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THE REACTION OF α-METHOXYVINYLLITHIUM WITH TRIALKYLBORANES *

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Summary

Several alkenyltrialkylborate salts derived from the reaction of α-methoxyvinyllithium (MVL) with trialkylboranes have been prepared. At —80°C, the initial complex is stable as indicated by its iodination to give moderate yields of enol ethers. Warming the complex to room temperature leads via an alkyl group migration to a new alkenyldialkylmethoxyborate salt. Oxidation of this complex leads to methyl ketones. Alternatively, treatment of this salt with various electrophiles, such as acid, iodine, or alkylating agents prior to oxidation leads to methyldialkylcarbinols, 1,1-dialkylethylenes and hindered tertiary alcohols, respectively. The products can be rationalized by electrophilic attack at the β carbon of an alkenylborate salt. The remarkable nucleophilicity of these salts appears to be comparable to that of enamines.

Introduction

The chemistry of unsaturated organoboranes often differs from that of their saturated analogs. For example, alkenyl- and alkynyl-boranes react readily with many electrophilic reagents. Under similar conditions, trialkylboranes are essentially inert [1,2]. From a mechanistic point of view, many of these reactions are believed to proceed via an alkenyl- or alkynyl-borate salt. Indeed, recently a number of investigators [3—14] have extensively examined the chemistry of alkynyltrialkylborate salts. In contrast, a sparcity of information about the chemistry of the corresponding alkenyl derivatives is available in the literature [3,14—20]. In part, this appears to be due to the relative inaccessibility of substituted vinyllithium derivatives. Thus, most of the reported work has involved the chemistry of borate salts derived from vinyllithium (eq. 1). Our recent interest in the synthetic applications of these complexes [20] stimulated a desire to study their

* Dedicated to Professor H.C. Brown on the occasion of his 66th birthday.

TABLE 1

PREPARATION OF METHYL KETONES FROM α-METHOXYVINYLLITHIUM AND TRIALKYLBORANES

R_3B R =	Product	Yield [a] (%)
n-Hexyl	2-Octanone	82
Tsobutyl	4-Metyl-2-pentanone	91
sec-Butyl	3-Methyl-2-pentanone	75
Cyclopentyl	Cyclopentylmethyl ketone	83
Cyclohexyl	Cyclohexylmethyl ketone	97

[a] Yields by GC.

such as $BF_3 : OEt_2$ to aid in the displacement of the methoxy group, subsequent iodination in the presence of sodium hydroxide leads to reasonable yields of VI (eq. 5).

$$I \xrightarrow{-78^\circ C \text{ to R.T.}} \xrightarrow{BF_3 : OEt_2} \xrightarrow[NaOH]{I_2} \underset{(VI)}{R_2C{=}CH_2} \qquad (5)$$

$$R = n\text{-}C_6H_{13}, 48\%, R = \text{cyclo-}C_5H_9, 75\%$$

Oxidation of I with basic hydrogen peroxide after warming to room temperature leads to mixtures of methyl ketones and dialkylmethylcarbinols. The product ratio can be controlled by varying the workup conditions. Thus addition of ethanol as cosolvent immediately prior to oxidaton leads to excellent yields of methyl ketones (eq. 6). Formally, this represents the alkylation of an acyl car-

$$\underset{(I)}{Li^+ [R_3B{-}\overset{OMe}{\overset{|}{C}}{=}CH_2]^-} \xrightarrow{-78^\circ C \text{ to R.T.}} \xrightarrow[NaOH/EtOH]{H_2O_2} \underset{(V)}{R{-}\overset{O}{\overset{\|}{C}}{-}CH_3} \qquad (6)$$

banion equivalent with an olefin, we have therefore investigated the scope of this reaction. The results for a number of boranes are summarized in Table 1. In all cases, excellent yields of ketones are obtained.

Alternatively, if one adds hydrochloric acid prior to the oxidation, only dial-

TABLE 2

THE FORMATION OF DIALKYLMETHYLCARBINOLS FROM TRIALKYLBORANES AND MVL

R_3B R =	Product	Yield [a] (%)
n-Hexyl	Di-n-hexylmethylcarbinol	100
Isobutyl	Diisobutylmethylcarbinol	94 (77) [b]
sec-Butyl	Di-sec-butylmethylcarbinol	92
Cyclopentyl	Dicyclopentylmethylcarbinol	87
Cyclohexyl	Dicyclohexylmethylcarbinol	94

[a] Yields by GC. [b] Isolated yields.

