Journal of Organometallic Chemistry, 434 (1992) 133–141
Elsevier Sequoia S.A., Lausanne
JOM 22656

Carbonylation of >B–H-boranes; evidence for a Fischer–Tropsch type reaction

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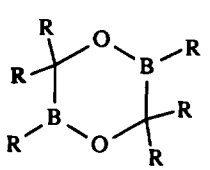
(Received November 21, 1991)

Abstract

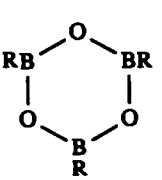
Bis(9*H*-9-borabicyclo[3.3.1]nonane) is readily carbonylated under about 50 bar pressure of carbon monoxide at 100°C. Bis(1,5-cyclooctanediyl)-2,5-dibora-1,4-dioxane (**1a**) is formed quantitatively. Reaction of **1a** at room temperature with acetic or propionic acid affords the corresponding 9,10-diacyloxybicyclo[3.3.2]decanes **2a** and **2b**. Thermolysis of **1a** gives the tris-(5-cyclononenyl-boroxine **4** as the main product. The expected tris(bicyclo[3.3.1]nonanylboroxine) **3** in formed only in a side reaction The carbonylation of tetraethyldiborane(6) is easier, requiring about 10–20 bar of carbon monoxide pressure at room temperature. The product consists of a mixture of 2,5-dibora-1,4-dioxanes with partially homologated alkyl substituents. The homologation proceeds in a manner analogous to that of the Fischer-Tropsch reaction.

Introduction

The direct carbonylation of trialkylboranes was first reported in 1960 [1] and explored in more detail in 1962–1963 [2,3]. Under very high pressure (500–1000 atm) 2,5-diboradioxanes of type I are formed at 50–70°C. These can be converted into the trialkylcarbinol boronic and anhydrides of type II at 150°C.



I



II

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Use of a higher initial temperature and atmospheric carbon monoxide pressure simplified the procedure and allowed it to be applied extensively to the synthesis of large varieties of alcohols, aldehydes, and ketones starting from simple olefins [5]. Mixtures of >B–H-boranes also react readily with carbon monoxide to form carbonylated products. Several years ago [6] we showed that bis(9*H*-9-borabicyclo [3.3.1]nonane) (9*H*-9-BBN)$_2$ was inert to carbon monoxide gas under atmospheric pressure, even at elevated temperature (130–150°C), but reacted readily with a number of metal carbonyls in a Fischer–Tropsch type reaction a homologous series of 9-alkyl-9-borabicyclo[3.3.1]nonanes was formed. In extension of that work we now report our results on the carbonylation of >B–H-boranes, including that of (9*H*-9-BBN)$_2$.

Results and discussion

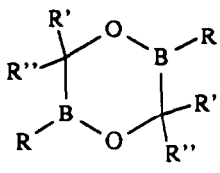
The rate of carbonylation of (9*H*-9-BBN)$_2$ is low below 100°C, but at 100°C its suspension in an inert solvent such as hexane and under 70 bar CO pressure absorbs one molar equivalent of the gas. The colourless solution yields a quantitative amount of a single microcrystalline solid (m.p. 99–101°C, after purification by sublimation) which shows a molecular ion at $m/z = 300$. The ^{1}H, ^{11}B, and ^{13}C NMR spectra (see Table 1) are in agreement with the 2,3:5,6-bis(1.5-cyclooctanediyl)-2,5-diboradioxane structure **1a**. This compound proved to be rather inert towards non acidic protic solvents. It could be quantitatively recrystallized from refluxing ethyl alcohol, and remained unaffected in boiling water or a primary amine.

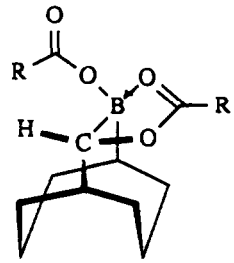
However **1a** reacted, very slowly, with glacial acetic or propionic acid at room temperature. After distillation the diacyloxy derivatives **2a** and **2b**, respectively, were obtained in about 80% yield. The structures of these compounds were established from their NMR (see Table 1) and other spectroscopic data. The ^{11}B

