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Studies of the Pyrolysis of Tetraethylammonium Tetrahydroborate

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Abstract

Tetraethylammonium tetrahydroborate, Et_4NBH_4, in suspension in refluxing decane–dodecane mixtures has been pyrolysed at temperatures between 175 and 190 °C. Et_3NBH_3, which is produced by partial decomposition of Et_4NBH_4, reacts with Et_4NBH_4 to give the intermediate $Et_4NB_3H_8$. Et_4NBH_4 and Et_3NBH_3 are also involved in the conversion of $Et_4NB_3H_8$ to $(Et_4N)_2B_9H_9$, $(Et_4N)_2B_{10}H_{10}$, $Et_4NB_{11}H_{14}$ and $(Et_4N)_2B_{12}H_{12}$ which are formed in varying proportions during the pyrolysis. A 1:1 Et_4NBH_4–Et_3NBH_3 mixture gives the same mixture of final products in the same proportions as Et_4NBH_4 alone, but the reaction time is shorter.

Results obtained under various conditions, for instance without solvent at 10^{-2} torr (50% yield), are explained by the transfer of BH_3 groups occurring not only through Et_3NBH_3, but also by solid–solid reactions involving Et_4NBH_4. A more complete reaction of Et_3NBH_3 is obtained, giving quantitative yields, only when Et_3N is evacuated from the reaction mixture. Optimum conditions for the formation of each hydroborate are examined.

Introduction

It was originally shown by Makhlouf [1, 2] that the pyrolysis of tetraethylammonium tetrahydroborate, Et_4NBH_4, proceeds according to the equation

$$10Et_4NBH_4 \longrightarrow (Et_4N)_2B_{10}H_{10} + 8Et_3N + 8EtH + 11H_2 \qquad (1)$$

Since $(Et_4N)_2B_{10}H_{10}$ can be used to prepare [3–5] carboranes with the general formula $C_2B_{10}H_{10}R_2$ (R = H or alkyl), which are of importance in the field of boron chemistry, it is not surprising that many studies have employed the above reaction. The pyrolysis has been carried out both in the presence [6] and absence [1, 2, 7–9] of heat-transfer solvents, and the method has also been studied using other tetraalkylammonium salts of BH_4^-. Recently it has also been demonstrated that similar results are obtained by using a mixture of KBH_4 and Et_4NCl [10].

The pyrolysis of Et_4NBH_4 is a complex reaction in which variable amounts of $B_{12}H_{12}^{2-}$, $B_9H_9^{2-}$ and $B_{11}H_{14}^-$ are obtained in addition to $B_{10}H_{10}^{2-}$. The mechanism by which these anions are formed is not clearly understood and is subject to dispute. We had suggested earlier that $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are produced in the reaction between triethylamine borane, Et_3NBH_3, and BH_4^- [5]. More recent studies have refuted this interpretation, and Et_3NBH_3 is no longer believed to be involved in the formation of $B_{10}H_{10}^{2-}$ [8, 6]; Et_3NBH_3 has even been used as a heat-transfer solvent. The purpose of the present work was to obtain a better knowledge of the mechanism, and to determine under which conditions the formation of each hydroborate is favoured. The tetrahydroborate has been pyrolysed both in suspension in hydrocarbides and in the absence of solvent. The role played by the amine borane has been deduced from kinetic studies of the pyrolysis of Et_3NBH_3 dissolved in hydrocarbide–Et_4NBH_4 mixtures.

