223. The Chromatography of Gases and Vapours. Part VII.* Some Substituted Borazoles.

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A number of alkyl borazoles have been prepared by reaction between lithium borohydride and a mixture of two alkylamine hydrochlorides, the products being separated by gas–liquid chromatography. Emphasis is laid on the identification of borazoles by gas-chromatographic retention data on squalane and Carbowax.

VERY few unsymmetrically substituted borazoles have been prepared.[1-3] The only reported syntheses of unsymmetrical *N*-alkylborazoles were achieved by Schlesinger, Ritter, and Burg,[4] who obtained *N*-methyl- and *NN'*-dimethyl-borazoles by pyrolysis of a mixture of the borane adducts from ammonia and methylamine. We have now found that all four possible products result on reaction between a mixture of two alkylamine hydrochlorides, $R{\cdot}NH_3Cl$ and $R'{\cdot}NH_3Cl$ ($R \neq R' =$ H, Me, Et, Pr^i, or Pr^n) and lithium borohydride. The mixtures of borazoles obtained have been examined by gas–liquid chromatography, with squalane and Carbowax as the stationary phases. A number of simple relationships which have been found for the borazole retention times suggest that a new borazole derivative may often be identified from gas-chromatographic data alone.

EXPERIMENTAL

Preparation of the Borazoles.—*N*-Alkylborazoles were prepared by the method of Schaeffer and Anderson.[5] Ammonium chloride (0·025 mole) and an alkylamine hydrochloride (0·025 mole) or two alkylamine hydrochlorides (0·025 mole of each) and lithium borohydride (0·05 mole) were used. The products from the pyrolysis were collected in a stream of dry nitrogen by means of a trap cooled in liquid oxygen, and the final traces were transferred from the reaction vessel to this trap by an oil-pump. Yields of mixed products were between 50% and 75%.

A mixture of tetra-, penta-, and hexa-methylborazole was prepared from tri-*N*-methylborazole, which was obtained as above, by the method of Smalley and Stafiej.[6] Trimethylborazole (0·76 g., 0·006 mole) in ether (15 ml.) was treated with methylmagnesium iodide [from magnesium (0·32 g. 0·013 mole) and methyl iodide (1·79 g., 0·012 mole)] and left overnight. After treatment of the residue with saturated ammonium chloride solution (1·25 ml.) and extraction with light petroleum (b. p. 30—40°) 0·93 g. (79%) of mixed products was obtained.

Preparation of Aromatic Hydrocarbons as Reference Substances.—The following hydrocarbons, required as reference compounds, were prepared by Norris and Rubenstein's method: [7] 5-ethyl- and 5-isopropyl-*m*-xylene, 3,5-diethyl- and 3,5-di-isopropyl-toluene, and 1,3,5-triethyl- and 1,3,5-tri-isopropylbenzene. The purity of these products was confirmed by gas chromatography on 13% squalane at 100°. Infrared spectra showed them to be the 1,3,5-substituted compounds, with characteristic bands at about 860 and 700 $cm.^{-1}$.[8]

Analytical Gas-chromatographic Apparatus.—Embacel (May and Baker; 60—100 mesh; acid-washed) was treated with hexamethyldisilazane as described by Bohemen *et al.*[9] to remove hydroxyl groups from this support. The analytical columns were 2 m. in length and 4 mm. in internal diameter. Two were packed, severally, with 4·0% and 13·2% squalane on treated

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* Part VI, *J.*, 1959, 18.

