46. *Borazoles. Part II.*[1] *The Preparation of Methyl and Ethyl Derivatives of Borazole with the Aid of Alkyl-lithiums.*

By P. Powell, J. A. Semlyen, R. E. Blofeld, and C. S. G. Phillips.

Various methyl and ethyl derivatives of borazole have been synthesised in good yield by the action of alkyl-lithium on borazole and *N*-alkylborazoles. These compounds have been separated and identified by gas–liquid chromatography in squalane and Carbowax columns.

Introduction of alkyl and aryl groups into borazoles that contain >BH groups, by means of Grignard or lithium reagents, has been described by Smalley and Stafiej,[2] who carried out reactions on tri-*N*-phenyl- and tri-*N*-methyl-borazoles. Wagner and Bradford[3] recently reported the formation of *N*-alkylborazoles by a two-stage synthesis involving the *N*-lithio-derivatives. We have investigated a general synthetic route to methyl and ethyl derivatives of borazole. *N*-Alkylborazoles were prepared by Schaeffer and Anderson's method.[4] They were identified and, in some cases isolated, by the gas-chromatographic techniques already described.[1] Methyl- and ethyl-lithium reacted with these *N*-alkylborazoles to give the corresponding *B*-alkyl derivatives; in many cases substitution gave all the possible products. As no other volatile compounds were formed, identification was effected by gas chromatography alone. In order to confirm the chromatographic peak assignments, several of the compounds arising in the reactions were synthesised by independent routes. Their retention data were identical with those compiled from the alkyl-lithium reactions.

Experimental

Preparation of Starting Materials.—Simple and mixed Schaeffer–Anderson reactions[4] were used to prepare borazole and its *N*-methyl and *N*-ethyl derivatives. Mono- and di-*N*-ethylborazoles were isolated by preparative gas chromatography.

Methyl- and ethyl-lithium were prepared from lithium and alkyl halides in diethyl ether.

Gas-chromatographic Apparatus.—In addition to the apparatus previously described,[1] an analytical column with 1·8% of squalane on treated Embacel was constructed. This was used

[1] Phillips, Powell, and Semlyen, *J.*, 1963, 1202, regarded as Part I of the series.
[2] Smalley and Stafiej, *J. Amer. Chem. Soc.*, 1959, **81**, 582.
[3] Wagner and Bradford, *Inorg. Chem.*, 1962, **1**, 93.
[4] Schaeffer and Anderson, *J. Amer. Chem. Soc.*, 1949, **71**, 2143.

for the less volatile products. All retention figures were calculated relative to mesitylene. Good agreement between results on the 1·8% and the 13·2% squalane column was obtained.

Reaction between N-Alkylborazoles and the Lithium Reagents.—Freshly prepared alkyl-lithium in ether was added dropwise at room temperature to the borazole (0·1—0·5 ml.), in a nitrogen-filled dry-box. The reactions proceeded spontaneously, with evolution of heat and formation of a grey precipitate. Gas-chromatographic analyses were carried out by capillary injection of about 1 mg. of the product.

Estimation of Yields.—The gas-density detector responds linearly to the molar concentration of a component in a carrier gas, multiplied by the difference in the molecular weights of the component and the carrier gas.[5] This detector was used to calibrate the flame-ionisation detectors employed in the routine analyses. A comparison of peak areas given by the two detectors showed that response from the flame-ionisation detector is related approximately to the carbon content of a borazole.

Yields in the alkyl-lithium reactions were calculated from chromatograms by using both detectors. Mesitylene was added, as an internal standard, to the borazole before reaction. Measurements in six cases gave an average yield of 60%.

Preparation of Borazoles for Confirmatory Purposes.—Several borazoles formed in the alkyl-lithium reactions were synthesised by interaction of Grignard reagents and *B*-trichloroborazole (1, $B_3Me_3N_3H_3$; 2, $B_3Et_3N_3H_3$),[6] alkylchloroborazoles (3, $B_3Me_3N_3H_2Me$; 4, $B_3Me_3N_3HMe_2$; 5, $B_3Me_3N_3Me_3$; 6, $B_3Et_3N_3H_2Et$; 7, $B_3Et_3N_3HEt_2$; 8, $B_3Et_3N_3Et_3$; 9, $B_3Et_3N_3Me_3$),[7] or tri-*N*-methylborazole (10, $B_3H_2MeN_3Me_3$; 11, $B_3HMe_2N_3Me_3$; also 5).[1]

Agreement between the retention on squalane and Carbowax for a compound prepared in two ways was used to confirm its identity. In some cases the borazoles were isolated and their structure established by physical measurement and analysis. [1, 3, 8, 9, 10, m.p.s in close agreement with published values; [3,6,7] 1, 3, 4, 10, infrared spectra identical with those published; [13] 2, 8, 9, (infrared) and 1, 8, 9 (proton nuclear magnetic resonance spectra) in agreement with structures postulated].