Results and Discussion

Hydrocarbide Suspensions of the Tetrahydroborate

The tetrahydroborate is pyrolysed at constant temperature in refluxing decane–dodecane mixtures at atmospheric pressure. The results obtained from pyrolysis at 185 °C are shown in Fig. 1. BH_4^- is quantitatively converted to $B_{10}H_{10}^{2-}$, $B_9H_9^{2-}$, $B_{12}H_{12}^{2-}$ and $B_{11}H_{14}^-$ after a reaction time of 12 h. $B_3H_8^-$, which had been considered to be involved in the formation of more condensed anions in an earlier work [1], appears to be the only stable intermediate. Et_3NBH_3 which is formed rapidly at the beginning of the reaction also plays an important role. Its higher concentration in the liquid phase is reached after a reaction time of two hours, and 25% of the boron atoms of the system are then accounted for by the Et_3NBH_3 in solution. The amine–borane is completely consumed at the end

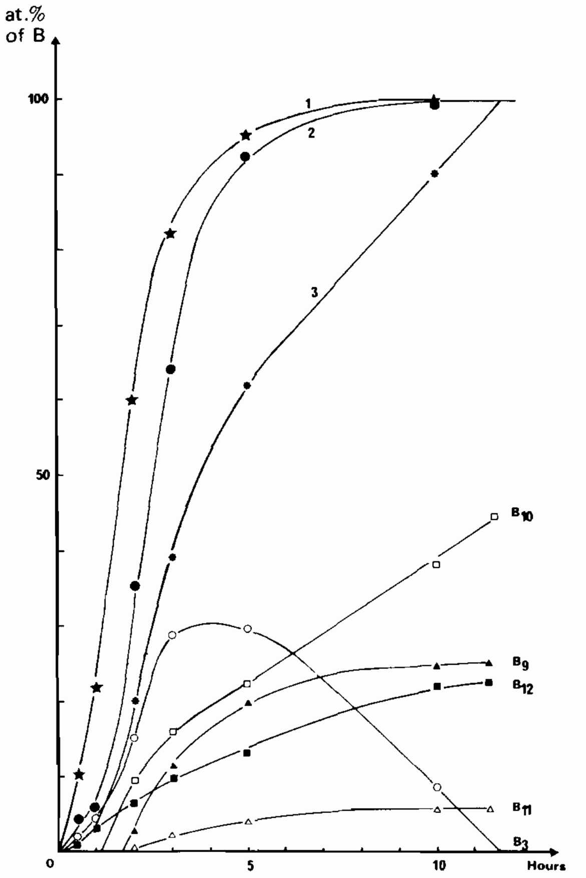

Fig. 1. Pyrolysis of Et_4NBH_4 (10 g) in suspension in 100 cm^3 of a refluxing decane–dodecane mixture at 185 °C. For the following curves, the percentages are given in boron atoms as a function of time (in hours): (1) total percentage of transformed Et_4NBH_4; (2) percentage of Et_4NBH_4 converted to the hydroborate anions $B_3H_8^-$, $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, $B_{11}H_{14}^-$ and $B_{12}H_{12}^{2-}$. (At any time the percentage of Et_3NBH_3 is the difference of the ordinates of the curves 1 and 2); (3) percentage of Et_4NBH_4 converted to $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, $B_{11}H_{14}^-$, and $B_{12}H_{12}^{2-}$. *Note*: (B_3), (B_9), (B_{10}), (B_{11}) and (B_{12}) give the percentages of $B_3H_8^-$, $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, $B_{11}H_{14}^-$ and $B_{12}H_{12}^{2-}$, respectively.

of the pyrolysis. At lower temperatures the reaction times are much longer: at 175 °C, $B_3H_8^-$ is still present in the reaction medium after 30 h. At higher temperatures (190 °C), the pyrolysis products become brown due to the slow decomposition of $B_9H_9^{2-}$.

Et_4NBH_4–Et_3NBH_3 in Decane–Dodecane Mixtures

The pyrolysis has been carried out under the same conditions as above; Et_3NBH_3, decane and dodecane are completely miscible. The thermolysis of Et_4NBH_4–Et_3NBH_3 in a 5:3 ratio for 30 h at 185 °C gives a solid product. The hydroborate distribution is approximately the same as in the pyrolysis of Et_4NBH_4 alone, but the amount of recovered product is larger since Et_3NBH_3 reacts quantitatively and participates in the formation of hydroborates (the yield calculated from the initial amounts of Et_4NBH_4 and Et_3NBH_3 is 97%). Results of the pyrolysis at 185 °C of Et_4NBH_4–Et_3NBH_3 in a 1:1 ratio are given in Fig. 2. Both reagents are almost completely consumed after 7 h, and the distribution of hydroborates in the final product is approximately the same as that when less amine-borane is used.