[1] Sheldon and Smith, *Quart. Rev.*, 1960, **14**, 200.
[2] Mikhailov, *Uspekhi Khim.*, 1960, 972.
[3] Lappert and Majumdar, *Proc. Chem. Soc.*, 1961, 425.
[4] Schlesinger, Ritter, and Burg, *J. Amer. Chem. Soc.*, 1938, **60**, 1296.
[5] Schaeffer and Anderson, *J. Amer. Chem. Soc.*, 1949, **71**, 2143.
[6] Smalley and Stafiej, *J. Amer. Chem. Soc.*, 1959, **81**, 582.
[7] Norris and Rubenstein, *J. Amer. Chem. Soc.*, 1939, **61**, 1163.
[8] McCaulay, *J. Amer. Chem. Soc.*, 1954, **76**, 2354.
[9] Bohemen, Langer, Perrett, and Purnell, *J.*, 1960, 2444.

Embacel, and the third with 13·2% Carbowax 4000 (May and Baker) on treated Embacel. Before the Carbowax column was used, a large injection of chlorotrimethylsilane was made on to it, to remove terminal hydroxyl groups from the column liquid. Each column was enclosed in a vapour jacket, which contained steam at 100°. Nitrogen was used as the carrier gas and was preheated. Tubes to the detector were electrically heated to prevent condensation. Flame-ionization detection was used for all analyses. An argon detector gave similar results, but gradually lost sensitivity owing to deposits on the anode. Capillary injection was employed.[10]

Preparative Gas-chromatographic Apparatus.—A column 2 m. in length and 18 mm. in internal diameter enclosed in a vapour jacket at 100° was used for preparative separations. The column was built in two sections, which were joined by a glass capillary U tube of 3 mm. internal diameter.[11] 13·5% Squalane coated on treated Embacel was the stationary phase.

Samples for injection were transferred under a vacuum to a U tube attached to the column, and injection was achieved by by-passing the nitrogen flow through this U trap and rapidly heating it to 200° in an oil-bath. The eluted vapours were condensed in traps attached to the column outlet; these traps formed part of a vacuum-system, and samples were transferred under a vacuum, after collection, in the usual way. About one part in 50 of the effluent gases was by-passed through a split stream to a flame-ionization detector, so that a simultaneous record of the collection was obtained.

Infrared Spectra.—Infrared spectra of individual borazoles separated on the preparative column were recorded on a Perkin-Elmer 21 infrared spectrophotometer between 2 and 12 μ. All other infrared spectra were measured on an Infracord spectrophotometer.

Nuclear Magnetic Resonance Spectra.—The spectrometer described by Lease, Richards, and Schaefer[12] was used for measurement of proton nuclear magnetic resonance spectra. Borazoles were dissolved in carbon tetrachloride and shifts measured relative to tetramethylsilane as internal standard.

Chemical Analyses.—Some of these were carried out in the Dyson Perrins Laboratory, South Parks Road, Oxford.

RESULTS AND DISCUSSION

Chromatogram Peaks and Products.—The chromatograms on 13% squalane at 100° showed that the reaction between a mixture of two alkylamine hydrochlorides, $R{\cdot}NH_3Cl$ and $R'{\cdot}NH_3Cl$ and lithium borohydride gave four products in the cases where R = Me and R = Et or Pr^i, and where R = Et and R' = Pr^i. A trace of ether remained from the preparations and appeared as an early peak. Two chromatogram records are reproduced in Fig. 1. However, when ammonium chloride was substituted for one of the amine hydrochlorides, with R' = Et, Pr^n, or Pr^i, only three peaks were obtained, together with the ether peak. There was no peak corresponding to borazole itself, but evidence was obtained that it was present and that it had approximately the same retention time as ether (see below).

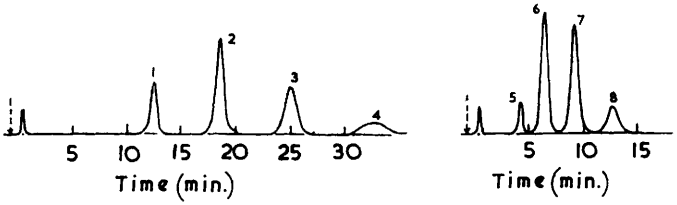

FIG. 1. Chromatograms of mixed borazoles.

