8, 29.4, 29.6, 31.9, 36.9, 37.2, 72.8, 108.7, 115.6, 120.2, 120.5, 122.0, 124.9, 125.1, 126.0, 126.4, 127.7, 129.7, 134.6, 152.3, 154.1. [8] 14.0, 22.6, 25.6, 29.4, 29.6, 31.9, 37.5, 72.0. [9] 13.9, 17.0, 18.8, 22.6, 26.0, 29.2, 29.6, 31.9, 33.4, 34.1, 76.7. [10] 13.7, 22.4, 25.4, 29.3, 31.7, 36.6, 41.7, 70.6, 117.7, 135.1. [11] 13.8, 14.0, 18.6, 22.2, 22.6, 25.2, 28.4, 29.3, 29.5, 31.0, 31.9, 38.2, 62.7, 81.5, 85.4.

c) Yield based on 1-alkyne utilized.

Although, the reactions described in Schemes 1 and 2 have known for a long time, the 1,1-diboryl compounds have not received much attention. We envisaged that the α-boramagnesium halide formed through the addition of Grignard reagent to 1,1-diboryl compounds on treatment with I_2/OH^- would lead to rearrangement of the alkyl group

through α-iodoboron intermediates, resulting in the formation of secondary alkyl boron compounds as shown in Scheme 3.

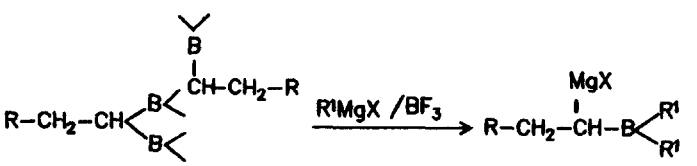
SCHEME 3



We have found that this is indeed the case. When the reaction was carried out with 1-decyne(7.5mM), BH_3:$N(C_2H_5)_2Ph$ (5mM), PhMgBr (10mM) and I_2 (10mM) the corresponding secondary alcohol has been obtained in moderate yield (50%) after H_2O_2/OH^- oxidation.

It is assumed that the 1,1-diboryl polymers breakdown to the α-boraalkylmagnesium bromide (Scheme 3) on reaction with RMgX . However, the alkyne and BH_3:$N(C_2H_5)_2Ph$ complex are used in 3:2 ratio and the stoichiometry (Scheme 3) requires involvment of alkyne and boron in 1:1 ratio. It was thought that the use of BF_3:OEt_2 and equivalent amount of RMgX to form BR_3 *in situ* would be helpful for the breakdown of the 1,1-diboryl polymers (Scheme 3).

SCHEME 4

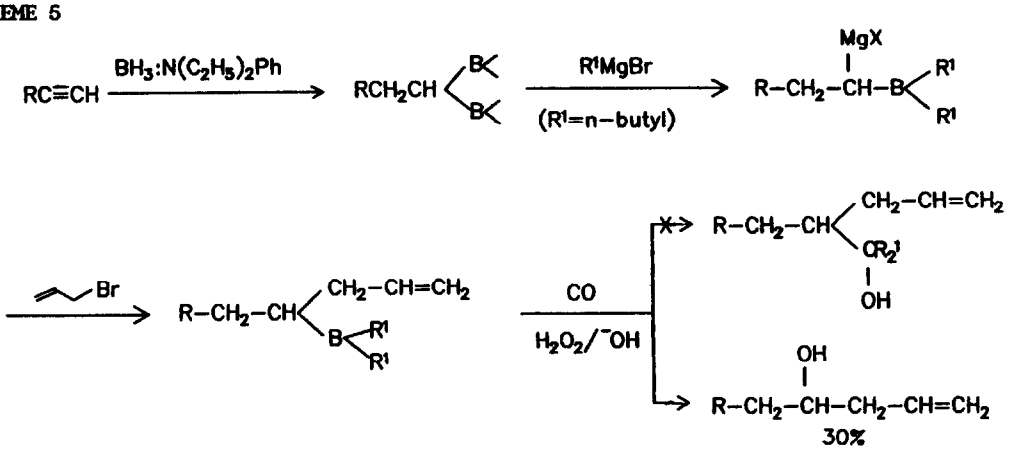


We have observed that the yield of the secondary alcohol is increased by about 10% when the reaction was carried out using 1-decyne (7.5mM), BH_3:$N(C_2H_5)_2Ph$ (5mM), PhMgX (30mM) and BF_3:OEt_2 (2.5mM). (See experimental section for details). Hence, we have carried out all transformations outlined in Table 2 in this way. Several mixed alkyl carbinols have been synthesized following this procedure (Table 2).

