1,5-Diborabicyclo[3.3.3]undecane; thermolysis of the product from hydroboration of triallylborane with triethylamine–borane

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Attempts to reproduce the reported preparation of 1,5-diborabicyclo[3.3.3]undecane 1 through hydroboration of triallylborane with triethylamine–borane, followed by thermolysis, have led to 1,5-dipropyl-1,5-diborocane 2 and other products, but the presence of 1 could not be detected by GC–MS. Treatment of triallylborane with monobromoborane, methanolysis and subsequent thermolysis gave 1,5-dimethoxy-1,5-diborocane 3 which could be converted to 2 by treatment with propylmagnesium bromide.

We have long been interested in the study of interactions between bridgehead atoms in bicyclic medium-ring compounds ('intrabridgehead chemistry'), especially with respect to the experimental investigation of unusual types of σ-bonding and antibonding.[1] Most of our work has been concerned with electron-rich bonding, *e.g.* in diamines, but it would clearly be of value to study various types of electron-deficient bonds in this unusually controlled environment. McMurry has made detailed studies of μ-hydrido bridging in bridgehead carbocations with inside-CH groups at the other bridgehead,[2] while we have reported the observation of a one-electron bonded radical cation from bicyclo[3.3.3]undecane.[3] Boron is clearly an element of interest in this regard and the compound 1,5-diborabicyclo[3.3.3]undecane **1**, whose preparation was reported in 1965 by Greenwood, Morris and Wright,[4] is an obvious target for study. We might expect that the formation of one- and two-electron bonds by reduction to a radical anion and dianion respectively would be accompanied by strain relief as the medium-ring bicyclic structure was converted into a [3.3.3]propellane. We have failed on several occasions to reproduce the preparation of **1** in spite of helpful advice from Professor Greenwood and Dr Wright, and we now report the result of a GC–MS examination of this preparation which suggests that the major product is 1,5-dipropyl-1,5-diborocane **2**.

Results and discussion

The reported preparation of **1** consists of the hydroboration of triallylborane[5] with triethylamine–borane to produce a polymeric material, and subsequent thermolysis of this polymer. The initial formation of a polymer is hardly surprising, since direct formation of **1** would involve the simultaneous creation of three eight-membered rings. Our experience is that cases of creation of medium-ring bicyclic compounds by ring closure reactions are rather rare and usually have special explanations. Presumably the formation of **1** during thermolysis could be ascribed to its volatility, with its removal by distillation displacing a highly-unfavourable equilibrium established through multiple reversible hydroboration reactions.

Triallylborane was prepared from allylaluminium bromide and boron trifluoride.[5] Hydroboration of triallylborane with borane–triethylamine complex in refluxing petroleum (bp 100–120 °C) gave an extremely pyrophoric solid polymer. Thermolyses of the polymer were carried out under various conditions as shown in Table 1 and a volatile fraction was collected. Very little volatile product was formed below 220 °C. The volatile fraction was purified by distillation under vacuum and examined by NMR. In the ^{1}H NMR spectrum of the main fraction there was a complex multiplet at δ 0.9–1.0, and several sets of multiplets in the range δ 1.2–1.7, the relative integration of these two areas being 5 : 4. The ^{13}C NMR spectrum displayed several lines in the range of δ 10–30. A DEPT spectrum showed several methyl carbon signals in the range of δ 15–20 ppm. However in the ^{11}B NMR spectrum, the pyrolysis product showed just one major peak at δ 84, suggesting that all boron atoms were connected to three alkyl groups.[6]

The thermolysis product was oxidised by alkaline hydrogen peroxide under normal conditions[7] and the alcohol products were extracted and converted to benzoate esters. NMR analysis showed the presence of propyl benzoate and propane-1,3-diyl dibenzoate, but propan-2-yl benzoate and propane-1,2-diyl dibenzoate were absent.