Peak	Subst.	Peak	Subst.
1	Et_3	5	Me_3
2	Et_2Pr^i	6	Me_2Et
3	$EtPr^i_2$	7	$MeEt_2$
4	Pr^i_3	8	Et_3

As the correct number of volatile compounds was present in each product mixture,

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[10] Scott, "Vapour Phase Chromatography" (ed. Desty), Butterworths Scientific Publns., London, 1957, p. 131.

[11] Atkinson and Tuey, "Gas Chromatography, 1958" (ed. Desty), Butterworths Scientific Publns., London, 1958, p. 270.

[12] Lease, Richards, and Schaefer, *J. Sci. Instr.*, 1959, **36**, 230.

it is likely that these correspond, in increasing retention time, to $R_3N_3B_3H_3$, $R_2R'N_3B_3H_3$, $RR'_2N_3B_3H_3$, and $R'_3N_3B_3H_3$.

When two reactions were carried out with the same alkylamine hydrochloride as one reactant, peaks were present in each chromatogram which were common to both reactions, *e.g.*, triethylborazole in Fig. 1. As these were always the compounds of lowest or highest retention times, it is reasonable to assign these peaks to the symmetrically substituted borazoles, $R_3N_3B_3H_3$ and $R'_3N_3B_3H_3$. The identity of the tri-*N*-methylborazole peak was confirmed by injecting the sample from a preparation involving methylammonium chloride alone: only one peak was obtained, the retention time of which agreed with that found in other reaction products. Further evidence for the nature of the products was obtained from peak areas. If the two alkylamine hydrochlorides react at approximately the same rate, a statistical distribution of the products would be expected, *i.e.*, they would be obtained in the ratio 1 : 3 : 3 : 1. By assuming that relative peak areas are an approximate measure of the relative quantities of borazoles present, approximately this distribution was found for the Me–Et, Me–Pr^i, and Et–Pr^i mixed reactions. The flame-ionization detector, however, may not respond equally to all the components; with hydrocarbons the response of this detector depends largely on the number of carbon atoms in the component,[13] and it may therefore be most sensitive to borazoles with large alkyl groups. Thus in, for example, the H–Pr^i reaction products, the peak areas increase with increasing carbon number.

If the mixed products were shaken in ether with dilute hydrochloric acid they were hydrolyzed, and injection of the ether layer from time to time showed that the lowest-boiling components were destroyed most rapidly.

Confirmation of the Nature of the Separated Products.—In order to confirm the individual peak assignments, samples of the products of the mixed reactions were separated into their components by preparative gas-chromatography, and some of the individual substances were investigated in the following ways to determine their structure.

(*a*) *Infrared spectra.* Infrared spectra of the individual components of the H–Et, H–Pr^n, and Me–Et reaction products were examined in carbon tetrachloride solution. These spectra all showed characteristic borazole ring vibrations at *ca.* 1450 cm.$^{-1}$ and B–H stretching bands at *ca.* 2500 cm.$^{-1}$.[14] The spectra of *N*-ethyl-, *N*-n-propyl-, *NN'*-diethyl; and *NN'*-di-n-propyl-borazole also contained N–H stretching bands at *ca.* 3450 cm.$^{-1}$, but this band was absent from the spectra of the trisubstituted borazoles. In addition, a sample of *NN'N''B*-tetramethylborazole was trapped out and its infrared spectrum taken. The spectra of this compound and of tri-*N*-methylborazole were identical with those recently published.[15]

Infrared spectra of the mixture of products from each reaction showed bands which could be assigned to B–N ring vibrations, B–H stretching vibrations and, where expected, N–H stretching vibrations.

Borazole itself could not be separated from ether by the preparative gas-chromatographic apparatus. However, the infrared spectrum of the mixed ether–borazole fraction was examined, and showed bands at 3500 (N–H str.), 2500 (B–H str.), and 1460 cm.$^{-1}$ (B–N ring) confirming the presence of a borazole in this fraction.