TABLE 3

ALKYLATION OF VINYLTRIALKYLMETHOXYBORATE SALTS (IX)

R_3B R =	Alkylating agent	Reaction time (h)	Yield [a,b]
n-Butyl	CH_3OSO_2F	1	81
	CH_3I		70
Isobutyl	CH_3OSO_2F	1	98
	CH_3I	1	89
	n-C_4H_9I	5 [c]	88
	n-C_4H_9Br	28 [c]	63
	n-C_4H_9Cl	24 [c]	—
	i-C_4H_9I	24 [c]	24
	$(CH_3)_2CHI$	24 [c]	—
	CH_2=$CHCH_2Br$	5	74
	CH_2=$CHCH_2Cl$	28 [c]	77 (52)
	$C_6H_5CH_2Br$	5	75
	$C_6H_5CH_2Cl$	5	78
sec-Butyl	CH_3OSO_2F	1	97
	CH_3I	1	84
Cyclopentyl	CH_3OSO_2F	1	67
		3	80
	CH_3I	24	86
Cyclohexyl	CH_3OSO_2F	24	77
		5 [c]	85
	CH_3I	24	66%

[a] GC yields. [b] Isolated yields in parentheses. [c] Reactions were carried out at reflux for the indicated amount of time.

kylmethylcarbinols result (eq. 7). The results for a variety of boranes are summarized in Table 2.

$$I \xrightarrow{-78^\circ C \text{ to R.T.}} \xrightarrow{2N\ HCl} \xrightarrow[NaOH/EtOH]{H_2O_2} R_2\overset{OH}{\overset{|}{C}}-CH_3 \quad (VII) \qquad (7)$$

Formation of VII is highly suggestive of electrophilic attack on an alkenylborate salt (vide infra). Previous work suggests that such intermediates may be nucleophilic [16—18]. Indeed, treatment of solutions of I with simple alkyl halides leads to moderate to good yields of highly hindered tertiary alcohols (eq. 8). The results for a variety of simple alkyl halides are summarized in Table 3.

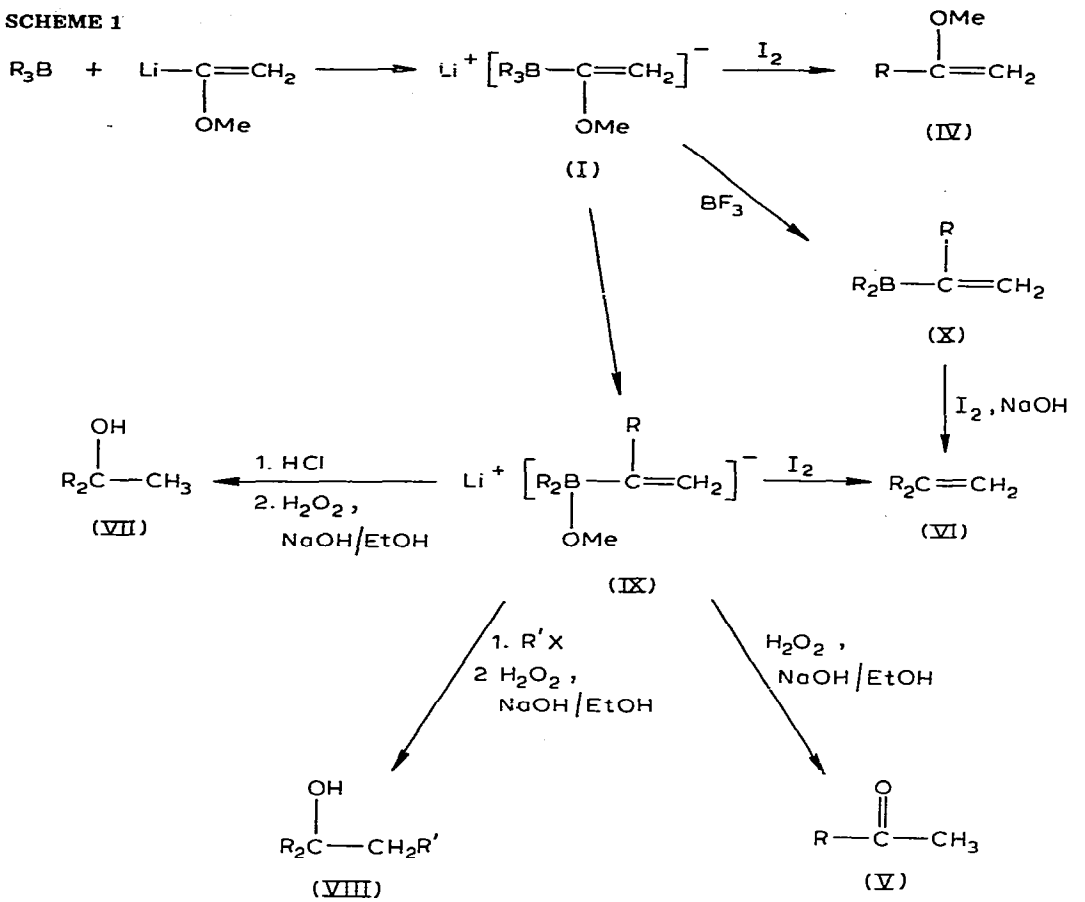
$$I \xrightarrow{-78^\circ C \text{ to R.T.}} \xrightarrow{R'X} \xrightarrow[NaOH/EtOH]{H_2O_2} R_2\overset{OH}{\overset{|}{C}}-CH_2R' \quad (VIII) \qquad (8)$$

