Pyrolysis of Di(isobutylamino)phenylboron

By J. A. Semlyen and P. J. Flory

When di(isobutylamino)phenylboron is pyrolysed, isobutylamine is eliminated and the trimer, *B*-triphenyl-*N*-tri-isobutylborazine, is produced. Contrary to claims in the literature, the pyrolysis does not provide a route to linear boron–nitrogen polymers.

ALTHOUGH boron–nitrogen chemistry is dominated by the ease with which the trimeric borazine ring is formed, it has been claimed that highly branched substituents suppress trimer formation by their steric influence, and thus favour the production of linear boron–nitrogen polymers. Burch, Gerrard, and Mooney [1] reported that linear condensates of the type $(PhB{\cdot}NR)_n$ (R = Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, or Bu^t) were produced by heating the corresponding $Ph{\cdot}B(NHR)_2$ compounds at 265—310° for 30—50 hr. These reactions have been interpreted as simple condensation polymerisations,[2,3] and average chain lengths of 20—40 units were estimated from viscosity measurements.[4] The proportion of amine eliminated from the various propyl and butyl derivatives was greatest for the isobutyl compound.[1] This fact would suggest that the polymer produced from the isobutyl compound should have the highest molecular weight.[5]

Contrary to these reports, we have found that the pyrolysis of $Ph{\cdot}B(NHBu^i)_2$ is not an exception to the rule that bis(amino)boranes yield borazines upon heating. The pyrolysis of di(isobutylamino)phenylboron at 260—315° proceeds with slow elimination of isobutylamine, but linear boron–nitrogen condensates could not be identified in the products. Instead, *B*-triphenyl-*N*-tri-isobutylborazine was formed. That linear condensates are produced by heating other bis(amino)-phenylboranes, $Ph{\cdot}B(NHR)_2$ with R = Pr^n, Pr^i, Bu^n, Bu^s, Bu^t, therefore appears questionable.

Samples of the starting material were prepared by the reaction of phenylboron dichloride and isobutylamine both in n-pentane and in diethyl ether,[1] in order to ensure that the origin of the samples would not influence the course of the reaction. Isobutylamine was eliminated more slowly than reported by Burch *et al.*,[1] and contrary to their findings appreciable amounts of benzene and a compound $C_8H_{17}N$ were eliminated in the pyrolyses. There is evidence that the production of benzene may be catalysed by impurities in the sample.

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[1] J. E. Burch, W. Gerrard, and E. F. Mooney, *J. Chem. Soc.*, 1962, 2200.

[2] F. G. R. Gimblett, "Inorganic Polymer Chemistry," Butterworths, London, 1963, p. 421.

[3] W. R. Moore, "An Introduction to Polymer Chemistry," University of London Press, 1963, p. 208.

[4] K. A. Andrianov, "Metalorganic Polymers," Interscience Publishers, New York, 1965, p. 357.

[5] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, 1953, ch. 8.

EXPERIMENTAL

Preparation of Ph·B(NHBu^i)$_2$.—Isobutylamine and phenylboron dichloride (in the mole ratio 4 : 1) were allowed to react in (i) n-pentane and (ii) diethyl ether at −60° under dry nitrogen. Isobutylamine hydrochloride was recovered in quantitative yields [Found (from reaction i): C, 43·5; H, 10·6; Cl, 31·9; N, 12·7; (from reaction ii): C, 43·9; H, 10·8; Cl, 31·4; N, 12·6. Calc. for $C_4H_{12}ClN$: C, 43·8; H, 11·0; Cl, 32·4; N, 12·8%]. After removal of the solvent, Ph·B(NHBu^i)$_2$ was distilled on a vacuum line and chemically analysed [Found (from reaction i): C, 72·2; H, 10·8; N, 11·8%; yield 32%; n_D^{20} = 1·4929; (from reaction ii): C, 72·3; H, 10·7; N, 11·5%; yield 54%; n_D^{20} = 1·4931. Calc. for $C_{14}H_{25}BN_2$: C, 72·4; H, 10·9; N, 12·1%]. Both the infrared and proton nuclear magnetic resonance spectra of the two Ph·B(NHBu^i)$_2$ samples were similar in all features and in agreement with the spectra expected.

Pyrolyses.—The samples of Ph·B(NHBu^i)$_2$ were pyrolysed in glass flasks on a vacuum line under dry nitrogen at reduced pressure (~0·5 atm.). Any volatile liquids formed were allowed to distil from the samples and condense in traps at −80°. No attempt was made to isolate any permanent gases produced. All manipulations were in a nitrogen dry-box from which oxygen and moisture were excluded.