Table 1

^{1}H-, ^{11}B- and ^{13}C-NMR data for compounds **1a**, **2a** and **2b**

Compound	δ^{13}C (50.4 MHz)						δ^{11}B 64.2 MHz $h_{1/2}$ (Hz)	δ^1H (200 MHz)		
	C^1	C^2 C^2	C^3 $C^{3'}$	C^4 $C^{4'}$	C^5	C^6		H^1	H^2–H^5	H^6
1a	73.0	30.0 28.0	22.2 22.1	27.8 27.6	35.9	26.0	50.3 (300)	2.48(2H)	1.0–1.8(26H)	3.60(2H)
2a	90.8	29.3 28.7	23.7 20.0	26.3 26.2	33.7	23.9	11.1 (200)	2.42(1H)	0.9–1.8(13H)	4.42(1H)
	C=O 188.7; 176.7 CH_3 8.9; 8.0							$CH_3CO_2^-$	2.30(3H); 1.95(3H)	
2b	90.7	29.3 28.7	23.7 20.0	26.3 26.2	33.7	23.8	11.6 (200)	2.42(1H)	0.8–1.9(13H)	4.42(1H)
	C=O 188.7; 176.8 CH_2 29.5, 23.4 CH_3 9.0; 8.0							$CH_3CH_2CO_2^-$	2.64(2H), 2.18(2H) 1.23(3H); 0.97(3H)	





1a R = R' = 1,5-C_8H_{14}, R'' = H

1b R = R' = Et, R'' = H

1c R = Et, R' = Pr, R'' = H

2a R = Me

2b R = Et

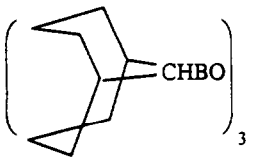
NMR chemical shifts for **2a** and **2b** at about $\delta = 11$ suggest intramolecular complexation of the oxygen atom of the ester group [7].

Treatment of **1a** in refluxing propionic acid resulted in deborylation and formation of a mixture of hydrocarbons, including cyclooctane, methylcyclooctane and all four possible isomers of methylcyclooctene. The significant amounts (*ca.* 20%) of cyclooctane formed show that the carbonylation of **1a** is rather easily reversed. This process is the predominant reaction in the alkaline hydroperoxide oxidation of **1a**, in which only 1,5-cyclooctanediol and cyclooctenoles are formed. The expected hydroxymethylcyclooctanol is only found in a significant quantity when **1a** is subjected to trimethylamine-N-oxide oxidation in an anhydrous solvent [8].

The 2,5-diboradioxane **1a**, like other derivatives of I, can be expected to be thermally unstable and to rearrange on further heating to form boroxines of the type II. Indeed when **1a** is heated for 1–2 h at 200°C a viscous liquid product is formed which shows only one signal at $\delta = 33.0$ in its ^{11}B NMR spectrum and the mass spectrum shows a molecular ion at $m/z = 450$. Both of these results are in agreement with the expected tris(bicyclo[3.3.1]nonanyl)boroxine **3**. However, both the ^1H and ^{13}C NMR spectra showed olefinic H and C atoms. Alkaline hydrogen peroxide oxidation of the thermolysis product gave cyclonon-5-enol, which on further oxidation by chromic acid was converted into cyclonon-5-enone **4** as the major (ca. 64%) product. An isomeric ketone was also shown to be present in 20% yield by GLC-MS analysis. This ketone is unreactive toward catalytic hydrogenation and is probably a bicyclic ketone. The expected bicyclo[3.3.1]nonanone **5** is typically formed in only about 10% yield. The major thermolysis product is thus the trialkylboroxine **6**, rather than **3**.

The driving force for the rearrangement of the bicyclo[3.3.2]decandiyl carbon skeleton of **1a** can be assumed to come from the lower ring strain in the cyclononenyl ring of **6** compared with that in the bicyclo[3.3.1]nonanyl structure of **3**.

Alkyldiboranes(6) with monofunctional residues are equilibrium mixtures of the dimers of tri-, di-, and mono-alkylboranes(3). Reaction of such mixtures with



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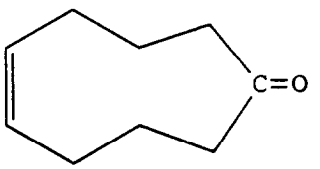

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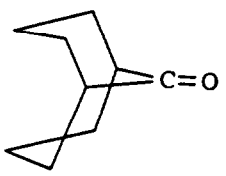

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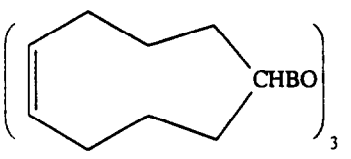
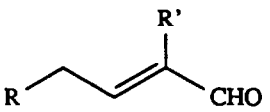