In order to examine the intermediacy of α-boraalkylmagnesium bromide, we have examined the alkylation-carbonylation process (Scheme 5)[18]. However, the expected trialkylcarbinol was not formed and the corresponding secondary alcohol, resulting

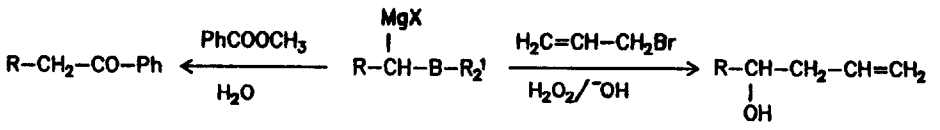
from alkylation of the intermediate α-boraalkylmagnesium bromide, was obtained in 30% yield.

SCHEME 5



This observation indicates that although the intermediate has the property expected for α-boraalkylmagnesium bromide, it may not be precisely the $RCH_2CH(MgX)BR_2^1$ species. The intermediacy of α-boraalkylmagnesium bromide was further ascertained by carrying out the alkylation with allyl bromide and the reaction with methylbenzoate (Scheme 6).

SCHEME 6



The mixed dialkyl carbinols and dialkyl ketones can be prepared through carbonylation[19] and cyanidation[20] of trialkyl boranes under certain conditions. The transformation described here is a good alternative to these methods, although in the present case three out of the four alkyl groups derived from the Grignard reagent are not utilized. Since one of the alkyl/aryl groups is prepared through a method not involving hydroboration, it is possible to prepare carbinols containing unsaturated moieties following the procedure reported here. Also, the zinc-boron organometallic species, structurally similar to the magnesium-boron derivatives suggested in Scheme 3, have been proved to be useful synthetic intermediates.[21] Although precise structure of the intermediate α-boraalkylmagnesium species is not understood, the reagent system should be useful for synthetic applications.

EXPERIMENTAL SECTION

General : Benzene distilled freshly over benzophenone-sodium ketyl was used as solvent for all experiments. Infrared spectra were recorded on a Perkin-Elmer spectrometer 1310 with polystyrene as reference. NMR spectra were recorded on JEOL-FX-100 and Bruker-AC-200 spectrometers in deuterated chloroform using tetramethylsilane as internal standard. The chemical shifts (δ) are expressed in ppm down field from the signal for internal Me_4Si. Elemental analyses were performed on a Perkin-Elmer elemental analyzer model-240 C. TLC plates coated with silica gel were used with hexane/ethyl acetate mixture as eluent and spots were developed in iodine. For column chromatographic purification under gravity, column grade silica gel (100-200 mesh size) was employed. 1-Decyne was prepared following a reported procedure.[22] The n-butyllithium was commercial sample supplied by Merck, Germany.

Reaction of 1,1-diboryldecane with n-BuLi / $PhCH_2Br$

The BH_3:$N(C_2H_5)_2Ph$ complex (5mM) was prepared *in situ* by bubbling diborane, generated by dropwise addition of iodine (1.27g, 5mM) in diglyme (10ml) to $NaBH_4$ (0.4g, 10mM) in diglyme (5ml) at 25°C, into a solution of N,N-diethylaniline (0.75g, 5mM) in dry benzene (50ml) for 1h.[8] 1-Decyne (1.04g, 7.5mM) was added at 25°C, stirred for 0.5h and refluxed for 6h. The reaction mixture was cooled to 10°C and n-butyllithium (8ml, 1.2M) was added slowly. The contents were further stirred for 2h at 25°C. Benzyl bromide (1.71g, 10mM) was added and further stirred for 6h. The reaction mixture was quenched with water (5ml) and oxidized using 3N NaOH (10ml) and H_2O_2 (30%, 10ml). The organic layer was washed with 3N HCl (20ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/90:10), 1-phenyl undecan-2-ol (1.15 g, 62%) was isolated. IR (neat) : ν_{max} 3350, 3050, 2950, 1600, 740, 700 cm^{-1}. ^{1}H-NMR (δppm/$CDCl_3$) : 7.40-7.15 (m,5H), 3.90-3.60 (m, 1H), 2.90-2.60 (m,2H), 2.30 (s,1H), 1.7-1.2 (m,16H), 0.95-0.80 (t,3H). The ^{13}C NMR data are summarized in footnote (b) Table 1. Anal. calcd. for $C_{17}H_{28}O$: C, 82.20 ; H, 11.36 Found C, 82.15 ; H, 11.41. This compound has been reported.[13]