Molecular Weight.—Number-average molecular weights were determined in chloroform or benzene using a Mechrolab model 301A vapour pressure osmometer.

Infrared Spectra.—These were recorded in carbon tetrachloride solution on a Perkin-Elmer 221 spectrophotometer between 2 and 12 μ.

Proton Nuclear Magnetic Resonance Spectra.—Varian A60 and HR100 spectrometers were used. Chemical shifts were measured in carbon tetrachloride relative to tetramethylsilane.

Mass Spectra.—Atlas CH4 and CEC 21–103C mass spectrometers were used.

Gas Chromatography.—Analytical gas chromatography was carried out in columns of 20% Silicone SF 96 on Chromosorb W at 90° and 15% Carbowax 20M on firebrick at 100° with helium as carrier gas. Katharometers and flame ionisation detectors were used for detection. Compounds were characterised by their relative retention times, t_R (benzene 1·00).

RESULTS AND DISCUSSION

Pyrolysis of Di(isobutylamino)phenylboron.—Samples were pyrolysed at 260—315° for several days (Table 1). The liquids eliminated were analysed as described below. The residues were clear yellow liquids at 300°; they crystallised slowly on cooling. After pyrolysis (*A*), 0·18 g. of the starting material was recovered, and identified by infrared and proton nuclear magnetic resonance spectra. No attempt was made to recover Ph·B(NHBu^i)$_2$ after pyrolysis (*B*).

Composition of the Liquid Fractions Eliminated.—(i) The infrared spectra of each of the liquid fractions showed bands characteristic of isobutylamine, and less intense bands characteristic of benzene. Isobutylamine and benzene (mixed in the mole ratio 10 : 1) gave a similar spectrum to those of the liquid fractions produced by pyrolysis (*A*). A band at 1665 cm.$^{-1}$ was observed in the spectra of some of the fractions from pyrolysis (*B*). This band was most intense in the spectrum of the last fraction.

(ii) The proton n.m.r. spectra of some of the liquid fractions were measured. All showed bands characteristic of benzene and isobutylamine. Integration of the peak areas gave the relative proportions of the constituents. The last fraction from pyrolysis (*B*) showed isobutyl proton resonance bands in its spectrum with different chemical shifts from the corresponding bands in the spectra of isobutylamine and di-isobutylamine.

TABLE 1

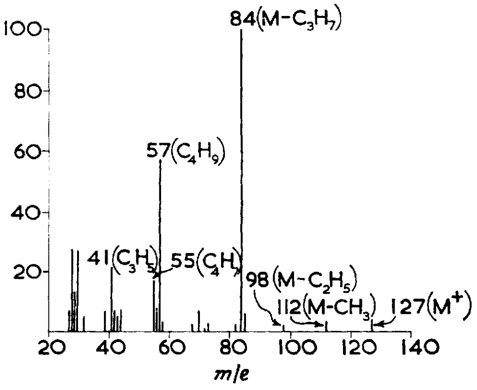
Pyrolysis (*A*) 5·18 g. of Ph·B(NHBu^i)$_2$ prepared in n-pentane (n_D^{20} = 1·4929)

Pyrolysis		Weight of liquid eliminated (g.)	Composition (mole %) of liquid fractions (*A*)		
Temp.	Time (hr.)		Bu^{i}NH$_2$	Benzene	Other compounds
260°	50	0·26	89	9	2
270	25	0·18	86	11	3
300	50	0·63	90	9	1
300	50	0·50	84	12	4
Residue (*A*) 3·23 g.					
Pyrolysis (*B*) 4·60 g. of Ph·B(NHBu^i)$_2$ prepared in diethyl ether (n_D^{20} = 1·4931)					
280	50	0·46	92	2	6
290	24	0·26	91	4	5
290	52	0·29	93	5	2
310	52	0·35	73	17	10
315	24	0·04	41	15	44
Residue (*B*) 3·11g.					

(iii) The mass spectra of the second and third liquid fractions from pyrolysis (*A*) showed molecular ions characteristic of isobutylamine and benzene. Ions of mass numbers 127, 112, 98, and 84 were also found, the last being the most intense. These may correspond to the molecular ion of $C_8H_{17}N$ and the fragments formed from it by the loss of methyl, ethyl and isopropyl groups. No ions of *m*/*e* greater than 127 were observed.

