Pyrolysis of Trimethylborane. Part I. The Preparation and Properties of 2,4,6,8,9,10-Hexamethyl-2,4,6,8,9,10-hexabora-adamantane

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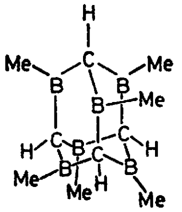
The preparation of 2,4,6,8,9,10-hexamethyl-2,4,6,8,9,10-hexabora-adamantane, $(MeB)_6(CH)_4$, in high yield (*ca.* 25%) by pyrolysis of BMe_3 is described. Degradation of the boron–carbon cage occurs in reactions of $(MeB)_6(CH)_4$ with oxygen, propanoic acid, and ammonia but no reaction occurs with water. It behaves as only a weak acceptor towards the donors, NMe_3, PMe_3, and PMe_2Ph, and stable complexes could not be isolated at room temperature.

PRIOR to the commencement of our investigation, the pyrolysis of trimethylborane had been little studied. Goubeau and Epple[1] in 1957 made the first study of the pyrolysis products and they succeeded in isolating one of the products, a crystalline compound to which they assigned the cyclic formula $(MeBCH_2)_4$. Buchanan and Creutzberg[2] studied the pyrolysis kinetically by measuring the rate of formation of CH_4 and H_2 and found the reaction to be first order in BMe_3. In recent preliminary communications,[3] we have reported the formation of carbaboranes and other boron–carbon compounds from this pyrolysis and in this paper we report in full on the compound $(MeB)_6(CH)_4$, the major product of pyrolysis under a wide range of conditions. The structure[3a] shown below, which we proposed for this compound, has now been confirmed by an *X*-ray diffraction study[4] and so there is now no doubt that it is correctly characterized as 2,4,6,8,9,10-hexamethyl-2,4,6,8,9,10-hexabora-adamantane. Other products and more general aspects of the pyrolysis of BMe_3 will be discussed in subsequent publications.



In contrast to the small amount of effort previously devoted to the study of trimethylborane, there have been extensive investigations of the pyrolysis of other alkylboranes, including cyclic compounds, notably by Köster and his co-workers,[5] and the formation of many polyboron compounds, including carbaboranes, has been reported. However, pyrolysis of BMe_3 is of particular interest because not only is it the simplest trialkylborane and therefore likely to give the least complex mixture of products, it is also the most stable, decomposing at an appreciable rate only at *ca.* 400 °C and above. Presumably this is because, unlike most other alkylboranes (which often decompose at temperatures as low as 200 °C or so), it is unable to decompose by dehydroboronation.

EXPERIMENTAL

(a) *Preparation of* $(MeB)_6(CH)_4$.—(i) *Sealed-tube pyrolysis.* In a typical experiment, trimethylborane (0·567 g, 10·15 mmol) was sealed in a Pyrex tube of *ca.* 120 cm³ in volume, fitted with a break seal on an extended 14/23 cone and previously flamed out *in vacuo*. The tube was placed in a thermostatically controlled furnace at 450 °C for 40 min. Initially this caused a drop in furnace temperature to *ca.* 400 °C, but the temperature of 450 °C was regained after *ca.* 15 min. After removing the tube from the furnace it was seen to be coated with a brown film and as it cooled a white frost-like deposit of the product together with oily droplets formed on the sides.

The reaction tube was connected to the vacuum line, cooled to −196 °C, the seal broken, and the non-condensable gases were pumped away. It was then allowed to warm to room temperature and the condensable products were removed, fractionated, and then refractionated on the vacuum line. Ethane was retained at −196 °C, un-

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[1] J. Goubeau and R. Epple, *Chem. Ber.*, 1957, **90**, 171.

[2] A. S. Buchanan and F. Creutzberg, *Austral. J. Chem.*, 1962, **15**, 744.

[3] (*a*) M. P. Brown, A. K. Holliday, and G. M. Way, *J.C.S. Chem. Comm.*, 1972, 850; (*b*) *ibid.*, 1973, 532.

[4] H. Shearer, unpublished work.