Reaction of 1,1 diboryldecane with n-BuLi / $PhCOOCH_3$

The BH_3:$N(C_2H_5)_2Ph$ complex (5mM) was prepared *in situ* as above.[8] 1-Decyne (1.04 g, 7.5mM) was added at 25°C, stirred for 0.5h and refluxed for 6h. The reaction mixture was cooled to 10°C and n-BuLi (8ml, 1.2M) was added slowly. The contents were further stirred for 2h at 25°C. Methyl benzoate (1.36g, 10mM) was added and further stirred for 6h. The reaction mixture was quenched with water (5ml). The

organic layer was separated and the aqueous layer was extracted with ether (2X20ml). The combined organic extract was washed with 3N HCl (20ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography, on silica gel column (hexane:ethyl acetate/90:10), 1-phenyl-1-undecanone (1.1g, 61%) was isolated. IR(neat): υ_{max} 3050, 2950, 1700, 1600, 700 cm^{-1}. ^{1}H-NMR (δppm/$CDCl_3$): 8.0-7.9 (d,2H), 7.60-7.40 (m,3H), 3.00-2.90 (t,2H), 1.80-1.15 (m,16H), 0.95-0.80 (t,3H). The ^{13}C-NMR data are summarized in footnote (b) Table 1. Anal. calcd. for $C_{17}H_{26}O$: C, 82 87; H, 10.64 Found C, 82.78; H,10.80. This compound has been reported in the literature.[16]

Reaction of 1,1-diboryldecane with PhMgBr / I_2-NaOH

The BH_3:$N(C_2H_5)_2Ph$ complex (5mM) was prepared *in situ* as above.[8] 1-Decyne (1.04g, 7.5mM) was added at 25°C and stirred for 0.5h. The contents were refluxed for 6h and cooled to 10°C. BF_3:OEt_2 (0.35g, 2.5mM) was added and the contents were brought to 25°C and stirred further for 1h. The PhMgBr, prepared using PhBr (30mM) and Mg (35mM) in THF (30ml) was added to the reaction mixture at 10°C. The reaction mixture was stirred for 1h at 25°C and refluxed for 2h. Iodine (5g, 20mM) in benzene (20ml) was added dropwise to the reaction mixture at 10°C and further stirred for 2h at 25°C. Aqueous NaOH (3N, 30ml) solution was added drop wise to the reaction mixture and stirred further for 2h. The reaction mixture was oxidized using H_2O_2(30%, 20ml). The organic layer was separated and the aqueous layer was extracted with ether (2x20ml). The combined organic extract was washed with 3N HCl (20ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/95:5), 1-phenyl-1-decanol (1.05g,60%) was isolated. IR (neat):υ_{max} 3300, 3050, 2950, 1600, 1480, 760, 700 cm^{-1}. ^{1}H-NMR (δppm/$CDCl_3$) 7.32-6.66 (m,5H), 3.84 (s,1H), 3.64 (t,1H), 1.68-1.00 (m,16H), 0.84 (t,3H). The ^{13}C-NMR data are summarized in footnote (b) Table 2. This compound has been reported.[17]

Reaction of 1,1-diboryldecane with allylmagnesium bromide / I_2-NaOH

The BH_3:$N(C_2H_5)_2Ph$ complex (5mM) was prepared *in situ* as above.[8] 1-Decyne (1.04g, 7.5mM) was added at 25°C and stirred for 0.5h. The contents were refluxed for 6h and cooled to 10°C. BF_3:OEt_2(0.35g, 2.5mM) was added and the contents were brought to 25°C and stirred further for 1h. Allylmagnesium bromide, prepared using allyl bromide (30mM) and Mg (35mM) in THF (30ml) was added to the reaction mixture at 10°C. The reaction mixture was stirred for 1h at 25°C and refluxed for 2h. Iodine (5g, 20mM) in benzene (20ml) was added dropwise at 10°C and the reaction mixture was further stirred for 2h at 25°C. Aqueous NaOH (3N, 30ml) solution was added drop wise

to the reaction mixture and stirred further for 2h. The reaction mixture was oxidized using H_2O_2(30%,20ml). The organic layer was separated and the aqueous layer was extracted with ether (2x20ml). The combined organic extract was washed with 3N HCl (20ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/95:5), tridec-1-en-4-ol (0.74g, 50%) was isolated. IR (neat) :υ_{max} 3360, 3080, 2935, 2860, 1645, 1465, 900 cm^{-1}.[1] H-NMR (δppm/$CDCl_3$): 5.89-5.73(m, 1H), 5.17-5.10(m, 2H), 3.61(m, 1H), 2.35-2.08(m, 2H), 1.80(s, 1H), 1.50-1.20(m,16H), 0.90-0.80(t, 3H). The ^{13}C-NMR data are summarized in footnote (b) Table 2. MS (EI) : (M^+-1) 197. Anal. calcd. for $C_{13}H_{26}O$: C, 78.72 ; H, 13.21 Found C, 78.65 ;H, 13.19. This compound has been reported in the literature.[14]