Results and Discussion

Reactions.—Reaction between tri-*N*-methylborazole and methyl-lithium gave the three *B*-substituted products, $N_3Me_3B_3H_2Me$, $N_3Me_3B_3HMe_2$, and $N_3Me_3B_3Me_3$. Reaction with ethyl-lithium gave the corresponding products, $N_3Me_3B_3H_2Et$, $N_3Me_3B_3HEt_2$, and $N_3Me_3B_3Et_3$. The relative proportions of these products depended on the amount of alkyl-lithium added. When a mixture of both alkyl-lithium reagents was added, the resulting chromatogram (Fig. 1) showed three peaks in addition to those corresponding to borazoles prepared by the simple reactions. These were assigned to the mixed borazoles, $N_3Me_3B_3HMeEt$, $N_3Me_3B_3Me_2Et$, and $N_3Me_3B_3MeEt_2$; their retention times accord with values calculated from the " simple " *B*-alkyl derivatives of tri-*N*-methylborazole. A plot of logarithms of the relative retention times on squalane against carbon content (Fig. 2) shows a network of straight lines linking all these borazoles in well-defined series, which is evidence that they have been correctly assigned. Tri-*N*-ethylborazole behaved similarly, and substitution resulted in the formation of all the possible products. Borazole itself rapidly gave tri-*B*-alkylborazoles with alkyl-lithiums; however, when only a small quantity of methyl-lithium was used, the mono- and di-*B*-methylborazoles were formed.

Mono- and di-*N*-ethylborazole were isolated by preparative gas chromatography, and similar quantities of methyl-lithium and ethyl-lithium were added separately to each. With methyl-lithium rapid substitution occurred, giving only one product in each case, namely, $N_3EtH_2B_3Me_3$ and $N_3Et_2HB_3Me_3$, respectively. With ethyl-lithium, however, in addition to the starting materials, all the *B*-ethylborazoles appeared in the chromatograms.

When partially *N*-methylated or partially *N*-ethylated borazoles were treated with

[5] Phillips and Timms, *Analyt. Chem.*, 1963, **85**, 505; Timms, personal communication.
[6] Haworth and Hohnstedt, *J. Amer. Chem. Soc.*, 1960, **82**, 3860.
[7] Ryschkewitsch, Harris, and Sisler, *J. Amer. Chem. Soc.*, 1958, **80**, 4515.

alkyl-lithiums, several new compounds were identified in the chromatograms. In such mixtures borazole always formed its tri-*B*-alkyl derivatives, whereas the tri-*N*-alkylborazoles gave all three possible *B*-substituted products. The mono- and di-*N*-alkylborazoles gave one, two, or three derivatives depending on the reactants concerned.

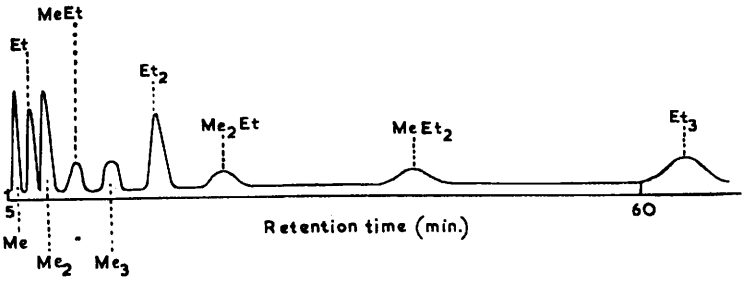

FIG. 1. Chromatogram on squalane at 100° of products from tri-*N*-methylborazole with a mixture of methyl-lithium and ethyl-lithium. The groups named on the plot are the *B*-substituents of the products.

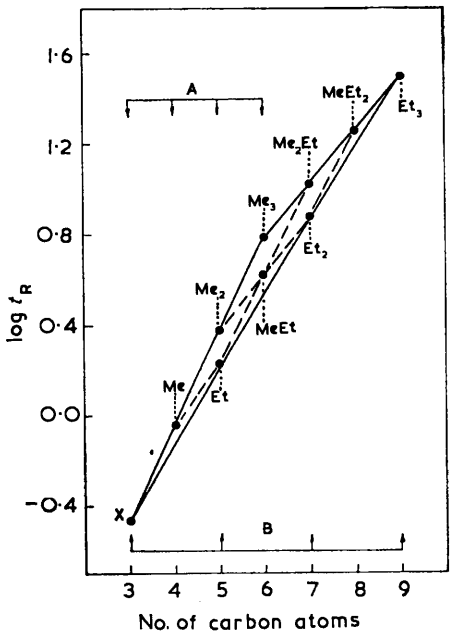

FIG. 2. Retention data, on squalane at 100°, of products from reaction of tri-*N*-methylborazole with (A) methyl-lithium and (B) ethyl-lithium. X = Unchanged tri-*N*-methylborazole; other symbols as in Fig. 1.