[5] R. Köster and G. W. Rotermund, *Tetrahedron Letters*, 1964, **25**, 1667; R. Köster, W. Larbig, and G. W. Rotermund, *Annalen*, 1965, **682**, 21; R. Köster and M. A. Grassberger, *Angew. Chem. Internat. Edn.*, 1967, **6**, 218.

reacted BMe_3 (7·9 mmol) at −140 °C, a small amount of a mixture of carbaboranes and other liquid products, which was not further examined in these experiments, at −107 °C, and the white solid product (18 mg, 23% based on BMe_3 consumed) at −40 °C. Since the vapour pressure of the product is only *ca.* 1 Torr at room temperature, it transferred only slowly on the vacuum line and care was needed to avoid losses. The use of i.r. lamps to warm the line was helpful.

The results of this and other similar experiments are summarized in Table 1. Generally it was found that the experiments were quantitatively not very reproducible and it was surprising that the amount of BMe_3 decomposed did not increase more markedly with the duration of the experiment. In terms of yield, there did not seem to be any advantage in increasing the pyrolysis time. The average yield was 21%. A further set of larger-scale experiments (*ca.* 20 mmol of BMe_3 in 300 cm^3 sealed tubes) gave essentially similar results although the pyrolysis time had to be increased to *ca.* 300 min. In a typical experiment, 69 mg (22%) of product was obtained from a charge of 21·05 mmol of BMe_3 from which 11·8 mmol was recovered unchanged. In a total of six experiments, yields varied from 10 to 27%, and the average was 18%.

TABLE 1

Pyrolysis at 450 °C

Pyrolysis time/min	Charge of BMe_3/mmol	BMe_3 decomposed/ mmol	Yield of $(MeB)_6(CH)_4$	
			mg	%
40	10·15	2·25	18	23
75	10·65	2·45	20	24
105	10·10	2·50	10	11·5
120	6·75	1·65	10	17·5
135	9·70	1·60	19	34
165	9·97	2·77	23	24
180	10·15	4·85	21	12

(ii) *Recirculatory-flow-system pyrolysis.* Initial experiments in BMe_3 pyrolysis were carried out in an apparatus essentially similar to that of Goubeau and Epple.[1] In these experiments, BMe_3 (usually 40—50 mmol) at 0·5 atm was slowly circulated through a silica combustion tube at 500 °C for 40 h or more.* Only small quantities (*ca.* 1—10 mg) of the crystalline $(MeB)_6(CH)_4$ were obtained on fractionation of the volatile products which consisted mainly of more volatile materials together with much polymeric solid on the walls. As a preparative method for $(MeB)_6(CH)_4$, this recirculatory flow system therefore appeared inferior to sealed-tube pyrolysis.

(iii) *Purification of the product.* Its ^{11}B n.m.r. spectrum (see below) appeared to show the presence of a trace of boron-containing impurity, which was almost impossible to remove by further fractionation, and close visual examination showed in fact the presence of a trace of oily contaminant. This could, however, be largely removed, as determined from visual observation and the ^{11}B spectrum, by treatment of the product with a small amount of water at room temperature for a few hours, followed by vacuum fractionation to remove traces of hydrolysed material and excess of water. The m.p. of 84 °C was however unchanged by this treatment.

(b) *Spectral properties of* $(MeB)_6(CH)_4$.—(i) *Mass spectrum.* The 70 eV spectrum (Micromass MM12) showed intense M^+ and $(M - CH_3)^+$ groups of peaks. The relative intensities within each group were in close agreement with those calculated for the multi-isotopic species $B_6C_{10}H_{22}^+$ and $B_6C_9H_{19}^+$, respectively, as shown in Table 2. The only other major peaks corresponded to much smaller fragments and were centred on *m/e* 89 (20·4), $B_3C_4H_8^+$, *m/e* 65 (50·4), $B_2C_3H_7^+$, *m/e* 51 (32·0), $B_2C_2H_5^+$, and *m/e* 41 (25·2), $BC_2H_6^+$ (relative intensities in parentheses). At 15 eV, the only fragmentation was loss of methyl groups and the spectrum essentially consisted of peaks due to two ions M^+ and $(M - CH_3)^+$. An accurate mass measurement (AEI-MS9 instrument) of the 208 peak gave 208·2269 (calc. for $^{11}B_6{}^{12}C_{10}{}^{1}H_{22}^+$: 208·2280).