The thermolysis products were examined by GC–MS; optimum conditions are given in the Experimental section. All thermolysis fractions gave several peaks on GLC, but results for a given fraction were repeatable, and products from different thermolysis conditions only differed in the relative amount of the major peaks. The mass spectrum of each peak was recorded, but none gave a major ion at *m/z* 148, corresponding to **1**. Under certain thermolysis conditions, *e.g.* heating at 250–260 °C under 22 Torr, a compound with a retention time of 9.7 min, *m/z* 192 is the dominant product in the thermolysis fraction (see Table 1). The GC–MS analysis showed that this compound, presumed to be **2** (see below), contained two boron

Table 1 Thermolysis of the polymer from hydroboration of triallylborane with triethylamine–borane

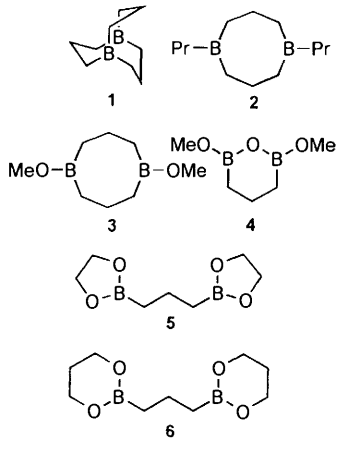
Run	Method of thermolysis	Bp on redistillation	Proportion of **2** in product (%)[a]
1	Oil bath, (220 °C/0.1 Torr)	50–60 °C/0.1 Torr	20
2	Oil bath (230–240 °C/0.1 Torr)	80–100 °C/0.1 Torr	20
3	Oil bath (250–260 °C/22 Torr)	100–120 °C/22 Torr	40
4	Sand bath (270 °C)	100–120 °C/22 Torr	30
5	Free flame	80–100 °C/22 Torr	20

[a] Area of the peak with retention time 9.7 min, *m/z* 192 as a percentage of the total area of peaks in GC trace.

atoms according to the boron isotopic pattern. The mass fragmentation analysis fits structure **2** (1,5-dipropyl-1,5-diborocane) reasonably well, with strong fragment ions at 149 (M–Pr, 40%) and 107 (100%, further loss of propene). Unfortunately, we were unable to obtain a HRMS, and the thermolysis product (which is highly pyrophoric) was clearly too complex for an elemental analysis to be useful.

We carried out a number of other reactions of triallylborane for comparison with products from thermolysis of the hydroboration product. Treatment of triallylborane with the commercially available monobromoborane–dimethyl sulfide complex was carried out by slow, simultaneous addition of equimolar dichloromethane solutions of the reactants, using a syringe pump, followed by methanolysis with two equivalents of sodium methoxide in methanol and removal of solvents under vacuum, leaving a sticky syrup-like polymer residue. Later it was found that the same product was obtained if quenched with methanol alone. Subsequent thermolysis of this polymer gave one major volatile fraction, from which 1,5-dimethoxy-1,5-diborocane **3** and 1,3-dimethoxy-1,2,6-oxadiborinane **4** could be isolated by fractional distillation. The ^{1}H NMR spectrum of **3** indicated the presence of two methoxy groups at δ 3.69, four methylene protons at δ 1.79 and eight methylene protons at δ 0.94. In the ^{13}C NMR spectrum, the methoxy carbon gave a peak at δ 53.14, a broad peak at δ 22 was assigned to the four methylene carbons adjacent to boron and the peak at δ 18.6 was assigned for the two central methylene carbons. In the ^{11}B NMR spectrum, **3** gave a peak at δ 53.8. The mass spectrum of **3** also agreed with the assigned structure. Compound **3** was oxidised by alkaline hydrogen peroxide and the product esterified with benzoyl chloride to give exclusively propane-1,3-diyl dibenzoate. The ^{1}H NMR spectrum of **4** indicated the presence of two methoxy groups at δ 3.57, two methylene protons at δ 1.48 and four methylene protons at δ 0.79. In ^{13}C NMR, the methoxy carbon appeared at δ 50.9, the methene carbon at δ 18.4 and the two methylene carbons next to boron appeared as a broad signal at δ 12. In the ^{11}B NMR spectrum, there was only one peak at δ 31.4.

The $B(CH_2CH{=}CH_2)_3/BBrH_2$ reaction was repeated, but with subsequent treatment with ethane-1,2-diol or propane-1,2-diol. When no further gas was released, volatiles were removed to give a sticky polymer in each case. Thermolyses of the polymers gave mainly products **5** and **6** with single



1 2 3 4 5 6

$BCH_2CH_2CH_2B$ units. Reaction of 1,5-dimethoxy-1,5-diborocane **3** with two equivalents of propylmagnesium bromide followed by quenching with a diethyl ether solution of hydrogen chloride gave a volatile product. GC–MS examinations showed that this product had an identical mass spectrum to that of the major peak from the triallylborane hydroboration/thermolysis, supporting the assignment of this as 1,5-dipropyl-1,5-diborocane **2**.