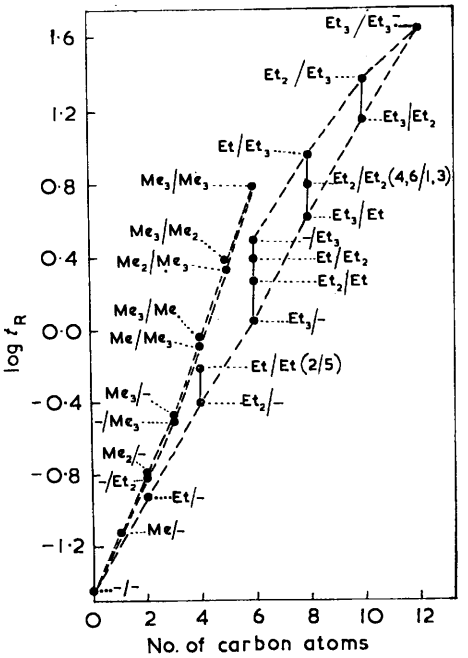

FIG. 3. Retention data on squalane at 100° for various methyl and ethyl derivatives of borazole. The first type of substituent named is on nitrogen, the second on boron; *e.g.*, Me_3/Et = tri-*N*-methyl-*B*-ethylborazole, $Me_2/-$ = di-*N*-methylborazole, $-/Et_2$ = di-*B*-ethylborazole.

E.g., mono-*N*-methylborazole and methyl-lithium formed only one product, $N_3H_2MeB_3Me_3$, whereas mono-*N*-ethylborazole with ethyl-lithium gave all three *B*-substituted products.

Separations.—A plot of the logarithms of retention times of " simple " methyl- and ethyl-borazoles on squalane against carbon number is shown in Fig. 3. As *N*-ethyl and *B*-ethyl groups have widely differing effects on the retention times, squalane is a suitable

Log (relative retention time) of some mixed alkylborazoles on squalane at 100°.

N-Subst.	Me	Me_2	Et	Et	Et_2	Et_2	Et_2	Et_3	Et_3
B-Subst.	Et_3	Et_3	Me_2	Me_3	Me	Me_2	Me_3	Me	Me_2
log t_R	0·83	1·19	−0·19	0·07	−0·07	0·23	0·60	0·39	0·75

stationary phase for separating and identifying ethylborazoles. On the other hand, *N*- and *B*-methylborazoles have similar retention times on this column. An efficient separation of the methyl series, however, is achieved on Carbowax (Fig. 4). It is thought that all these borazoles, except the tri-*N*-methyl derivatives, are specifically retarded owing to hydrogen bonding of free NH groups with oxygen atoms in the stationary phase,

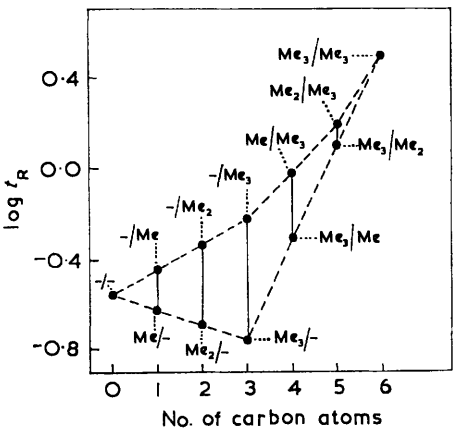

FIG. 4. Retention data on Carbowax at 100° for various methyl derivatives of borazole. Symbols as in Fig. 3.

so that replacement of NH by NMe reduces the retention time on the Carbowax column. The retention data of methyl- and ethyl-borazoles formed in the alkyl-lithium reactions and not appearing in the graphs are collected in the Table.

We are indebted to the Harmsworth Trust, Merton College, the D.S.I.R. (P. P.), and to the Salters' Company and Merton College (J. A. S.) for senior scholarships and maintenance grants. We thank Imperial Chemical Industries Limited for the loan of recorders, and Gow-Mac Ltd. for the gift of a gas-density balance.

INORGANIC CHEMISTRY LABORATORY,
THE UNIVERSITY, OXFORD.

[*Received, May 6th,* 1963.]