TABLE 2

Isotope patterns for the M^+ and $(M - CH_3)^+$ ions

M^+ ion ($B_6C_{10}H_{22}^+$)			$(M\text{-}CH_3)^+$ ion ($B_6C_9H_{19}^+$)		
	Relative intensity			Relative intensity	
m/e	obs.	calc.	*m/e*	obs.	calc.
209	3·0	3·6	195	0·6	0·3
208	34·0	35·9	194	7·3	6·9
207	47·5	47·5	193	74·0	74·0
206	28·3	28·1	192	100·0	100·0
205	10·0	9·0	191	60·3	59·3
204	2·0	1·6	190	20·2	19·0
203	0·4	0·2	189	4·0	3·6

(ii) *N.m.r. spectra.* The ^1H n.m.r. spectrum (Varian A-60) of the compound as a melt (100 °C), containing 3% benzene as an internal reference, showed just two singlets, δ 0·69 (BCH_3) and 4·14 p.p.m. (CH) (relative to $SiMe_4$). In solution, with $SiMe_4$ as internal reference, the resonances were at δ 0·57 and 3·98 [$(D_3C)_2CO$] and δ 0·62 and 4·08 p.p.m. (C_6D_6), respectively. The area ratios were close to 9 : 2 as expected.

The ^{11}B n.m.r. spectrum (Brooker 90 instrument) in $(D_3C)_2CO$ consisted of one intense and fairly broad peak, δ −63·2 p.p.m. (28·9 MHz, F_3B,OEt_2 external reference) together with a weak doublet on the high-field side. The spectrum of the compound in the molten state was similar, but after purification of the sample with water as described above the relative intensity of the doublet was much decreased showing that this resonance was obviously due to an unidentified impurity.

The ^{13}C n.m.r. spectrum (Varian XL-100) obtained from the melt (90 °C) was weak but the proton-decoupled spectrum (20 575 scans) showed two broad and irregularly shaped bands δ (25·2 MHz, $SiMe_4$ reference) −11·6 (BMe) and −82·2 p.p.m. (CH).

(iii) *I.r. spectrum.* Fluorolube and Nujol mulls gave the following peaks: 448m; 727m; 805m,br; 822br (sh); 875s; 1 003s; 1 163s; 1 185w,br; 1208s; 1260vw; 1 192s; 1 428m,br; 1 558w; 1 730m,br; 1 830w,br; 2 830 (sh); 2 928s; and 2 955s cm^{-1}. A full vibrational study is being undertaken and the results will be published later.

(c) *Reactions of* $(MeB)_6(CH)_4$.—The following reactions of the air-sensitive $(MeB)_6(CH)_4$ were carried out using conventional vacuum-line techniques.

(i) *With oxygen.* The compound (0·05 mmol) was treated with oxygen (0·48 mmol) in a weighed bulb at room temperature for several hours. It quickly blackened and an oily liquid appeared. The unreacted oxygen (0·22 mmol) was removed and, from the products, trimethylboroxin (0·09 mmol) was recovered by vacuum fractionation and identified by its mass spectrum.

(ii) *With propanoic acid.* The compound (0·039 g, 0·19 mmol) was treated with excess of propanoic acid (*ca.*

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* 1 atm = 101 325 Pa; 1 eV ≈ 1·60 × 10^{-19} J.

20 mmol) in a sealed vessel at 120 °C for 1 week. The gaseous product consisted of methane (1·65 mmol). The ratio of $CH_4 : (MeB)_6(CH)_4$ was therefore 8·7 : 1. A similar treatment for a period of 24 h gave less methane (7·4 : 1).