Discussion

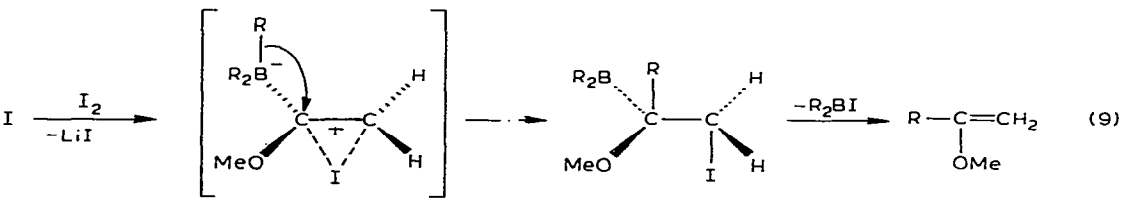
The results described above can be rationalized in terms of Scheme 1. Thus, iodination of an alkenylborate such as I should lead directly to enol ethers [20] by an addition—elimination sequence (eq. 9).

The products derived from I after warming to room temperature can only be

SCHEME 1



rationalized in terms of an "α-transfer" * reaction to give the new borate salt

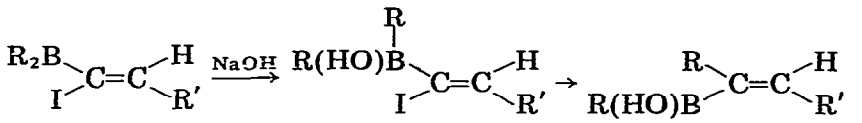


(9)

IX. There is ample precedent for this in the related work of Zweifel and coworkers [24] (eq. 10). Subsequent oxidation of IX should give directly methyl ketones. Formation of IX cannot be complete, however, at room tem-

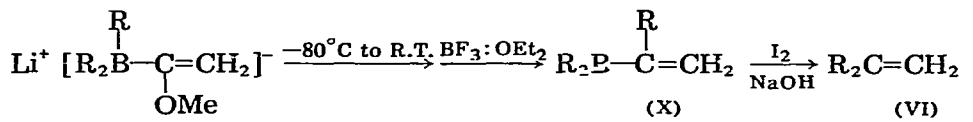
* We use "α-transfer" to denote any reaction involving transfer of an alkyl group from tetracoordinate boron to an adjacent atom bearing a leaving group, i.e.

perature because iodination leads to mixtures of IV and VI. However, if one adds



(10)

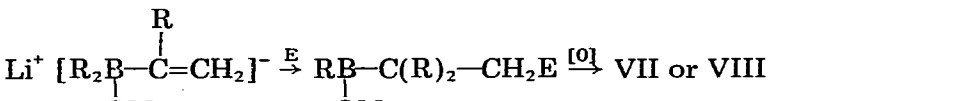
a Lewis acid, such as $BF_3 : OEt_2$, the alkenylborane X is formed in moderate yield as indicated by its iodination to VI (eq. 11). Presumable this is due to Lewis acid complexation of BF_3 with the methoxy group, making it a better