Reaction of 1,1-diboryldecane with isopropylmagnesium bromide / I_2-NaOH

The BH_3:$N(C_2H_5)_2Ph$ complex (5mM) was prepared *in situ* as above.[8] 1-Decyne (1.04g, 7.5mM) was added at 25°C and stirred for 0.5h. The contents were refluxed for 6h and cooled to 10°C. BF_3:OEt_2 (0 35g, 2.5mM) was added and the contents were brought to 25°C and stirred further for 1h. Isopropylmagnesium bromide, prepared using isopropyl bromide (30 mM) and Mg (35mM) in THF (30ml) was added to the reaction mixture at 10°C. The reaction mixture was stirred for 1h at 25°C and refluxed for 2h. Iodine (5g, 20mM) in benzene (20ml) was added dropwise at 10°C and the reaction mixture was further stirred for 2h at 25°C. Aqueous NaOH (3N, 30ml) solution was added dropwise and stirred further for 2h. The reaction mixture was oxidized using H_2O_2 (30%, 20ml). The organic layer was separated and the aqueous layer was extracted with ether (2x20ml). The combined organic extract was washed with 3N HCl (20ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/95:5), 2-methyl,3-dodecanol (0.78g,52%) was isolated. IR (neat) ν_{max} 3250, 2900, 1440 cm^{-1}. ^{1}H-NMR (δppm/$CDCl_3$) 3.24(m,1H), 1.64-0.92(m,16H), 0.88-0.60(m,9H). The ^{13}C-NMR data are summarized in footnote (b) Table 2. MS (EI) : (M^+-1) 199.

Reacton of 1,1-diboryldecane with $H_3C(CH_2)_2CH_2MgBr$ / H_2C=CH-CH_2Br

The BH_3:$N(C_2H_5)_2Ph$ complex (5mM) was prepared *in situ* as above.[8] 1-Decyne (1.04g, 7.5mM) was added at 25°C and stirred for 0.5h. The contents were refluxed for 6h and cooled to 10°C. BF_3:OEt_2 (0.35g, 2.5mM) was added and the contents were brought to 25°C and stirred further for 1h. The $H_3C(CH_2)_2CH_2MgBr$, prepared using $H_3C(CH_2)_2CH_2Br$ (30mM) and Mg (35mM) in THF (30ml) was added to the reaction mixture at 10°C. The mixture was stirred for 1h at 25°C and refluxed for 2h. Allyl bromide (1.20g, 10mM) was added dropwise to the reaction mixture at 25°C and further stirred for 3h at

25°C. The contents were oxidized by the addition of 3N NaOH (10ml) followed by dropwise addition of H_2O_2 (16%, 15ml). The mixture was stirred for 2h at 25°C. The organic layer was separated and the aqueous layer was washed with ether (2x20ml). The combined organic extract was washed with 3N HCl (2x20ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate / 95:5), tridec-1-en-4-ol (0.47g, 32%) was isolated. Spectral data were identical with the data of this product obtained in the earlier experiment (Table 2).

Reaction of 1,1-diboryldecane with $H_3C(CH_2)_2CH_2MgBr$ / $PhCOOCH_3$

The BH_3:$N(C_2H_5)_2Ph$ complex (5mM) was prepared *in situ* as above.[8] 1-Decyne (1.04g, 7.5mM) was added at 25°C and stirred for 0.5h. The contents were refluxed for 6h and cooled to 10°C. BF_3:OEt_2 (0.35g, 2.5mM) was added and the contents were brought to 25°C and stirred further for 1h. The $H_3C(CH_2)_2CH_2$-MgBr prepared using $H_3C(CH_2)_2CH_2Br$ (30mM) and Mg (35mM) in THF (30ml) was added to the reaction mixture at 10°C. The reaction mixture was stirred for 1h at 25°C and refluxed for 2h. Methyl benzoate (1.36g, 10mM) was added dropwise to the reaction mixture at 25°C, and further stirred for 3h at 25°C. The mixture was quenched with water (5ml). The organic layer was separated and the aqueous layer was washed with ether (2x20ml). The combined organic extract was washed with 3N HCl (2x20ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate / 90:10), 1-Phenyl- 1-undecanone (0.68g, 38%) was isolated. Spectral data were identical with the data of this product obtained in the earlier experiment (Table 1).