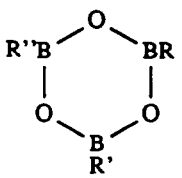
6

carbon monoxide should result in the formation of various carbonylation products [5]. The reaction of a toluene solution of tetraethyldiborane(6) proceeds rapidly and exothermically at room temperature when 10–20 bar of carbon monoxide pressure is applied, and also proceeds slowly at about 80°C under atmospheric pressure. A mixture is formed consisting of tetraethyldiboroxane (typically 10–20%) and of derivatives of **1** as deduced from the ^{11}B NMR spectra ($\delta^{11}B \approx 49$) [9] and GLC-MS analysis. The two main products (yields typically *ca.* 22.0 and 25.0%) both give molecular ions with $m/z = 196$, consistent with being the *cis* and *trans* isomers of the tetraethyl derivative **1b**. The next two most abundant products (typically about 5–7% each) both have molecular ions with $m/z = 210$ (196 + CH_2), consistent with being the *cis* and *trans* triethylpropyl derivatives **1c**. The GLC-MS spectrum also indicates the presence of small amounts of higher homologues of **1c**, but their molecular weights are uncertain because of the absence of a molecular ion peak. The formation of **1c** and the higher homologues imply the insertion and reduction of more than one carbon monoxide molecule into the B–C bond. This was confirmed by analyzing the products of the alkaline hydrogen peroxide oxidation of the carbonylation mixture; in addition to ethyl-, propyl-, and 3-pentyl alcohols (2, 12, and 10%, respectively) *ca.* 2% of butanol was also detected. The main products identified by GLC-MS (involving comparison with authentic materials) are, however, the α,β-unsaturated aldehydes **7a–d**, the aldol products formed in the alkaline reaction medium from self- and cross-condensations of propanal, 1-butanal, and 1-pentanal.

When the carbonylation mixture was kept at 200°C for 8 h, complete conversion into the boroxine derivatives **8** ($\delta^{11}B = 33.0$) was achieved, as expected. The GLC-MS analysis revealed at least nine major compounds. Owing to absence of a molecular ion peak, molecular masses could not be determined, but the presence



7a R = R' = Me
7b R = Et, R' = Me
7c R = Pr, R' = Me
7d R = R' = Et
7e R = Pr, R' = Me



8
R = R' = R''
R ≠ R' = R''
R = R' ≠ R''
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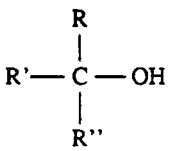
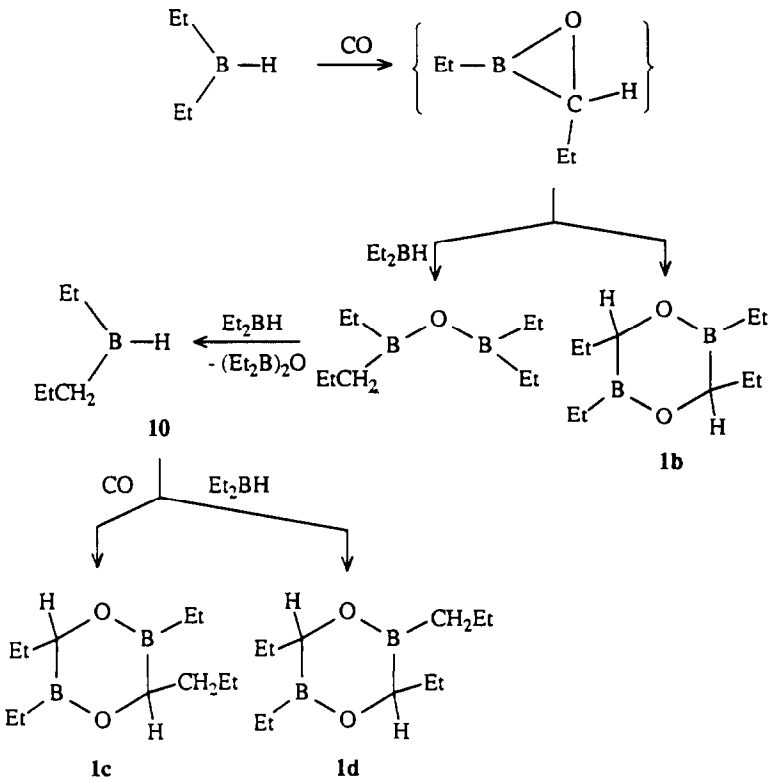