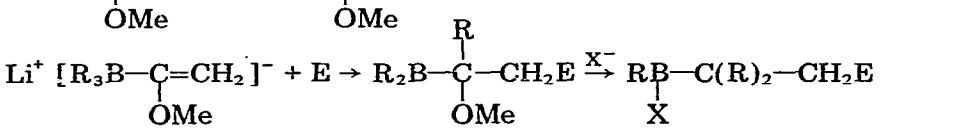
(11)

leaving group. Furthermore, the quantitative formation of V upon oxidation of a mixture of I and IX suggests that even hydrogen bonding may provide enough assistance to allow quantitative formation of IX or the vinyl borane X.

The exact mechanism of formation of VII and VIII is not as clear. One can rationalize their formation by attack of an electrophile on IX directly, followed by oxidation (eq. 12) or equally as well by attack of an electrohile on I followed by a rapid second transfer to displace methoxide (eq. 13). An analogous displace-



(12)



(13)

ment of methoxide has previously been reported [25]. Since our evidence suggests that both I and IX are present simultaneously, it may be that both mechanisms are occurring simultaneously.

Conclusion

These results clearly demonstrate that alkenylborate salts react with electrophiles at the olefinic carbon β to boron. Furthermore, the fact that these complexes react readily with simple alkyl halides demonstrates a remarkable nucleophilicity for what is formally a simple olefin. Presumably this effect is due to the full negative charge on boron strongly polarizing the π orbitals.

In view of these salts remarkable nucleophilicity and the fact that these reactions allow the simultaneous formation of two new carbon—carbon bonds, we are exploring their utility in organic synthesis. In particular we are studying their application to the synthesis of simple macrocyclic lactones and to the synthesis of Markovnikov alkenylboranes.

Experimental

General

The techniques described in Chapter 9 of ref. 1 were used extensively. All

glassware was dried at 150°C for at least 4 h, assembled hot, and allowed to cool under a purge of prepurified nitrogen. All reactions were carried out under a static pressure of nitrogen. Gases were delivered using a gas-tight syringe [26].

Materials

Borane/dimethylsulfide was obtained from Aldrich chemical company and used as received after standardization. Methyl vinyl ether was obtained from Linde Specialty Gases and used as received. t-Butyllithium was obtained from Alfa/Ventron and standardized prior to use by the method of Watson and Eastham [27]. The various alkylating agents were obtained from Aldrich Chemical Company and used as received. Triethyl- and triisobutyl-borane were obtained from Callery Chemical Co. and used without further purification. The other boranes were prepared by hydroboration with boranemethylsulfide [28]. All solvents were distilled from benzophenone ketyl under nitrogen. All products were isolated by preparative gas chromatography and were at least 98% pure by GC. The ketones were identified by comparison of their spectral properties with samples obtained from Chemical Samples Company or with the literature.

Analyses

^{1}H NMR were recorded on a Varian EM-360 spectrometer. All ^{1}H chemical shifts are relative to tetramethylsilane (δ 0 ppm). ^{11}B NMR spectra were recorded on a Varian XL-100-FT spectrometer (32.1 MHz). The spectra were recorded using ^{2}H internal lock and all chemical shifts are relative to $BF_3 : OEt_2$ (δ 0 ppm). ^{13}C NMR spectra were recorded on a Varian CFT-20 instrument using ^{2}H internal lock. All chemical shifts are relative to TMS (δ 0 ppm). Infrared spectra were recorded on a Pye Unicam SP 1000 spectrometer using liquid films.

VPC analyses were carried out on a Varian 1400 or Hewlett—Packard 5700 gas chromatograph equipped with a Hewlett—Packard 3380 integrating recorder. All analyses were carried out on 6′ × 1/4″ stainless steel columns filled with 10% loaded liquid phases on AW-DMCS 60/80 Chromosorb W. SE-30 and XE-60 were used as liquid phases for all analyses. Preparative gas chromatography was carried out on a Varian 920 instrument equipped with a 6′ × 1/2″ stainless steel column filled with 20% loaded packing on AW-DMCS treated 40—60 Chromosorb W. Low resolution mass spectra were recorded on a Hewlett—Packard 5980A mass spectrometer. High resolution data were obtained on an AEI MS-30 instrument.