We have reluctantly concluded that 1,5-diborabicyclo-[3.3.3]undecane **1** is not formed in appreciable amounts in the thermolysis of the triallylborane hydroboration polymer, and that the most abundant product from that thermolysis is probably 1,5-dipropyl-1,5-diborocane **2**. Unfortunately, there are few, if any, plausible alternative routes to **1**. Based on our experience with medium-ring bicyclic nitrogen and phosphorus chemistry, one may speculate that the 1,5-diboratricyclo-[3.3.3.0]undecanediyl dianion, with an intrabridgehead B–B bond, might be reasonably stable, but synthetic routes to this species are still very speculative.

Experimental

All NMR spectra were obtained on JEOL JNM-GX270 or JEOL JNM-GX400 spectrometers. Chemical shifts (δ) are reported in ppm relative to an internal tetramethylsilane reference for ^{1}H and ^{13}C spectra, and to BF_3–Et_2O for ^{11}B spectra unless otherwise noted. *J* Values are given in Hz. Mass spectra were recorded on a Fisons VG AutoSpec Mass Spectrometer. GC–MS analyses were performed on a Fisons Instruments MD800. The following conditions were used for GC:SGE BPX5 column, 25 m × 0.32 mm, 0.25 μm film thickness. Helium was used as carrier gas with flow pressure 8 psi.† Column temperature was programmed: 40 °C × 3 min, 15 °C min^{-1}, 220 °C × 5 min. All reactions, except those carried out in aqueous media, were performed under an atmosphere of nitrogen using flame-dried glassware. All transfers and additions were performed with flame-dried syringes and needles. All solvents were freshly distilled over drying agents before use. Reagents were obtained from commercial suppliers (Aldrich and Lancaster) and used without purification.

Triallylborane was prepared from allylaluminium bromide and boron trifluoride.[5] The product was obtained as colourless liquid, bp 42 °C/15 Torr (lit.,[5] 45 °C/19 Torr), δ_H(270 MHz, $CDCl_3$) 2.2 (6 H, br s, CH_2), 4.9 (6 H, br s, CH_2) and 5.9 (3 H, m, CH); δ_C(68 MHz, $CDCl_3$) 34 (br s), 114.8 (br s), 134.7; δ_B(128 MHz, $CDCl_3$) 79.2 (br s).

Hydroboration of triallylborane

Solutions of triallylborane (3.9 g, 29.1 mmol) in light petroleum (20 cm^3) and borane–triethylamine (4.3 cm^3, 29.1 mmol) in light petroleum (20 cm^3) were added simultaneously to refluxing light petroleum (100–120 °C, 40 cm^3) during a period of about 1 h. The mixture was then refluxed under N_2 for 16 h. During that time, a precipitate formed. The solvent was removed first by distillation at normal pressure and then under reduced pressure (80 °C/0.1 Torr) to give a white powdery polymeric solid (4.6 g), mp 220–230 °C. The solid was barely soluble in organic solvents and is spontaneously flammable when exposed to air.

Thermolysis of the polymer and isolation of 1,5-dipropyl-1,5-diborocane

Pyrolysis of the polymeric material was carried out by heating the solid (4.6 g) at 250–260 °C (oil bath) at a reduced pressure (22 Torr). A volatile fraction was collected (2.1 g, 100–120 °C/22 Torr) and a non-volatile residue remained. The volatile fraction is air-sensitive and was further purified by distillation (70–90 °C/15 Torr), although this effected no simplification of the ^{1}H NMR spectrum: δ_H(400 MHz, $CDCl_3$) 0.9–1 (1 H, m) and 1.2–1.7 (0.8 H, m); δ_C(100 MHz, $CDCl_3$) 15–19 (m) and 25 (br s); a DEPT spectrum showed that both methyl and methylene groups were present in the δ 15–20 region; δ_B(128 (MHz, $CDCl_3$) 84 (br s); GC–MS analysis showed several

† 1 psi ≈ 6.894 757 × 10^3 Pa; 1 Torr ≈ 133.322 Pa.

products to be present with retention times‡ of 3.5 (20), 4.6 (8), 5.8 (15), 6.6 (15), 9.0 (8), 9.7 (50), 10.1 (20) and 10.3 min (8% of total ion current). The major constituent (40% by area), with the retention time of 9.7 min, showed *m/z* 192 (10), 149 (40), 107 (100), 53 (75) and 41 (80%).