9a R = R' = H, R'' = Me
9b R = R' = H, R'' = Et
9c R = R' = H, R'' = Pr
9d R = H, R' = R'' = Et
9e R = R' = R'' = Et
9f R = H, R' = Et, R'' = Pr
9g R = Et, R' = R'' = Pr
9h R = R' = Et, R'' = Bu
9i R = Et, R' = R'' = Pr
9j R = Et, R' = Pr, R'' = Bu
9k R = R' = Et, R'' = Pent

of boron-free peaks at $m/z = 70$, 84, 98, and 112 in some of the spectra, suggests the presence of homologous alkyl substituents. More information on the nature of these substituents is obtained by studying the products **9a–k** of the alkaline hydrogen peroxide oxidation. In the GLC-MS analysis of the alcohols formed the primary C_2–C_4 alcohols (**9a–c**) together with a number of homologous secondary and tertiary alcohols prevailed, giving MS peaks ranging from m/z 102 to 158. As expected, the most abundant are 3-pentanol (**9d**) and 3-ethyl-3-pentanol (**9e**) (18 and 25%, respectively). Other alcohols found are, in decreasing order of concentration, 3-hexanol (**9f**), 3-ethyl-3-hexanol (**9g**), 3-ethyl-3-heptanol (**9h**), 4-ethyl-4-heptanol (**9i**), 4-ethyl-4-octanol (**9j**), and 3-ethyl-3-octanol (**9k**).

Although some of these alcohols are formed only in small amounts (1–10%) their presence clearly demonstrates that homologation is involved in this reaction. It is a process analogous to the Fischer–Tropsch reaction [10]. In the >B–H-borane-induced homologation reaction that we studied previously [6] a metal centre was believed to be involved. A metal atom also participates in the recently described Fischer–Tropsch type homologation of trialkylboranes [11]. The reaction now observed shows that in principle no metal centre is required for repeated carbon monoxide insertion-reduction steps.

Two factors limit the efficiency of this reaction. These are the occurrence of the competitively rapid reaction to form **1b** and the need to absorb the oxygen atom of



Scheme 1. Proposed steps leading to **1b** and its homologues **1c** and **1d**

the carbon monoxide molecule released in this reaction. The oxygen becomes incorporated into the tetraethyldiboroxide found as a side product. This process is comparable with the formation of $(9\text{-BBN})_2O$ in the reaction of $(9H\text{-}9\text{-BBN})_2$ with metal carbonyls [1]. The possible steps involved are shown in Scheme 1.

The proposed intermediate ethylhydropropylborane **10** undergoes further carbonylation leading to one of two derivatives of **1c**. In one an ethyl, and in the other a propyl, group undergoes the migration. Depending on whether the propyl group is located on carbon or boron, oxidation should yield either propanol or propanal. The isolation of both can be taken as an indication that the carbon monoxide insertion and reduction steps (Fischer–Tropsch type reaction) precede the formation of **1c**, as shown in Scheme 1. Repetition of the above sequence will lead to the formation of the next higher homologue. Alkyl exchange reactions of the dialkylhydroboranes should result in the formation of homologous trialkylboranes with elongated alkyl chains. Carbonylation of these followed by thermal conversion and oxidation will result in the homologous tertiary alcohols observed.

Experimental

Instruments: Büchi melting point apparatus, sealed tubes. IR: Perkin Elmer 297. MS: MAT CH 5. ^1H, ^{11}B, ^{13}C NMR: Bruker AC 200 with Me_4Si as internal

and $Et_2O \cdot BF_3$ as external standards. GLC: Siemens Sichromat 1, OV-1 capillary column (25 m) programmed at 6°C/min, 80–290°C, carrier gas H_2/0.5 bar. All operations were carried out under oxygen-free dry argon. Solvents were freshly dried and distilled.

*2,3:5,6-Bis(1,5-cyclooctanediyl)-2,5-dibora-1,4-dioxane (**1a**).* A suspension of 9.0 g (36.9 mmol) of (9*H*-9-BBN)$_2$ [12] in 75 ml hexane was placed in a 200 ml stainless steel autoclave, pressurized to 70 bar with CO gas, and kept for 4 h at 100°C (pressure decrease: ≈ 15 bar). The solution was evaporated to dryness. The colourless solid residue was sublimed at ≈ 100°C/10^{-1} torr, 10.8 g (98% yield), m.p. 99–101°C. MS: $m/z = 300$ (M^+, B_2, 10), 272 (8), 177 (25), 150 (35), 122 (55), 109 (55), 81 (100). For NMR data see Table 1. Found: C, 71.88; H, 10.22; B, 7.52. $C_{18}H_{30}B_2O_2$ (300.1). calcd.: C, 72.05; H, 10.08; B, 7.21%.