(iii) *With ammonia.* The compound (0·22 mmol) was treated with ammonia (10·6 mmol) at −46 °C for 2 h when the unreacted ammonia was removed *in vacuo.* On allowing the white oily residue to warm to room temperature, it foamed giving unidentified volatile and involatile products which however contained a small amount of unreacted starting material. Mass-spectral examination of the volatile components showed strong groups of peaks at *m/e* 122 and 107 with isotope patterns corresponding to ions containing three boron atoms, but the material was obviously impure and could not be further characterized.

(iv) *With trimethylamine, trimethylphosphine, and dimethylphenylphosphine.* When the compound was treated, in separate experiments, with measured amounts of each of these three Lewis bases at room temperature no stable complexes could be isolated. With trimethylamine and trimethylphosphine the reactants were recovered almost quantitatively when the reaction mixtures were subjected to vacuum fractionation. With the less-volatile dimethylphenylphosphine complete recovery was not achieved. Whereas most of the PMe_2Ph passed to a trap at −78 °C, some (slightly less than one molar proportion) was trapped at −18 °C together with the $(MeB)_6(CH)_4$, presumably as a weak complex. No evidence of complex formation could however be obtained by mass-spectral examination of this material. With trimethylamine, a further experiment was carried out in which $(MeB)_6(CH)_4$ (0·31 mmol) was treated with the amine (1·23 mmol) at −78 °C. The excess of trimethylamine (0·93 mmol) was removed *in vacuo* at −78 °C. On allowing the reactants to warm to room temperature, a further sample (0·28 mmol) of amine was recovered suggesting that a 1 : 1 complex may be stable at −78 °C but not at room temperature.

The possibility of complex formation was also studied by ^1H n.m.r. spectroscopy with $SiMe_4$ as internal reference, in sealed 5 mm tubes containing the following mixtures: trimethylamine (5·4 mmol) and $(MeB)_6(CH)_4$ (0·31 mmol) with no added solvent; trimethylamine (1·0 mmol), $(MeB)_6(CH)_4$ (0·31 mmol), and $(D_3C)_2CO$ (0·5 cm^3); dimethylphenylphosphine (0·13 mmol), $(MeB)_6(CH)_4$ (0·09 mmol), and C_6D_6 (0·5 cm^3); and trimethylphosphine (0·65 mmol), $(MeB)_6(CH)_4$ (0·12 mmol), and $(D_3C)_2CO$ (0·5 cm^3). The results of these experiments are discussed below.

DISCUSSION

In so far as we find that BMe_3 pyrolysis proceeds readily at *ca.* 400—450 °C and gives mostly an involatile polymeric product and a mixture of volatile liquid products together with a readily isolated crystalline solid, our work confirms that of Goubeau and Epple.[1] Although they characterized the solid, obtained in yields of 4%, as a cyclic tetramer $(MeBCH_2)_4$, it seems likely that it is in fact identical to the compound which we obtain and characterize as $(MeB)_6(CH)_4$ despite the fact that there are some apparent differences in properties. Thus we find an identical m.p. (84 °C) but a lower vapour pressure (*ca.* 1 compared to 11 Torr) at 25 °C and differences in the i.r. spectrum.

The compound is formed by pyrolysis either in sealed tubes or in a recirculatory flow system; under the conditions of our experiments yields, although varying between 10 and 30%, are much higher using the former. Discounting formation of polymer which must account for much of the decomposed BMe_3, the yield of $(MeB)_6(CH)_4$ greatly exceeds the combined yields of all the other products. Such a high yield of a single compound is surprising, especially when compared with the pyrolysis of tetramethylsilane[6] which also gives a complex mixture of compounds but with no single compound in such exceptional yield. This may be due to the more-labile character of B–Me bonds, as compared to Si–Me bonds, permitting polymeric or condensed materials, possibly containing $CH(BMe)_3$ units, to rearrange at high temperature. Conversion to a more-volatile and lower-molecular-weight material, *viz.* $(MeB)_6(CH)_4$, could well be thermodynamically favoured. This would explain the lower yields in the flow apparatus where the polymer is mostly deposited on the walls of the cooler parts of the apparatus and not subject to further heating, unlike the sealed-tube method where the entire tube is within the furnace.