Where appropriate, elemental compositions were determined by elemental analysis. All elemental analyses were performed by Galbraith Laboratories.

General procedure for the formation of I

A dry 100 ml round-bottom flask equipped with a septum-capped inlet, water condenser and magnetic stirring bar was flushed with nitrogen. To this flask was added 5 ml of THF. The flask was cooled to —80°C and 8.25 mmol of methyl vinyl ether was added as a gas [1]. To this solution was added 6.52 ml (7.50 mmol) of t-butyllithium. The mixture was allowed to warm in air until the bright yellow color disappeared. The reaction mixture was cooled to —80°C and 5 mmol of the appropriate borane added.

Iodination of I to give enol ethers

The preformed complex of I was treated with 1.90 g of iodine in 6 ml of THF at −80°C. The solution was stirred for 1 h at −80°C and the excess iodine destroyed by titration with n-butyllithium. The solution was allowed to warm to R.T., washed 3 times with 5 ml of 3 *N* sodium hydroxide under nitrogen, and oxidized with 2 ml of 30% hydrogen peroxide and 5 ml of 3 *N* sodium hydroxide. The enol ethers were not isolated as such. Their presence was inferred by GC/MS and their subsequent hydrolysis to the known ketones.

Hydrolysis of enol ethers

The solution obtained after oxidation was separated, and the organic layer treated with 10 ml of 10% hydrochloric acid for 5 min, neutralized with 3 *N* sodium hydroxide and the yield of ketone measured versus an appropriate internal standard by gas chromatography.

Formation of 1,1-dialkylethylenes (VI)

The preformed solution of I was allowed to warm to 0°C and 15 ml of 3 *N* sodium hydroxide was added. Finally, 1.27 g (5 mmol) of iodine was added in 6 ml of THF over a 20 min period. By the time the addition of iodine was complete, the iodine color disappeared. The aqueous layer was removed, the organic layer washed three times under nitrogen and oxidized with 7 ml of 3 *N* sodium hydroxide and 2 ml of 30% hydrogen peroxide. The organic layer was separated, dried ($MgSO_4$) and the solvent removed under vacuum. The products were isolated by preparative gas chromatography.

Formation of dialkylmethylcarbinols

To the preformed solution of I was added 6.25 ml of 2 *N* hydrochloric acid. The solution was stirred for 30 min then neutralized with 6.5 ml of 3 *N* sodium hydroxide. The borane was oxidized by the addition of 20 ml of ethanol followed by 2.8 ml of 30% hydrogen peroxide. To insure complete oxidation, the reaction mixtures was heated under reflux for 1 h. The reaction mixture was cooled, the organic layer dried ($MgSO_4$), the solvent removed under vacuum, and the alcohol isolated by preparative gas chromatography.

Alkylations of IX to give the tertiary alcohols VIII

To the preformed solution of I was added 7.5 mmol of the appropriate alkylating agent. The solution was stirred for the time and at the temperature indicated in Table 3, then washed three times under nitrogen with 3 *N* sodium hydroxide, and oxidized with 3 ml of 3 *N* sodium hydroxide, 10 ml of ethanol, and 2 ml of 30% hydrogen peroxide. To ensure complete oxidation the solution was heated under reflux for 1 h. The reaction mixture was cooled, the organic layer separated, dried ($MgSO_4$), and the solvent removed under vacuum. The alcohol was isolated by preparative gas chromatography.

1,1-Di-n-hexylethylene: IR (Film): 3080 ($C=CH_2$), 3000—2860, 1646, 1467, 1380, 893 cm^{-1}; PMR ($CDCl_3$): δ 0.7—1.7 (m, 22 H), 1.8—2.3 (M, 4 H), 4.66 (s, 2 H) ppm. (Found: C, 85.45; H, 14.44. $C_{14}H_{28}$ calcd.: C, 85.72; H, 14.27%).

1,1-Dicyclopentylethylene: IR (Film): 3090 ($C=CH_2$), 3000—2860, 1637, 1449, 1203, 886 cm^{-1}; PMR ($CDCl_3$): δ 1.0—2.0 (m, 16 H), 2.0—2.7 (m, 2 H),

4.76 (s, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ 25.11, 32.55, 45.95, 104.22, 157.69 ppm. (Found: C, 87.65; H, 12.22. $C_{12}H_{20}$ calcd.: C, 87.81; H, 12.18%).