*9,10-Diacetoxy-9-borabicyclo[3.3.2]decane (**2a**).* A mixture of 2.05 g (6.8 mmol) of **1a** and 1.65 g (27.5 mmol) of glacial acetic acid in 10 ml hexane was stirred for 20 h at room temperature. The slightly turbid solution was filtered, the solvent and volatiles were removed in vacuum, and the residue was distilled, b.p. ≈ 85°C/10^{-3} torr, 3.1 g (92.0% yield) of a colourless liquid (**2a**). IR (film): νC=O = 1690, 1575 cm^{-1}. MS: $m/z = 252$ (M^+, 1), 224 (11), 209 (5), 192 (8), 87 (20), 43 (100). Found: C, 61.88; H, 8.51; B, 4.35. $C_{13}H_{21}BO_4$ (252.1). calcd.: C, 61.94; H, 8.40; B, 4.29%.

*9,10-Dipropionyloxy-9-borabicyclo[3.3.2]decane (**2b**).* As above, a mixture of 2.05 g (6.8 mmol) of **1a** and 2.02 g (27.3 mmol) of propionic acid in 10 ml hexane was stirred at room temperature for 20 h. The product, b.p. 96–100°C/10^{-3} torr, 3.2 g (86.4% yield), colourless liquid. IR (film): νC=O = 1695, 1580 cm^{-1}. MS: $m/z = 280$ (M^+, 1), 252 (10), 223 (4), 57 (100). Found: C, 64.50; H, 8.81; B, 3.95. $C_{15}H_{25}BO_3$ (280.2). calcd.: C, 64.31; H, 8.99; B, 3.86%.

*Protolysis of **1a** with propionic acid.* A solution of 9.4 g (31.3 mmol) of **1a** in 50 ml of propionic acid was kept for 100 h at 140°C. The volatile components were distilled at 110°C, 1 torr. The distillate was made slightly basic by adding 6 N NaOH and extracted with ether. The extract gave on evaporation of the ether 6.7 g of a colourless liquid. GLC-MS: cyclooctane (18%), Σ methylcyclooctenes (38.8%), methylcyclooctane (4.0%), and cyclononene (30%).

*Alkaline hydrogenperoxide oxidation of **1a**.* A solution of 2.0 g **1a** in 50 ml THF was added to 50 ml of 6 *N* NaOH and the mixture was cooled to 0°C and 10 ml of 30% hydrogen peroxide solution was added dropwise. The mixture was heated for 1 h under reflux then saturated with Na_2CO_3, and the organic layer was separated, and thoroughly washed with water and dried. The residue after evaporation of the solvent was acetylated with acetic anhydride/pyridine. Analysis by GLC-MS showed: acetoxycyclooctane (10%), acetoxycyclooctene (4%), 1,5-diacetoxycyclooctane (70%).

*Trimethylamine-N-oxide oxidation of **1a**.* To a refluxing toluene solution of 2.0 g (6.8 mmol) of **1a** was added, slowly during 16 h, 2.0 g (27.0 mmol) of dry trimethylamine-N-oxide [2]. On completion of trimethylamine evolution, 50 ml of H_2O were added and the organic layer was separated, and the solvent evaporated and the residue acetylated with acetic anhydride/pyridine. Analysis by GLC-MS showed: acetoxymethylcyclooctane (20%), 5-(acetoxymethyl)acetoxycyclooctane (2 isomers Σ 72%).

*Thermolysis of **1a**, formation of the boroxines (**3** + **6**).* 5.2 g of **1a** was kept at 200°C for 2 h. The viscous liquid did not solidify on cooling. MS: $m/z = 450$ (M^+,

B3, 70), 422 (30), 408 (30), 122 (35), 81 (100). ^{1}H NMR ($CDCl_3$): δ = 5.48 (m, 2H), 2.33 (m, 2H), 2.00 (m, 2H), 1.2–1.8 (m, ≈ 10H). ^{11}B NMR ($CDCl_3$): δ = 33.0 ($h_{1/2}$ = 900 Hz). ^{13}C NMR ($CDCl_3$, main signals): δ = 129.8 (d, 2C), 26.0 (t, 2C), 25.9 (t, 2C), 24.6 (t, 2C), 21.5 (br, d, 1C).