Pyrolysis conditions were varied (see Table 1). The polymer was unmelted and unchanged below 220 °C. Stronger heating (> 270 °C) of the polymer gave a higher boiling fraction (> 120 °C/15 Torr); GC–MS analysis of this fraction showed it to be very complex and no constituent could be recognized. We think it very unlikely that this material contained **1**.

Oxidation of the pyrolysis product followed by identification of the alcohols formed as esters

Oxidation. To a stirred solution of the thermolysis fraction (1.4 g) in THF (50 cm^3) was added aqueous NaOH (3 mol dm^{-3}; 25 cm^3) at 0 °C, followed by slow addition of H_2O_2 (30%; 25 cm^3). The reaction mixture was stirred at room temperature for 16 h and then filtered. The filtrate was neutralized by addition of aq. HCl to pH 7, saturated with NaCl and extracted with Et_2O (2 × 30 cm^3). The combined organic layers were washed with saturated aqueous NaCl (2 × 30 cm^3), dried ($MgSO_4$) and used directly for the esterification reaction (solution **A**).

Alternatively, the combined aqueous layers were concentrated to about 0.5 cm^3 by distillation (150 °C oil bath with a 20 cm column) at normal pressure. The residue was extracted with THF (50 cm^3), and the THF layer dried ($MgSO_4$) and used directly for esterification (solution **B**).

Esterification of solution A. Solution **A** was stirred at 0 °C under N_2, and pyridine (20 cm^3) and benzoyl chloride (10 cm^3) added. After stirring for 16 h at room temperature, Et_2O (40 cm^3) was added; the precipitate was removed by filtration. The filtrate was washed with aq. HCl, then NaOH (2 mol dm^{-3} 2 × 40 cm^3), dried and evaporated to an oil (0.64 g). ^1H NMR showed this was propyl benzoate containing a small amount (< 10%) of propane-1,3-diyl dibenzoate.

Esterification of solution B. Solution **B** was esterified by a similar procedure and gave a thick oil (1.67 g) which was identified as propane-1,3-diyl dibenzoate by ^1H NMR.

Treatment of triallylborane with monobromoborane and methanol; isolation of 1,5-dimethoxy-1,5-diborocane 3 and 1,3-dimethoxy-1,2,6-oxadiborinane 4

Monobromoborane–dimethyl sulfide complex (8.4 cm^3, 78 mmol) was added to a stirred solution of triallylborane (10.5 g, 78 mmol) in dichloromethane (90 cm^3) at 0 °C and the mixture stirred for 16 h at room temperature under nitrogen. Methanol (9 cm^3) was added and stirring continued for 2 h. The solvent was removed by distillation under reduced pressure to give a gel-like product. Thermolysis was carried out by heating the product at 170 °C under vacuum. A volatile liquid was collected (5.18 g, 90–94 °C/12–14 Torr), which was further purified by vacuum distillation to give 1,5-dimethoxy-1,5-diborocane **3** (2.2 g), bp 50 °C/14–16 Torr, δ_H(400 MHz, $CDCl_3$) 3.69 (6 H, s, OCH_3), 1.79 (4 H, m, $CH_2CH_2CH_2$) and 0.94 (8 H, t, *J* 6.6, BCH_2); δ_C(100 MHz, $CDCl_3$) 53.1 (OCH_3), 21.8 (BCH_2, br s) and 18.6 ($CH_2CH_2CH_2$); δ_B(128 MHz, $CDCl_3$) 53.8; *m/z* (GC–MS, EI) 168 (M^+, 10%), 153 (60), 140 (50), 125 (60) and 112 (100) and 1,3-dimethoxy-1,2,6-oxadiborinane **4** (0.6 g), bp 60 °C/18 Torr; δ_H(400 MHz, $CDCl_3$) 3.57 (6 H, s, OCH_3), 1.48 (2 H, m, *J* 6.8, $CH_2CH_2CH_2$) and 0.79 (4 H, t, *J* 6.8, BCH_2); δ_C(100 MHz, $CDCl_3$) 50.9 (OCH_3), 18.4 ($CH_2CH_2CH_2$) and 12 (BCH_2, br s); δ_B(128 MHz, $CDCl_3$) 31.4.

‡ For comparison, tripropylborane and tributylborane were made by treatment of corresponding Grignard reagents with boron trifluoride,[8] and analysed by GC–MS under the same temperature–pressure program used for the thermolysis products; the retention times were 4.3 and 9.1 min respectively.