Di-n-hexylmethylcarbinol: IR (Film): 3540—3150 (OH), 3040—2780, 1470, 1380, 1150, 1100, 1085, 925, 720 cm^{-1}; PMR ($CDCl_3$): δ 0.40—1.7 (m, 30 H) ppm; ^{13}C NMR; ($CDCl_3$): δ 14.07, 22.65, 23.90, 29.95, 31.88, 41.97 ppm (Found: C, 78.62; H, 14.29. $C_{14}H_{30}O$ calcd.: C, 78.43; H, 13.99%).

Diisobutylmethylcarbinol: B.p. 96—98°C/28 mmHg (lit. [30] 94—96°C/25 mmHg). IR (Film): 3700—3100 (OH), 3050—2750, 1470, 1370, 1160, 1080, 1030, 920, 860, 760 cm^{-1}; PMR ($CDCl_3$): δ 0.6—2.1 (m, 22 H) ppm; ^{13}C NMR ($CDCl_3$): δ 14.9, 23.4, 24.7, 27.50, 51.25, 74.0 ppm.

Di-sec-butylmethylcarbinol: IR (Film): 3750—3200 (OH), 3090—2800, 1460, 1380, 1160, 1110, 910, 860, 785 cm^{-1}; PMR ($CDCl_3$): δ 0.4—2.1 (m, 22 H) ppm. (Found: C, 75.73; H, 13.91. $C_{10}H_{22}O$ calcd.: C, 75.97; H, 13.92%).

Dicyclopentylmethylcarbinol: IR (Film): 3200—3650 (OH), 3080—2800, 1500, 1380, 1260, 1200—1000, 885, 740 cm^{-1}; PMR ($CDCl_3$): δ 1.0—2.5 (m, 22 H) ppm. (Found: C, 78.97; H, 12.05. $C_{12}H_{22}O$ calcd.: C, 79.13, H, 12.08%).

Dicyclohexylmethylcarbinol: IR (Film): 3650—3300 (OH), 3050—2790, 1450, 1380, 1220, 1200, 1060, 995—870, 740 cm^{-1}; PMR ($CDCl_3$): δ 0.7—2.3 (m, 26 H) ppm. (Found: C, 79.92; H, 12.35. $C_{14}H_{26}O$ calcd.: C, 80.01; H, 12.37%).

Di-n-hexylethylcarbinol: IR (Film): 3430 (OH), 3000—2860, 1460, 1380, 1145, 953 cm^{-1}; PMR ($CDCl_3$): δ 0.9 (m, 9 H), 1.32 (m, 23 H) ppm; ^{13}C NMR ($CDCl_3$): δ 7.84, 14.09, 22.68, 23.12, 23.46, 30.02, 31.67, 31.92, 38.87 ppm. (Found: C, 78.67; H, 14.03. $C_{15}H_{32}O$ calcd.: C, 78.96; H, 14.02%).

Diisobutylethylcarbinol: IR (Film); 3500 (OH), 3000—2880, 1470, 1370, 1165, 1010, 970, 860 cm^{-1}; PMR ($CDCl_3$): δ 0.93 (d, 12 H), 0.7—1.9 (m, 12 H) ppm; ^{13}C NMR ($CDCl_3$): δ 8.38, 23.84, 24.89, 32.33, 48.09 ppm. (Found: C, 76.73; H, 13.75. $C_{11}H_{24}O$ calcd.: C, 76.76%; H, 13.94%).

4-Isobutyl-2-methyl-4-nonanol: IR (Film): 3480 (OH), 3000—2900, 2870, 1467, 1364, 1155, 1010 cm^{-1}; PMR ($CDCl_3$): δ 0.9 (d, 15 H), 1.1—2.0 (m, 15 H) ppm. (Found: C, 78.60; H, 13.96. $C_{14}H_{30}O$ calcd.: C, 78.43; H, 13.96%).

4-Isobutyl-2,7-dimethyl-4-octanol: IR (Film): 3450 (OH), 3000—2860, 1465, 1380, 1362, 1168, 1150, 1005 cm^{-1}; PMR ($CDCl_3$) δ 0.7—2.1 (m, 30 H) ppm. (Found: C, 78.56; H, 14.19; $C_{14}H_{30}$ calcd.: C, 78.52; H, 14.01%).