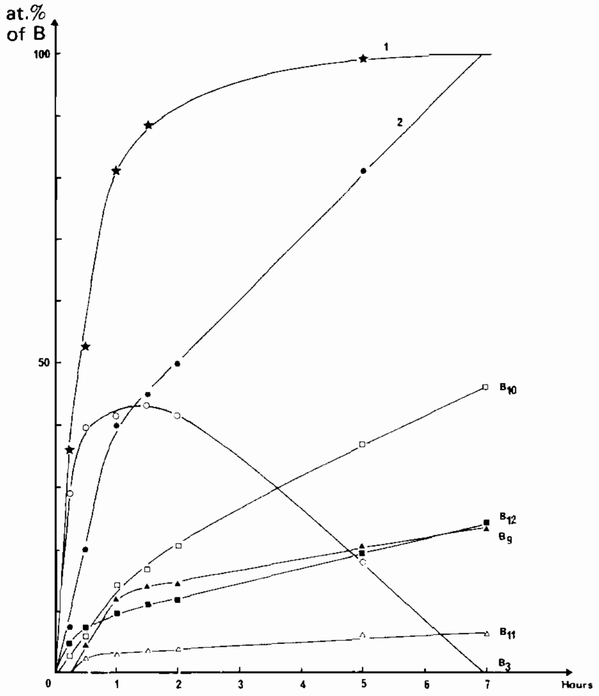

Fig. 2. Pyrolysis of Et_4NBH_4 (0.069 mol) and Et_3NBH_3 (0.069 mol) at 185 °C in 100 cm^3 of a decane–dodecane mixture. The percentages are given in boron atoms as a function of time, in hours: (1) gives the total percentage of BH_4^- and Et_3NBH_3 converted to $B_3H_8^-$, $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, $B_{11}H_{14}^-$ and $B_{12}H_{12}^{2-}$; (2) represents the percentage of BH_4^- and Et_3NBH_3 converted to $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, $B_{11}H_{14}^-$ and $B_{12}H_{12}^{2-}$. *Note*: (B_3), (B_9), (B_{10}), (B_{11}) and (B_{12}) give the percentages of $B_3H_8^-$, $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, $B_{11}H_{14}^-$ and $B_{12}H_{12}^{2-}$, respectively.

$Et_4NB_3H_8$ Formation

The reaction of Et_4NBH_4 with Et_3NBH_3 gives the intermediate $Et_4NB_3H_8$. Figure 1 shows that a high Et_3NBH_3 concentration is required to form $B_3H_8^-$ in large amounts. The pyrolysis of 1:1 Et_4NBH_4–Et_3NBH_3 (Fig. 2) also demonstrates that high rates of formation are observed for $B_3H_8^-$ in the presence of Et_3NBH_3. For a reaction time of 15 min, 41.5% of Et_4NBH_4 and 30% of Et_3NBH_3 have been used giving mainly $B_3H_8^-$ which contains more than 80% of the boron atoms of the conversion product; the other anions formed are $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$. These data do not suffice to determine

TABLE I. Pyrolysis of Et_4NBH_4 (10 g) in 100 cm^3 of a Refluxing Decane–Dodecane Mixture at 185 °C. Reaction Time: 120 min

Starting materials	Et_3BNH_3 recovered after reaction (% in boron atoms)	Unreacted BH_4^- (in %)	$B_3H_8^-$ produced (% of the initial boron atoms)	Distribution of the condensed hydroborates (in boron atoms)			
				$B_9H_9^{2-}$	$B_{10}H_{10}^{2-}$	$B_{11}H_{14}^-$	$B_{12}H_{12}^{2-}$
Et_4NBH_4	24.5[a]	40.0	43.5	13.8	49.8	4.2	32.2
Et_4NBH_4–Et_3NBH_3 (1:1 ratio)	7.0[b]	12.5	45.6	28.2	40.7	7.5	23.5
Et_4NBH_4–Et_3NBH_3 (1:2 ratio)	28.5[b]	14.0	26.9	33.2	38.7	8.6	19.5