Treatment of triallylborane with monobromoborane and ethane-1,2-diol; isolation of 1,3-bis(1,3,2-dioxaboralan-2-yl)-propane 5

Monobromoborane–dimethylsulfide complex (3.6 cm^3, 33.6 mmol) was added to a stirred solution of triallylborane (4.5 g, 33.6 mmol) in dichloromethane (50 cm^3) at 0 °C and the mixture stirred for 16 h at room temperature under nitrogen. Ethane-1,2-diol (3.8 cm^3) was added and stirring continued for 16 h. The solvent was removed by distillation under reduced pressure to give a gel-like product. Thermolysis was carried out by heating the product at 220 °C under vacuum. Compound **5** was collected as a colourless oil (1.8 g) bp 110 °C/1 Torr, δ_H(400 MHz, $CDCl_3$), 4.17 (8 H, s, OCH_2), 1.58 (2 H, m, *J* 7.7, $CH_2CH_2CH_2$) and 0.87 (4 H, t, *J* 7.7, BCH_2); δ_C(100 MHz, $CDCl_3$) 64.1 (OCH_2), 17.4 ($CH_2CH_2CH_2$) and 13 (BCH_2, br s); δ_B(128 MHz, $CDCl_3$) 32.5; *m/z* (GC–MS, EI) 156 (M^+ − 24, 25%), 141 (10), 126 (20), 114 (35), 99 (40) and 45 (100); *m/z* (CI, NH_3) 185 (M + H^+ 100%), 155 (20), 141 (40), 113 (80) and 87 (90) [HRMS (EI) Found: M + H^+, 185.1160; calc. for $C_7H_{15}B_2O_4$: *M*, 185.1156].

Treatment of triallylborane with monobromoborane and propane-1,3-diol; isolation of 1,3-bis(1,3,2-dioxaborin-2-anyl)-propane 6

Compound **6** was obtained by using a similar procedure to **5**, but using propane-1,3-diol (2.1 g), bp 120 °C/1 Torr; δ_H(400 MHz, $CDCl_3$) 3.96 (8 H, t, *J* 5.5, OCH_2), 1.92 (4 H, q, *J* 5.5, CH_2CH_2O), 1.41 (2 H, m, *J* 7.9, $BCH_2CH_2CH_2B$) and 0.68 (4 H, t, *J* 7.9, BCH_2); δ_C(100 MHz, $CDCl_3$) 60.4 (OCH_2), 26.2 (CH_2CH_2O), 17.4 ($BCH_2CH_2CH_2B$) and 17 (BCH_2, br s); δ_B(128 MHz, $CDCl_3$) 28.7; *m/z* (GC–MS, EI) 184 (M^+ − 28, 25%), 156 (30), 126 (30) and 85 (40); *m/z* (CI) 213 (M + H^+, 40%), 184 (45), 155 (100), 143 (80) and 127 (75).

Treatment of 1,5-dimethoxy-1,5-diborocane 3 with propylmagnesium bromide

A solution of propylmagnesium bromide (0.85 mol dm^{-3}; 7.8 cm^3) was added to a stirred solution of 1,5-dimethoxy-1,5-diborocane **3** (0.5 g, 3 mmol) in pentane (10 cm^3) and diethyl ether (3 cm^3) at 0 °C and the mixture stirred for 6 h at room temperature. The reaction mixture was quenched by addition of a diethyl ether solution of hydrogen chloride (1 mol dm^{-3}; 6 cm^3) or chlorotrimethylsilane and filtered under nitrogen. The clear solution was concentrated under reduced pressure to give a clear oil (0.44 g); δ_H(400 MHz, $CDCl_3$) 1.43 (4 H, dt, *J* 15.4 and 7.7, $CH_3CH_2CH_2B$), 1.30 (8 H, t, *J* 7, $BCH_2CH_2CH_2B$), 1.19 (4 H, t, *J* 7.7, $CH_3CH_2CH_2B$) and 0.9–0.87 (10 H, m, $CH_3CH_2CH_2B$ and $BCH_2CH_2CH_2B$); δ_C(100 MHz, $CDCl_3$) 29.8 (br s, $CH_3CH_2CH_2B$), 16.7 (CH_3), 16.6 ($CH_3CH_2CH_2B$), 16.4 ($BCH_2CH_2CH_2B$) and 13.6 (br s, $BCH_2CH_2CH_2B$); δ_B(128 MHz, $CDCl_3$) 85; *m/z* (GC–MS, EI) 192 (10), 149 (40), 107 (100) and 53 (80).

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