(iv) Gas chromatography was used to separate the components of the liquid fractions, and their approximate mole percentages were estimated from peak areas (Table 1). Isobutylamine and benzene were identified by their retention times in the polar Carbowax column, and in the less polar Silicone column. In addition, pure samples of both constituents were isolated by preparative gas chromatography and their nature established from infrared spectra.

Gas chromatography showed that, in addition to isobutylamine and benzene, only one other component was present in all fractions in appreciable amounts (>1%). In the last fraction from pyrolysis (*B*) it was the largest constituent of the mixture. Its relative retention time in the Silicone column is 3·33, and it is retarded relative to benzene in Carbowax (t_R = 5·60). The compound was isolated by preparative gas chromatography. Its smell is lachrymatory and amine-like. Its mass spectrum (Figure) indicated that it is probably an unsaturated amine, of empirical formula $C_8H_{17}N$, corresponding to di-isobutylamine with the loss of one hydrogen molecule. Its infrared spectrum agrees with this; a strong band at 1665 cm.$^{-1}$ may correspond to either a C=C or C=N stretching mode. Both $(CH_3)_2CH{\cdot}CH{=}N{\cdot}Bu^i$ and $(CH_3)_2C{=}CH{\cdot}NHBu^i$ are in agreement with the spectroscopic evidence, and either or both may be present in the pyrolysis mixtures.



Traces of two other compounds were found in some fractions. These have relative retention times of 2·63 and 4·27 in the Silicone column. One of them may be di-isobutylamine which also has a retention time of 4·27 in this column.

Nature of Residue (A).—The solid residue (*A*) (Table 1) was soluble in warm carbon tetrachloride. On cooling it precipitated as a white solid, melting over the range 25—131°. Its number-average molecular weight (in $CHCl_3$) was 365.

(i) The infrared spectrum of residue (*A*) shows C–H stretching bands characteristic of phenyl and isobutyl groups in the region 3100—2800 cm.$^{-1}$. There is no band in the N–H and B–H stretching regions. The most intense vibrational modes in the remainder of the spectrum lie at 1407 and 702 cm.$^{-1}$, and both have shoulders on the high-frequency side. No other band of appreciable intensity is present in the region 800—500 cm.$^{-1}$.

(ii) The proton nuclear magnetic resonance spectrum of (*A*) shows an unresolved band due to phenyl group protons, and bands with coupling patterns characteristic of *N*-isobutyl group protons (Table 2). No N–H proton resonance band was observed. The ratio of the peak areas of the responses due to the isobutyl and phenyl group protons was 1·87 (±0·02) : 1; Calc. for $B_3Ph_3N_3Bu^i{}_3$: 1·80 : 1. The difference may be due in part to elimination of benzene in the pyrolysis.

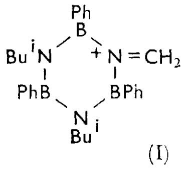
A solution of residue (*A*) in carbon tetrachloride was shaken with excess of deuterium oxide, and the proton nuclear magnetic resonance spectrum was monitored on the 100 Mc./sec. spectrometer. No change in the spectrum was observed with the sample after 60 min., and after three days only about 40% of the sample had deuterolysed. This behaviour is in contrast to that of di(isobutylamino)phenylboron which under similar conditions was completely deuterolysed in less than 30 sec. A borazine with three phenyl groups and three isobutyl groups attached to its ring would be expected to hydrolyse very slowly.[6]

(iii) The mass spectrum of the solid residue (*A*) shows a molecular ion of mass 477 corresponding to the borazine $B_3Ph_3N_3Bu^i{}_3$. The spectrum is dominated by a more intense fragment of (*m*/*e*) 434. This may correspond to the loss of an isopropyl group from the borazine, with formation of (I). By analogy with other nitrogenous ring compounds,[7] (I) would be expected to be a stable fragment in the mass spectrum of $B_3Ph_3N_3Bu^i{}_3$. The absence of mass ions at 159 and 318 indicates that the molecular ion corresponding to the borazine nucleus was not produced by random fragmentation of long-chain condensation polymers, $(PhB{\cdot}NBu^i)_n$, for fragments corresponding to $n = 1$ and $n = 2$ would be expected to be at least as abundant as those corresponding to $n = 3$. Ions of *m*/*e* 420, 390, 356, 312, 278, and 190 are present. Their origin may have been the borazine or other compounds formed in the pyrolysis.

