Formation of Carboranes by Pyrolysis of Trimethylborane

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Summary Pyrolysis of trimethylborane at 475—520 °C yields $Me_2BCH_2BMe_2$ and the carboranes $C_2H_2(BMe)_3$ and $C_4H_4(BMe)_6$; mass spectral evidence suggests also the formation of $(MeBCH_2)_3$ and $(MeBCH_2)_4$ and other less-volatile carboranes.

We report the presence of significant amounts of carboranes in the volatile products of the pyrolysis of trimethylborane. Previous work on the pyrolysis of trimethylborane has been limited to co-pyrolysis[1] with carboranes and to the preparation and characterisation of a cyclic tetramer[2] $(MeBCH_2)_4$.

Pyrolysis of trimethylborane (2 g) through a vertical silica tube, at 475—520° and 0·5 atm. for 40—100 h, gave hydrogen, methane, a trace of ethylene, unchanged trimethyl-borane (25—66% recovery), and a less-volatile fraction (0·1—0·2 g).

Three components (1)—(3) of this latter fraction have been obtained pure by the use of trap-to-trap distillation and a low-temperature fractionation column. The mass spectrum of each component is remarkably simple. Most of the ion current is carried by the M^+ and $(M - 15)^+$ ions, there being no significant contribution from a $(M - 1)^+$ fragment; this supports a *B*-permethylated formulation[1] (Table). Analysis of the isotope patterns (^{10}B and ^{13}C) and accurate mass measurements on the molecular ions of (2) and (3) support their formulation as carboranes $C_2H_2(BMe)_3$ and $C_4H_4(BMe)_6$.

Table

Component	Trap temp., (°C)	Mass spectrum[a] (70 eV) *m/e* (relative intensity values)	Molecular formula
(1)	−110	96(5·7), 81(100)	$B_2C_5H_{14}$
(2)	−100	104(50), 89(100)	$B_3C_5H_{11}$
(3)	−40	208(49), 193(100)	$B_6C_{10}H_{22}$

[a] Corrected for ^{10}B contributions.

The mass spectrum of (1) indicates it to be $Me_2BCH_2BMe_2$, the linear dimer corresponding to the previously observed[2] cyclic tetramer.

The remainder of the third fraction could only be partially separated but mass spectral evidence (peaks corresponding to M^+ and $(M - 15)^+$ with the correct isotopic abundances) indicates presence of the cyclic trimer $(MeBCH_2)_3$ and the previously reported tetramer $(MeBCH_2)_4$, together with other less volatile carboranes.

The ^1H n.m.r. spectrum (100 MHz) of (2) (in C_6D_6) shows that the two CH groups (δ 5·54 p.p.m.) and the three CH_3 groups (δ 1·48 p.p.m.) are equivalent and establishes the compound as the previously unreported *B*-trimethyl derivative of the 1,5-$C_2B_3H_5$ carborane.[3] The i.r. spectrum shows the absence of B–H absorption.

Although no structural evidence is available at present, (3) seems likely to be the *B*-permethyl derivative of the predicted[4] *nido*-$C_4B_6H_{10}$ carborane; no derivative of this carborane has previously been fully characterised but it has been suggested that a compound, $C_{20}B_6H_{42}$, obtained and given another structure by Köster,[5] is in fact an alkyl derivative of $C_4B_6H_{10}$, namely $Me_4C_4B_6Et_6$.

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