Oxidation of (3 + 6). A solution of 2.2 g of the above thermolysis product in 20 ml of THF was added to 20 ml 6 *N* NaOH solution and the mixture was cooled to 0°C and treated with 5 ml of 30% H_2O_2 solution. The mixture was heated for 2 h under reflux then saturated with K_2CO_3 and the organic phase was separated and slowly added to a stirred solution of 2.0 g of $K_2Cr_2O_7$ in 20 ml of 6N H_2SO_4 at room temperature. From the organic phase 1.6 g of a colourless liquid was recovered. GLC-MS: cyclooctane (8%), mol.wt. 138 (unchanged by catalytic hydrogenation) (20%), 5-cyclononenone (after catalytic hydrogenation, cyclononanone) (64%), bicyclo[3.3.1]nonanone (7%).

Carbonylation of tetraethyldiborane (6); formation of mixtures of 1b and 1c, etc. (typical procedure). A solution of 8.0 g of tetraethyldiborane(6) (18.0% hydride, 144.0 mmol >B–H-borane) in 10 ml of toluene was placed in a 100 ml stainless steel autoclave and initially pressurized at room temperature with 20 bar of carbon monoxide. After 1/2 h of magnetic stirring the pressure had dropped to about 5 bar, and the temperature had risen to *ca.* 35°C. Again 20 bar of carbon monoxide pressure was applied and the mixture stirred for 1 h. The final pressure was 5 bar. The remaining gas was vented and the colourless solution removed. ^{11}B NMR (toluene): δ = 59.1, 49.2, 37.4, 33.0 (≈ 1 : 6 : 1 : 1 : 1). GLC-MS showed the following major products [M^+ (m/z), % area]: tetraethyldiboroxide (154, 21.6), **1b** (196, 24.5), **1b'** (196, 22.2), **1c** (210, 6.2), **1c'** (210, 5.2).

Trialkylboroxine mixture (8) from carbonylation of tetraetyldiborane(6). An aliquot (*ca.* 10 ml) of the carbonylation product solution (see above) was heated in the autoclave at 200°C for 8 h. The colourless solution showed in the ^{11}B NMR spectrum (toluene) a signal at δ = 33.0. GLC-MS revealed eight major components (area%L 38.2, 4.7, 20.7, 4.2, 12.8, 2.9, 2.7, 1.1). Except for the first peak (triethylboroxine), none of the others showed molecular ions, not even under CI conditions.

Alkanal and alkenal mixtures (9 + 7) from the alkaline hydrogen peroxide oxidation of the products of the carbonylation of tetraethyldiborane(6). To a solution of 5 ml of the carbonylation product mixture in 20 ml of tetrahydrofuran at 0°C was added 5 ml of 6 *N* NaOH, and this was followed by dropwise addition of 5 ml of 30% hydrogen peroxide. After 1 h stirring at room temperature and 1 h under reflux, the organic layer was separated and analyzed by GLC-MS. This revealed the following alcohols (area%): ethanol (**9a**, 1.9), propanol (**9b**, 12.5), butanol (**9c**, 1.5), 3-pentanol (**9d**, 10.4), 3-pentanone (3.6) and the following α,β-unsaturated aldehydes: 2-methyl-2-pentenal (**7a**, 28.8), 2-methyl-2-hexenal (**7b**, 4.3), 2-ethyl-2-hexenal (**7d**, 14.5), 2-ethyl-2-heptenal (**7c**, 1.1), 2-methyl-2-heptenal (**7c**, 1.0).

Alkanols (9) from alkaline hydrogenperoxide oxidation of mixtures of trialkylboroxines 8. A solution of 5 ml of the trialkylboroxine mixture **8** in 20 ml of tetrahydrofuran was treated with alkaline hydrogenperoxide as above. The organic layer was analyzed by GLC-MS. This showed the following alcohols (area%): ethanol (**9a**, 10.2), propanol (**9b**, 18.1), butanol (**9c**, 2.7), 3-pentanol (**9d**, 18.3), 3-hexanol (**9f**, 2.4), 3-ethyl-3-pentanol (**9e**, 24.5), 3-ethyl-3-hexanol (**9g**, 10.3), 4-ethyl-4-heptanol (**9i**, 1.4), 3-ethyl-3-heptanol (**9h**, 0.8), 4-ethyl-4-octanol (**9j**, 0.5), 3-ethyl-3-octanol (**9k**, 0.4).

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