The n.m.r. spectra, which have already been discussed,[3b] are remarkably simple for a compound containing so many atoms (38) and show only one ^{11}B resonance, two ^1H resonances, and two proton-decoupled ^{13}C resonances, although there is some doubt about the latter because of the poor quality of the spectrum. The i.r. spectrum is consistent with an organoborane-type of structure in that the C–H stretching absorptions fall in the range 2 830—2 955 cm^{-1} whereas carbaboranes containing CH groups as part of the cage have average C–H frequencies[7] at greater than 3 000 cm^{-1}. In the mass spectrum, calculated relative intensities for the groups of peaks corresponding to the M^+ and $(M - CH_3)^+$ ions are in good agreement with the observed (Table 2), showing that fragmentation by loss of H atoms does not occur to a significant extent. This is unusual in higher boron compounds which usually contain B–H groups and undergo H loss as a major fragmentation process giving complex overlapping groups of peaks.[8] Similar resistance to H loss has also been noted in another B-permethylated compound, the carbaborane $(MeB)_5(CH)_2$, prepared by Seklemian and Williams.[9]

The reactions of the compound are generally similar to those of an alkylborane. Thus sensitivity towards oxygen is to be expected, and so too is cleavage of the boron–carbon bonds with propanoic acid. Cleavage of only the terminal B–C bonds would give a 6 : 1 mol ratio of $CH_4 : (MeB)_6(CH)_4$, whereas cleavage of all the B–C bonds, including those of the cage, would give a

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[6] G. Fritz, J. Grobe, and D. Kummer, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 403.

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[8] R. H. Cragg and C. F. Weston, *J. Organometallic Chem.*, 1974, **67**, 161.

[9] H. V. Seklemian and R. E. Williams, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 289.

10 : 1 mol ratio [equation (1)]. The experimental mol ratios of 7·4 : 1 (24 h) and 8·7 : 1 (1 week) show that the

$$(\mathrm{MeB})_6(\mathrm{CH})_4 + 18\ \mathrm{EtCO_2H} \longrightarrow 6\ \mathrm{B(O_2CEt)_3} + 10\ \mathrm{CH_4} \quad (1)$$

B–C bonds of the cage have reacted but apparently only incompletely. The products of the reaction with ammonia could not be characterized, but it seems clear from the formation of volatile material containing boron and the rather intractable nature of the residue that the reaction is not one of simple addition but that, surprisingly, degradation of the cage has taken place.

Complexes formed with NMe_3, PMe_3, and PMe_2Ph are too weak for them to be isolated at room temperature and the compound $(MeB)_6(CH)_4$ must therefore be a weaker acceptor than, for example, BMe_3 which forms quite stable adducts with these donors. That donor–acceptor interactions do occur, however, was shown by the ^1H n.m.r. results. The ^1H resonances of $(MeB)_6(CH)_4$ were shifted from δ 0·69 (BCH_3) and 4·14 (CH) to δ 0·38 and 3·05 p.p.m., respectively, upon interaction with NMe_3 and to δ 0·36 and 2·80 p.p.m. upon interaction with PMe_3. Smaller shifts to δ 0·60 and 3·96 p.p.m. were observed with PMe_2Ph suggesting that complexing is even weaker with this donor, probably for steric reasons. The Me groups of the donors only gave one resonance showing that exchange in each of these three systems is rapid. Trimethylphosphine gave a doublet, δ 1·05 p.p.m. (*J* 3 Hz), whereas with dimethylphenylphosphine the P–CH_3 coupling was lost and a singlet, δ 0·96 p.p.m., was observed.[10] This is a further indication of interaction in this particular case. Trimethylamine gave a single peak at δ 2·1 p.p.m., although at −85 °C a new peak, δ 2·53 p.p.m., presumably due to complexed NMe_3, was observed; it was too close to the intense peak of the uncomplexed NMe_3, used in large excess as solvent, for integration to be reliable. Further study of the complexes of $(MeB)_6(CH)_4$ will be carried out when larger samples have been prepared.

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