[a] Calculated from Et_4NBH_4 used initially. [b] Calculated from Et_3NBH_3 used initially.

in which ratio Et_3NBH_3 and Et_4NBH_4 react to give $B_3H_8^-$, because at the same time some Et_3NBH_3 is formed:

$$Et_4NBH_4 \longrightarrow Et_3NBH_3 + EtH \qquad (2)$$

However, by considering the pyrolysis of Et_4NBH_4 alone (Fig. 1), the yield of Et_3NBH_3 after 15 min via reaction 2 can be evaluated. It is correct to deduce that, in bulk, as much Et_4NBH_4 as Et_3NBH_3 is used for the formation of $Et_4NB_3H_8$.

The conversion rate of Et_4NBH_4 stops increasing when the Et_3NBH_3 concentration exceeds a certain limit; the percentage of reacted Et_4NBH_4 (Table I) is approximately the same after a reaction time of 2 h for the pyrolysis of Et_4NBH_4–Et_3NBH_3 either in a 1:1 or 1:2 ratio. It is believed that the Et_3NBH_3 attack on Et_4NBH_4 is the first step in the process; when the Et_3NBH_3 concentration is high, the rate of the reaction depends only on the concentration of reacting Et_4NBH_4. In agreement with previous studies [10], it is suggested that $Et_4NB_2H_7$ is the first anion formed. Due to its instability in the reaction mixture, it has not been characterized by ^{11}B NMR [11].

$$Et_4NBH_4 + Et_3NBH_3 \rightleftarrows Et_4NBH_4, Et_3NBH_3 \rightleftarrows Et_4NB_2H_7 + Et_3N \qquad (3)$$

The process by which $B_2H_7^-$ is obtained is reversible because the concentration of Et_3N in the reaction mixture determines the course of the pyrolysis. When Et_3N is efficiently removed, the hydroborates are quantitatively formed; otherwise the pyrolysis yields mainly Et_3NBH_3 from reaction 2. $B_2H_7^-$ can be converted to $B_3H_8^-$ in several ways which may be concurrent. The sodium salt NaB_2H_7 decomposes [12]

$$2B_2H_7^- \longrightarrow B_3H_8^- + BH_4^-$$

but taking account of the behaviour of tetraethylammonium salts (see below the pyrolysis of $Et_4NB_3H_8$), and also of the amount of Et_3NBH_3 used to form $B_3H_8^-$, the following reaction is more probable:

$$2Et_4NB_2H_7 \longrightarrow Et_4NB_3H_8 + Et_3NBH_3 + H_2 + EtH \qquad (4)$$

$B_2H_7^-$ can also react with Et_4NBH_4 or Et_3NBH_3 to give $B_3H_8^-$.

In general in the pyrolysis, Et_4NBH_4 acts as the BH_4^- anion and gives Et_3NBH_3 via reaction 2. This dual behaviour makes the formation of hydroborates possible from Et_4NBH_4 (and more generally R_4NBH_4) at temperatures below 200 °C. Results obtained under various conditions lead to the conclusion that transfer of BH_3 groups can occur not only through Et_3NBH_3, but also by solid–solid reactions involving Et_4NBH_4. Formation of hydroborates during pyrolysis at 10^{-2} torr pressure (Table III) can be interpreted in this way since Et_3NBH_3 is a volatile compound at 185 °C. From similar results, Hill [8] concluded that Et_3NBH_3 is not an intermediate in the formation of $B_{10}H_{10}^{2-}$. It is worth noting that under these conditions the yield is only 50%, and that it is difficult to control the pressure during the exothermic phase of the reaction (reaction of Et_3NBH_3 would then take place). A more general examination of the results shows that according to the conditions of the experiment, the amine–borane is directly involved in the formation of $B_3H_8^-$ to varying degrees.