5-Isobutyl-5-hydroxy-7-methyl-1-octene: IR (Film): 3490 (OH), 3080 ($CH=CH_2$), 3000—2870, 1641, 1468, 1383, 1366, 1350, 992, 911 cm^{-1}; PMR ($CDCl_3$) δ 0.90 (d, 12 H), 1.1—2.3 (m, 10 H), 4.6—6.0 (m, 3 H) ppm. (Found: 78.81; H, 13.01. $C_{13}H_{26}O$ calcd.: C, 78.80; H, 13.12%).

2,6-Dimethyl-4-phenethyl-4-heptanol: IR (Film): 3560, 3475 (OH), 3070, 3060, 3025, 3000—2860, 1600, 1495, 1460, 1450, 1385, 1363, 745, 700 cm^{-1}; PMR ($CDCl_3$) δ 0.96 (d, 12 H), 1.3—2.3 (m, 9 H), 2.56 (m, 2 H), 7.20 (s, 5 H) ppm. (Found: C, 83.41; H, 11.40. $C_{17}H_{28}O$ calcd.: C, 83.62; H, 11.46%).

3,5-Dimethyl-4-ethyl-4-heptanol: IR (Film): 3495 (OH), 3000—2890, 1460, 1380, 1260, 1158, 1110, 950, 860, 786 cm^{-1}; PMR ($CDCl_3$) δ 0.7—2.0 (m, 24 H) ppm. (Found: C, 76.50; H, 13.87. $C_{11}H_{24}O$ calcd.: C, 76.76; H, 13.94%).

Dicyclopentylethylcarbinol: IR (Film): 3490 (OH), 2990—2860, 1450, 1380, 1303, 1268, 1170, 1014, 927, 888 cm^{-1}; PMR ($CDCl_3$): δ 0.93 (t, 3 H), 1.20 (s, 1 H), 1.58 (m, 20 H) ppm. (Found: C, 79.35; H, 12.15. $C_{13}H_{24}O$ calcd.: C, 79.61; H, 12.23%).

Dicyclohexylethylcarbinol: IR (Film); 3490, 2980—2900, 2855, 1448, 1382, 1315, 1268, 1238, 1189, 1128, 1072, 1035, 973, 957, 894 cm^{-1}. PMR ($CDCl_3$): δ 0.7—2.2 (m, 31 H) ppm.

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ORGANOBORANES IN ORGANIC SYNTHESIS

IX *. CARBONYLATION PRODUCTS OF ORGANOBORANES DERIVED FROM MYRCENE

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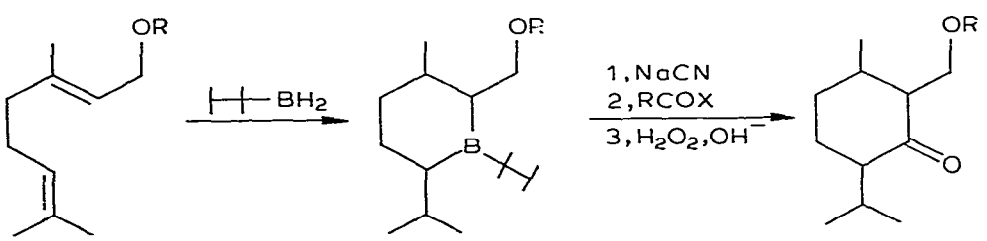
Summary

Myrcene and thexylborane react in the ratio 2/3 to give a mixture of two boranes, only one of which is carbonylated with cyanide/trifluoroacetic anhydride, followed by oxidation, to give 3-hydroxymethyl-6-isopropyl-2-methylcyclohexanone (A). The positions of hydroboration are established by synthesis of the hydroboration/oxidation products. The cyanidation of the organoboranes derived from myrcene and diborane leads to a 2/3 mixture of A and 5-(2′-hydroxyethyl)-2-isopropylcyclohexanone, the structures of which are established by independent synthesis. The hydroboration of myrcene is shown to be relatively non-stereospecific.

Introduction and discussion

In Part IV of this series [1] we investigated the utility of the readily available diene geraniol as a precursor of cyclic ketones via hydroboration—cyanidation [2]. We now report the extension of this work to the readily available triene,



myrcene (I).

* Dedicated to Professor H.C. Brown on the occasion of his 66th birthday. (For Part VIII, see ref. 7).