(*b*) *Nuclear magnetic resonance spectra.* The proton nuclear magnetic resonance spectra of some of the products were examined, chemical shifts being measured relative to tetramethylsilane. In 10—25% carbon tetrachloride solution, the compounds gave spectra listed in Table 1 which were compatible with the proposed structure. For instance, the intensities of the bands due to *N*-methyl groups and CH_3 groups in the *N*-ethyl groups

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[13] Desty, Geach, and Goldup, " Gas Chromatography, 1960 " (ed. Scott), Butterworths Scientific Publns., London, 1960, p. 46.

[14] *E.g.*, Gerrard, " The Organic Chemistry of Boron," Academic Press, Inc., New York, 1961, p. 230.

[15] Wagner and Bradford, *Inorg. Chem.*, **1962**, **1**, 89.

in dimethylethylborazole were in the ratio 2 : 1. The chemical shifts agreed well with the values obtained by Ito, Watanabe, and Kubo[16] for *N*-alkyl groups attached to a borazole ring [$\tau(C_6H_{12})$ taken as 8·56[17]].

TABLE 1.

Chemical shifts (τ-values).

Borazole *N*-Deriv.	*N*-CH_3	*N*-Ethyl CH_3 triplet	*N*-Ethyl CH_2 quartet
Ethyl	—	$8{\cdot}8_6 \pm 0{\cdot}1$	$6{\cdot}6_5 \pm 0{\cdot}1$
Diethyl	—	$8{\cdot}8_6$	$6{\cdot}6_5$
Trimethyl	$6{\cdot}9_0$	—	—
Ethyldimethyl	$6{\cdot}9_5$	$8{\cdot}8_7$	$6{\cdot}7_0$
Diethylmethyl	$6{\cdot}8_8$	$8{\cdot}8_6$	$6{\cdot}6_6$
Literature[17]	$6{\cdot}9_6$	$8{\cdot}9_6$	$6{\cdot}5_8$

$J(CH_2/CH_3) = 7{\cdot}1$ c./sec.

(*c*) Molecular-weight determinations. The molecular weights of *N*-ethylborazole and isopropyldimethylborazole were measured by using a gas-density balance:[18]

	Found	Calc.
Ethylborazole	109·4, 111·0, 113·8, 111·4	108·4
Isopropyldimethylborazole	153·0	150·4

(*d*) *Chemical analyses.* As a further check on the order of elution of the mixed compounds, chemical analyses were performed on the suspected *ethyldimethylborazole* (Found: C, 35·5; H, 10·2; N, 29·7. $C_4H_9B_3N_3$ requires C, 35·2; H, 10·3; N, 30·8%) and *diethylmethylborazole* (Found: C, 40·0; H, 10·9; N, 28·0. $C_5H_{11}B_3N_3$ requires C, 39·9; H, 10·6; N, 27·9%).

(*e*) *Other evidence.* Boron compounds burn with an intense green flame. It was found that the flame of the flame-ionization detector became green simultaneously with the peak response when a boron compound passed through it. All the peaks assigned to alkylborazoles gave positive results with this test. In addition, when the products from reactions involving ammonium chloride were chromatographed, the flame of the detector became bright green just after the emergence of the ether peak, indicating that borazole itself was present in these samples.

The output gas-stream from the gas-chromatographic column[19] was bubbled through Nessler's reagent. When a borazole containing free N–H groups emerged from the column, it was hydrolyzed by the reagent solution to form ammonia, which was detected by the intense orange colour it produces with this reagent. Trialkylborazoles which were hydrolyzed to primary amines gave less definite colours, and gradually mercury was deposited.

Relative Retention Times on Squalane.—A plot of the logarithms of retention times of the borazoles and the corresponding aromatic hydrocarbons on 13% squalane at 100° against the number of carbon atoms in the alkyl side chains is shown in Fig. 2. Essentially the same relative retention times were obtained with 13% and 4% squalane columns at 100°.