In order to clarify the situation concerning the conversion of the intermediate $B_3H_8^-$ to more condensed hydroborates, we have compared the results of Et_4NBH_4 and $Et_4NB_3H_8$ pyrolysis. The transformation of $Et_4NB_3H_8$ alone (Table II) is different from that of CsB_3H_8, which gives [13] $Cs_2B_9H_9$, $Cs_2B_{10}H_{10}$, $Cs_2B_{12}H_{12}$ and $CsBH_4$ without any change in the total number of anionic charges; in the case of $Et_4NB_3H_8$, the amine-borane is formed instead of Et_4NBH_4. The conversion of the intermediate $Et_4NB_3H_8$ in the pyrolysis of Et_4NBH_4 is very complex; we have not been able to separate the different stages or characterize the intermediates, but it appears that Et_4NBH_4 and Et_3NBH_3 are involved. Comparing results of the pyrolysis of Et_4NBH_4–Et_3NBH_3 in a 1:1 and 1:2 ratio (Table I),

TABLE II. Pyrolysis of $Et_4NB_3H_8$ (2 g) at 185 °C

Conditions	Reaction time (h)	% of Unreacted $Et_4NB_3H_8$	Et_3NBH_3 recovered after reaction as % boron atoms	Distribution of condensed as % boron atoms			
				$B_9H_9^{2-}$	$B_{10}H_{10}^{2-}$	$B_{11}H_{14}^{-}$	$B_{12}H_{12}^{2-}$
10^{-2} torr without solvent	24	15	19.0[a]	50.5	26.5	9.0	14.0
Suspension in 50 cm^3 of a refluxing decane–dodecane mixture	10	23	3.2[a]	49.0	28.0	8.0	15.0
$Et_4NB_3H_8$–Et_3NBH_3 (1:3 ratio) in 50 cm^3 of a refluxing decane–dodecane mixture	10	0	0.1[b]	13.0	27.0	18.0	42.0

[a]Calculated from $Et_4NB_3H_8$ used initially. [b]Calculated from Et_3NBH_3 as above.

TABLE III. Pyrolysis of Et_4NBH_4 (10 g) in the Absence of Solvent at 185 °C for 24 h

Pressure (torr)	Yield of condensed hydroborates (%)	Distribution of condensed hydroborates (as % boron atoms)			
		$B_9H_9^{2-}$	$B_{10}H_{10}^{2-}$	$B_{11}H_{14}^{-}$	$B_{12}H_{12}^{2-}$
760	74	<1	33.0	4.0	63.0
30	91	28.7	49.6	5.0	16.7
10^{-2}	50	25.9	41.9	8.4	23.8