Attempted carbonylation reaction with Alkylated α-boraalkylmagnesium bromide

The BH_3:$N(C_2H_5)_2Ph$ complex (5mM) was prepared *in situ* as above.[8] 1-Decyne (1.04g, 7.5mM) was added at 25°C and stirred for 0.5h. The contents were refluxed for 6h and cooled to 10°C. BF_3:OEt_2 (0.35g, 2.5mM) was added and the contents were brought to 25°C and stirred further for 1h. The $H_3C(CH_2)_2CH_2$-MgBr prepared using $H_3C(CH_2)_2CH_2Br$ (30mM) and Mg (35mM) in THF (30ml) was added to the reaction mixture at 10°C. The reaction mixture was stirred for 1h at 25°C and refluxed for 2h. Allyl bromide (1.20g, 10mM) was added dropwise to the reaction mixture at 25°C and further stirred for 3h at 25°C, ethylene glycol (10ml) was added and the reaction mixture was brought to 100°C. It was stirred further for 6h at 100°C while bubbling carbon monoxide through it. The reaction mixture is then brought to 25°C, 3N NaOH (20ml) was added and the oxidation carried out by the dropwise addition of H_2O_2 (16%, 10ml). The organic layer was separated and the aqueous layer was washed with ether (2x20ml).

The combined organic extract was washed with 3N HCl (2x20ml),3N NaOH (2x20ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate / 95:5), tridec-1-en-4-ol (0.44g, 30%) was isolated. Spectral data were identical with the data of this product obtained in the earlier experiments.

Acknowledgement : This research work was supported by the DST & UGC (New Delhi). We are also grateful to the UGC Special Assistance and COSIST Programmes.

References :

1. Brown,H.C.; Zweifel,G. J. Am. Chem. Soc.,1961,83,3834.
2. Zweifel,G.; Arzoumanian,H. J. Am. Chem. Soc.,1967,89,291.
3. Zweifel,G.; Arzoumanian,H. Tetrahedron Lett.,1966,2535.
4. Zweifel,G.; Fisher,R.P.; Horng,A. Synthesis.,1973,37.
5. Cainelli,G.; Dal Bello,G.; Zubiani,G. Tetrahedron Lett.,1965,3429.
6. Cainelli,G.; Dal Bello,G.; Zubiani,G. Tetrahedron Lett.,1966,4315.
7. Mukaiyama,T.; Murakami,M.; Oriyama,T.; Yamaguchi,M. Chem. Lett.,1981,1193.
8. Narayana,C.; Periasamy,M. J. Organomet. Chem.,1987,323,145.
9. Bhaskar Kanth,J.V.; Periasamy,M. J. Org. Chem.,1991,56,5964.
10. Kishan Reddy,Ch.; Periasamy,M. Tetrahedron Lett.,1989,5663.
11. Kishan Reddy,Ch.; Periasamy,M. Tetrahedron,1992,8329.
12. Kishan Reddy,Ch.; Periasamy,M. Tetrahedron Lett.,1990,1919.
13. Shankaran,K.; Talekar,D.G.; Rao,A.S. Indian J. Chem., sect.B 1982,21B,408.
14. Roush,W.R.; Hoong,L.K.; Palmer,M.A.J.; Park,J.C. J. Org. Chem.,1990,55,4109.
15. Shunsuke,H.; Yoshinori,Y.; Haruo,M.; Sumio,M. Kogyo Kagaku Zasshi.,1968,71,704.
16. Mazid,M.A.; Walker,S.; Weir,N.A. Relaxation Interact. process.,1981,19,249.
17. Brown,H.C.; Chandrasekharan,J.; Ramachandran,P.V. J. Am. Chem. Soc.,1988,110, 1539.
18. We thank a refree for suggesting this experiment.
19. Brown,H.C.; Rathke,M.W. J. Am. Chem. Soc.,1967,89,2738..
20. Pelter,A.; Hutchings,M.G; Smith,K. J. Chem. Soc. Chem. Commun.,1970,1529.
21. Knochel,P. J. Am. Chem. Soc.,1990,112,7431.
22. Dehmlow,E.V.; Lissel,M. Tetrahedron.,1981,37,1653.