The similarity between the two plots is very close. For example, the relative retention times for the substituents with three carbon atoms in the alkyl side chains are in both series in the order trimethyl > n-propyl > isopropyl. James and Martin[20] showed that for a homologous series

$$\frac{\text{Retention distance of the } (n+1)\text{th member}}{\text{Retention distance of the } n\text{th member}} = \text{a constant}$$

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[16] Ito, Watanabe, and Kubo, *J. Chem. Phys.*, 1961, **34**, 1043.

[17] Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 47.

[18] Phillips and Timms, *J. Chromatog.*, 1961, **5**, 131.

[19] Walsh and Merritt, *Analyt. Chem.*, 1960, **32**, 1378.

[20] James and Martin, *J. Appl. Chem.*, 1956, **6**, 105.

Values of this constant for some of the borazoles and the corresponding aromatic hydrocarbons are listed in Table 2, to show the close similarities between these two series.

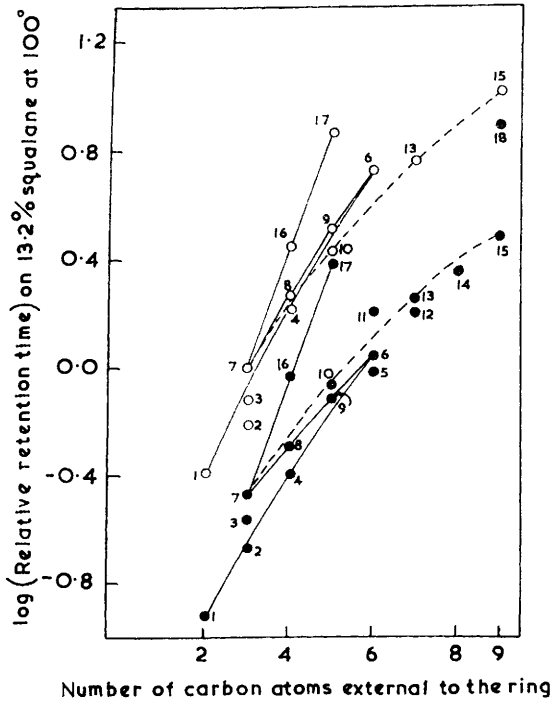

Fig. 2. Relative retention times on squalane at 100° for substituted borazoles (●) and substituted benzenes (○).

Peak	Subst.	Peak	Subst.
1	Et	10	Me$_2$Pr^i
2	Pr^i	11	Pr$^n_2$
3	Pr^n	12	Et$_2$Pr^i
4	Et$_2$	13	MePr$^i_2$
5	Pr$^i_2$	14	EtPr$^i_5$
6	Et$_3$	15	Pr$^i_3$
7	Me$_3$	16	Me$_4$
8	Me$_2$Et	17	Me$_2$
9	MeEt$_2$	18	Pr$^n_3$

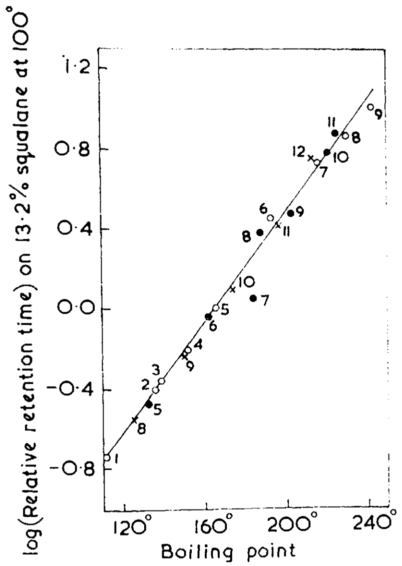

Fig. 3. Log (relative retention times) plotted against boiling points. For benzene (○) and borazole derivatives (●) the key is: 1, Me; 2, Et; 3, Me$_2$; 4, Pr^i; 5, Me$_3$; 6, Me$_4$; 7, Et$_3$; 8, Me$_5$; 9, Pr$^i_3$; 10, Me$_6$; 11, Pr$^n_3$. For n-alkanes (×) the numerals denote the number of carbon atoms.