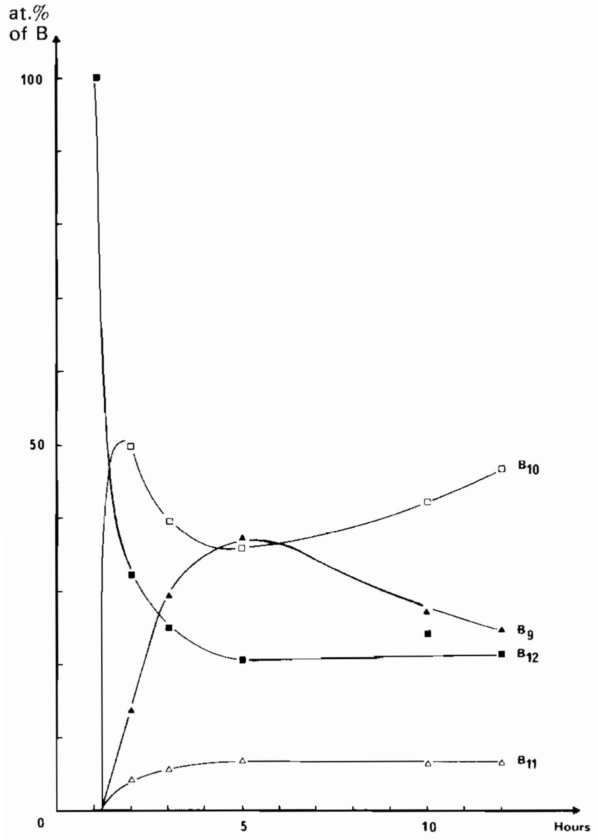

Fig. 3. Distribution variation of the species $B_9H_9^{2-}$ (B_9), $B_{10}H_{10}^{2-}$ (B_{10}), $B_{11}H_{14}^{-}$ (B_{11}) and $B_{12}H_{12}^{2-}$ (B_{12}) during the pyrolysis of Et_4NBH_4 (10 g) in 100 cm^3 of refluxing decane–dodecane. Percentages are calculated as % boron atoms.

it is clear that a high Et_3NBH_3 concentration increases the conversion rate of $B_3H_8^-$. Pyrolysis of $Et_4NB_3H_8$–Et_3NBH_3 mixtures (Table II) confirms that Et_3NBH_3 reacts during the conversion of $B_3H_8^-$. Conversely, Et_3NBH_3 is produced by the pyrolysis of $Et_4NB_3H_8$ under vacuum. Due to the role played by unreacted Et_4NBH_4 in the conversion of the intermediate $Et_4NB_3H_8$, a complete reaction is observed in the pyrolysis of Et_4NBH_4 at 10^{-2} torr for a reaction time of 24 h (Table III). Under the same conditions $Et_4NB_3H_8$ is partly converted, giving a different distribution of the stable hydroborates in the final product (Table II).

Conditions for the Formation of Various Species

$B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, $B_{11}H_{14}^{-}$ and $B_{12}H_{12}^{2-}$ are never formed in the same ratios at any one time. The distribution of these species during the pyrolysis of a Et_4NBH_4 suspension in a decane–dodecane mixture is given in Fig. 3. Similar results are obtained for the 1:1 Et_4NBH_4–Et_3NBH_3 mixture, but the rate is faster. The percentage of $B_{12}H_{12}^{2-}$ is highest at the beginning of the reaction; the conversion of $B_3H_8^-$ takes place in the presence of a large amount of Et_4NBH_4. The formation of $B_{10}H_{10}^{2-}$ is favoured when most of the Et_4NBH_4 has reacted and when the Et_3NBH_3 concentration in the reaction mixture is high. $B_9H_9^{2-}$ is mostly obtained by conversion of $B_3H_8^-$ without significant involvment of Et_4NBH_4 or Et_3NBH_3 (the result of the $Et_4NB_3H_8$ pyrolysis in Table II confirms this interpretation). There is no maximum value for the formation of $B_{11}H_{14}^-$. After five hours reaction time there is less

$B_3H_8^-$ in the reaction mixture, and so the rate of the formation of condensed hydroborates decreases, but the distribution of these species varies. Due to the presence of Et_3NBH_3 and perhaps Et_4NBH_4, a conversion of $B_9H_9^{2-}$ to $B_{10}H_{10}^{2-}$ and a less rapid conversion of $B_{10}H_{10}^{2-}$ to $B_{12}H_{12}^{2-}$ take place. To form $B_{12}H_{12}^{2-}$ in a good yield, the last stage of the pyrolysis must be carried out in the presence of an excess of Et_3NBH_3 (this can be added to the reaction mixture). The maximum $B_{10}H_{10}^{2-}$ yield (about 55%) is more difficult to obtain owing to kinetic effects.