TABLE 2

Chemical shifts (τ-values)

		$>$N-isobutyl		
	$>B{-}C_6H_5$ (unresolved multiplet)	$>N{-}CH_2{-}$ (doublet)	$-CH<$ (multiplet)	$-<{CH_3 \atop CH_3}$ (doublet)
$Ph{\cdot}B(NHBu^i)_2$	$2{\cdot}7_7$	$7{\cdot}3_5$	$8{\cdot}4_3$	$9{\cdot}1_2$
$B_3Ph_3N_3Bu^i{}_3$	$2{\cdot}7_0$	$7{\cdot}1_7$	$8{\cdot}7_7$	$9{\cdot}5_4$



(I)

Spectroscopy indicates, that residue (*A*) is mainly *B*-triphenyl-*N*-tri-isobutylborazine. Its symmetrical isomer, *B*-tri-isobutyl-*N*-triphenylborazine, was prepared by Groszos and Stafiej.[8]

Isolation of B-*Triphenyl*-N-*tri-isobutylborazine*.—A sample of the trimer was isolated from residue (*A*) by dissolving it in warm n-pentane and allowing the solution to cool whereupon a crop of white crystals separated. Trimer was obtained from residue (*B*) by dissolving 3 g. of it in chloroform and precipitating the timer with ethyl alcohol. A single recrystallisation gave 1·2 g. of $B_3Ph_3N_3Bu^i{}_3$. The samples were characterised by chemical analyses and molecular weight (Table 3).

Small amounts of a brown oil were separated from residue (*B*). This gave the residue its light yellow colour.

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[6] R. J. Brotherton and A. L. McCloskey in "Boron–Nitrogen Chemistry," Advances in Chemistry Series, No. 42, American Chemical Society, 1964, p. 131.

[7] A. M. Duffield, R. Beugelmans, H. Budzikiewicz, D. A. Lightner, D. H. Williams, and C. Djerassi, *J. Amer. Chem. Soc.*, 1965, **87**, 805.

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Quantities of the starting material $Ph\cdot B(NHBu^i)_2$ were found on the walls of both reaction flasks at the end of the pyrolyses. These hydrolysed rapidly on exposure to air and isobutylamine and phenylboric acid were formed. No dimeric, tetrameric, or polymeric boron–nitrogen compounds were found in the residues.

TABLE 3

Characterisation of the borazine $B_3Ph_3N_3Bu^i_3$

From residue	M. p.	Found (%) C	H	N	B	M.W.*
A	135—135·2°	75·3	8·8	9·1	6·4	442
B	136·2—136·4	75·5	8·8	8·8	6·8	477
	Calc.	75·5	8·9	8·8	6·8	477

* Number-average, in benzene.

The infrared spectrum of the borazine was essentially the same as that of the solid residues (*A*) and (*B*). Its proton nuclear magnetic resonance spectrum was similar to that of residue (*A*) (Table 2). However, for the purified trimer the areas of bands due to isobutyl and phenyl group protons were in the ratio 1·82 : 1.

Elimination of Benzene in Pyrolysis.—This investigation leads us to different conclusions from those of Burch, Gerrard, and Mooney.[1] A striking difference is the very much smaller amount of amine eliminated from our samples of $Ph\cdot B(NHBu^i)_2$ when pyrolysed at 280° for 50 hr. One sample of di(isobutylamino)phenylboron, prepared in diethyl ether, had a higher refractive index than those of others ($n_D^{20} = 1\cdot4945$) (Found: C, 72·3; H, 10·6; N, 11·8%), and its pyrolysis at 280° for 50 hr. led to the elimination of about the same amount of isobutylamine as with the other samples, but with proportionally more benzene (68%) and other compounds (6%). The residue was a clear brown highly viscous gum, which spectroscopy indicated might be polymeric. Small quantities of impurities or by-products from the preparation appear to catalyse the rate at which benzene is eliminated in the pyrolysis. Radical polymerisation processes might then take place. The production of benzene by the pyrolysis of boron–nitrogen compounds containing $>B-Ph$ groups has been reported by several authors.[9,10]

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DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY,
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[9] H. C. Newsom, W. D. English, A. L. McCloskey, and W. G. Woods, *J. Amer. Chem. Soc.*, 1961, **83**, 4134.

[10] U.S. Borax and Chemical Corporation, *Chem. Abs.*, 1965, 7890f.