The logarithms of the relative retention times for both aromatic hydrocarbons and those borazoles for which the boiling points have been estimated are plotted against the boiling points in Fig. 3. These lie fairly closely on a straight line except that triethylborazole has a shorter retention time than would be predicted from its boiling point.

TABLE 2.

Ratio of retention times for adjacent members of homologous series.

Substituents			Benzene	Borazole	Substituents			Benzene	Borazole
Me	Me	Me	—	—	Me	Pr^i	Pr^i	2·2	2·1
Me	Me	Et	1·8	1·7	Pr^i	Pr^i	Pr^i	1·8	1·7
Me	Et	Et	1·8	1·6	H	H	Et	—	—
Et	Et	Et	1·7	1·5	H	Et	Et	4·4	3·3
Me	Me	Pr^i	2·6	2·5	Et	Et	Et	3·1	2·8

The *N*-ethyl group has a slightly anomalous effect, as may be seen by a close comparison of the effect of an ethyl group on retention times in the borazole and in the aromatic series (Fig. 2). However, the boiling point of triethylborazole quoted depends upon a considerable extrapolation.

Relative Retention Times on Carbowax.—Carbowax 4000, a polyethylene oxide, was chosen as a second column liquid, as it is known to form hydrogen bonds with free N–H groups, for example, with pyrroles.[21] The borazoles investigated emerged in order of molecular weight; their identity was checked by comparing peak areas on Carbowax and squalane, by duplication of peaks, by injection of tri-n-propylborazole, and by re-injection of the H–Et and Me–Et series after the separate components had been trapped and their identity confirmed by nuclear magnetic resonance and infrared spectra.

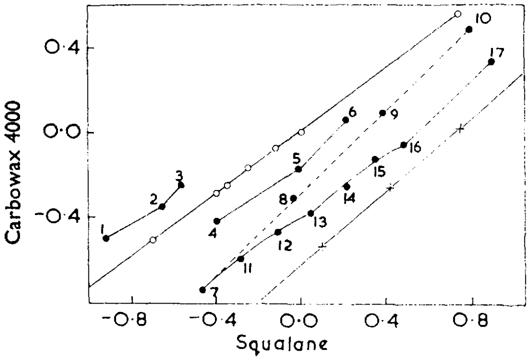

FIG. 4. Effect of hydrogen bonding: comparison of log (relative retention times) on Carbowax 4000 and on squalane (both with 13·2% at 100°). (○) Aromatic hydrocarbons. (×) Aliphatic hydrocarbons. (●) Borazoles, for which the key is: 1, Et; 2, Pr^i; 3, Pr^n; 4, Et_2; 5, Pr^i_2; 6, Pr^n_2; 7, Me_3; 8, Me_4; 9, Me_5; 10, Me_6; 11, Me_2Et; 12, $MeEt_2$; 13, Et_3; 14, Et_2Pr^i; 15, $EtPr^i_2$; 16, Pr^i_3; 17, Pr^n_3.

The logarithms of the relative retention times on Carbowax are plotted against the corresponding quantity on squalane in Fig. 4.

These results show that borazoles which contain free N–H groups are retarded by Carbowax, and it is suggested that this is caused by hydrogen bonding from these groups to the oxygen atoms of the column liquid. As expected, *N*-monoalkylborazoles which contain two free N–H groups are more strongly retarded than dialkylborazoles and both than trialkylborazoles.

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[21] Fessenden and Crowe, *J. Org. Chem.*, 1960, **25**, 598.