Comparison of the Pyrolysis Processes

The formation of $B_9H_9^{2-}$ and $B_{11}H_{14}^-$ has not been discussed in earlier work for two reasons: (i) they were obtained by pyrolysis at atmospheric pressure in the absence of solvent in too low a concentration to be characterized [1, 11], and (ii) in other cases they were destroyed in the pre-treatment before analysis [5]. More recently, after having characterized these reductive species in the pyrolysis products, Hill [8] found conditions to avoid their formation and to obtain $B_{10}H_{10}^{2-}$ quantitatively. He pyrolysed small amounts of Et_4NBH_4 (purity 98%) in metallic reactors in order to control the temperature during the exothermic phase of the reaction. We have not been able to reproduce these results and, in common with Sayles [9], have always obtained hydroborate mixtures. The condensed hydroborates were not quantitatively produced in the pyrolysis performed by Sayles in the presence of Et_3NBH_3 or mineral oil. The complete conversion that we obtain on refluxing decane–dodecane mixtures is due to an efficient evacuation of Et_3N from the reaction mixture. An other advantage of this process is that it can be used either for large- or small-scale pyrolysis.

On amounts greater than 100 g, the pyrolyses performed without solvent present were difficult to carry out owing to the exothermic stage at the start of the reaction. At atmospheric pressure (Table III), Et_3N is only partly removed from the reaction mixture, and enough Et_3NBH_3 is produced to form $B_{12}H_{12}^{2-}$ in good yield during the last part of the pyrolysis. More $B_{10}H_{10}^{2-}$ can be converted to $B_{12}H_{12}^{2-}$ with longer reaction times. Pyrolysis at 40 torr gives, with a slightly lower yield, the same distribution of hydroborates as the pyrolysis in decane–dodecane mixtures. In both cases Et_3NBH_3 remains in the reaction mixture whereas Et_3N is removed. At 10^{-2} torr, the percentage of $B_{12}H_{12}^{2-}$ in the final product is higher than at 40 torr because the conversion of the intermediate $B_3H_8^-$ occurs mainly by reaction with Et_4NBH_4.

Experimental

Starting Materials

Et_4NBH_4 was prepared from KBH_4 (Prolabo) by exchange on a cationic resin (Duolite C 20), as reported previously [14]. Purification was carried out by dissolving in CH_3CN and precipitation with diethylether. The product was subsequently recrystallised from isopropanol. Titration by IO_3^- [15] indicated at least 98% purity. Et_3NBH_3 was obtained from Aldrich. NaB_3H_8 was prepared from $NaBH_4$ and Et_2OBF_3 [12] and converted to $Et_4NB_3H_8$ by metathesis.

Decane and dodecane (Prolabo) were dried on $LiAlH_4$ before use and were mixed in suitable proportions to give a particular boiling point.

All the chemicals were handled in an inert atmosphere using a glove box or nitrogen blanket.

Pyrolysis in Decane–Dodecane Mixtures

An Et_4NBH_4 suspension was pyrolysed in a three-necked round bottom flask connected to a 20-plate distillation column. The reaction vessel was placed in an oil bath. The mixture was stirred with a mechanical stirrer and the temperature was measured in the flask and at the head of the column. The triethylamine produced during the reaction was collected in a trap. The apparatus could be connected to vacuum, or to an inert gas inlet or a mercury manometer for the escape of the gas formed during the reaction (H_2, C_2H_6). The solid products were collected by filtration and washed with diethylether prior to being dried under vacuum. Et_4NBH_4 and the solvent mixture could be used over a range of proportions (from 2.5 cm^3 to 10 cm^3 of liquid per gram of Et_4NBH_4) without notable changes in the results of the pyrolysis.

Pyrolysis without Solvent

Et_4NBH_4 was pyrolysed in a pyrex pipe reactor; and the volatile compounds were condensed in a trap cooled by liquid air. The temperature was gradually increased to 185 °C, especially over 150–185 °C region in order to avoid a too vigourous start to the reaction. For pyrolysis on a 100 g scale, 3 h were necessary to reach 185 °C. The pyrolysis products were washed with diethylether and dried under vacuum before analysis.

Analysis

Qualitative results concerning the distribution of hydroborates were obtained from IR spectra (nujol mulls), but the percentages were determined from the ^{11}B NMR spectra recorded on an XL-100 Varian instrument at 32.1 MHz. A chemical titration was used for Et_3NBH_3. The amine borane was first oxidised by hydrogen peroxide in a basic medium, followed by a second stage involving titration of the boric acid in an acidic medium as usual [16].

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