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Borazines. VI.[1] Reaction of Unsymmetrically 1,3,5-Substituted Borazines with Grignard Reagents. Identification of Position Isomers

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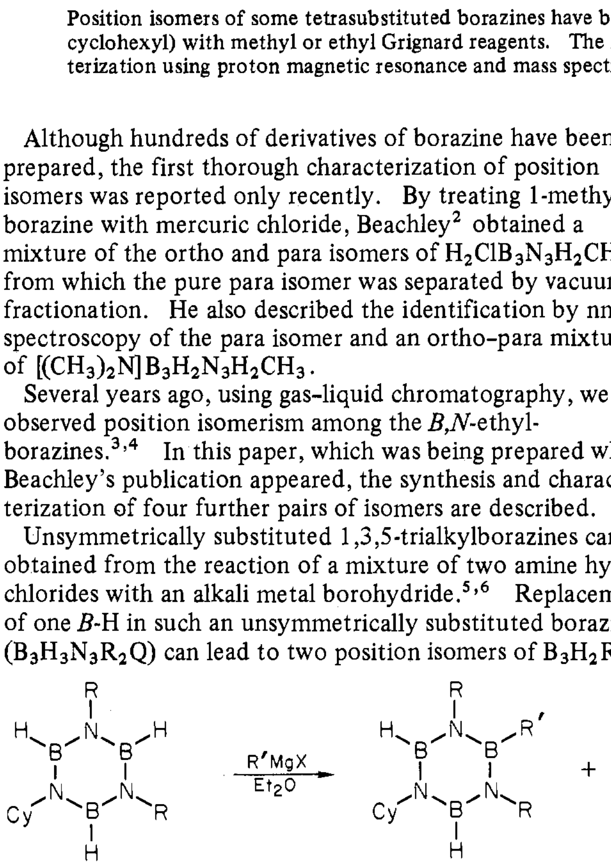
Position isomers of some tetrasubstituted borazines have been prepared by treating $B_3H_3N_3R_2Cy$ (where R = Me, Et; Cy = cyclohexyl) with methyl or ethyl Grignard reagents. The isomers were separated by gas chromatography. Their characterization using proton magnetic resonance and mass spectroscopy is discussed.

Although hundreds of derivatives of borazine have been prepared, the first thorough characterization of position isomers was reported only recently. By treating 1-methylborazine with mercuric chloride, Beachley[2] obtained a mixture of the ortho and para isomers of $H_2ClB_3N_3H_2CH_3$, from which the pure para isomer was separated by vacuum fractionation. He also described the identification by nmr spectroscopy of the para isomer and an ortho-para mixture of $[(CH_3)_2N]B_3H_2N_3H_2CH_3$.

Several years ago, using gas-liquid chromatography, we observed position isomerism among the *B,N*-ethylborazines.[3,4] In this paper, which was being prepared when Beachley's publication appeared, the synthesis and characterization of four further pairs of isomers are described.

Unsymmetrically substituted 1,3,5-trialkylborazines can be obtained from the reaction of a mixture of two amine hydrochlorides with an alkali metal borohydride.[5,6] Replacement of one *B*-H in such an unsymmetrically substituted borazine ($B_3H_3N_3R_2Q$) can lead to two position isomers of $B_3H_2R'N_3R_2Q$. Thus treatment of 1,3-dimethyl-5-cyclohexylborazine (I) or 1,3-diethyl-5-cyclohexylborazine (VIII) with a Grignard reagent in a 1:1 molar proportion affords two mono-B-substituted products in each case, which have been identified as the 2- and 4-substituted isomers B and C. Some of the disubstituted compound D is also obtained.

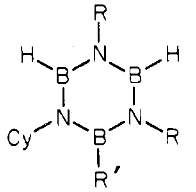


A

I, R = Me
VIII, R = Et

B

II, R = Me, R′ = Me
V, R = Me, R′ = Et
IX, R = Et, R′ = Me
XII, R = Et, R′ = Et



+ $B_3HR'_2N_3R_2Cy$

C

III, R = Me, R′ = Me
VI, R = Me, R′ = Et
X, R = Et, R′ = Me
XIII, R = Et, R′ = Et

D

IV, R = Me, R′ = Me
VII, R = Me, R′ = Et
XI, R = Et, R′ = Me
XIV, R = Et, R′ = Et

Table I. Analytical and Gas Chromatographic Retention Data[a]

Compd	Bp, °C (mm)	% calcd C	% calcd H	% calcd N	% found C	% found H	% found N
I	111-113 (14)	50.4	10.5	22.0	50.4	10.2	22.0
II	68-69 (0.25)	52.8	10.8	20.5	53.2	10.3	20.5
V	74-78 (0.05)	54.9	11.1	19.2	55.0	10.7	19.2
VIII	55-57 (0.01)	54.9	11.1	19.2	54.8	11.1	19.3
IX + X	70-75 (0.05)	56.8	11.3	18.0	56.8	11.3	18.1
XII		58.4	11.4	17.0	58.5	11.2	17.2
XIII		58.4	11.4	17.0	58.5	11.1	17.1
XIV		61.2	11.7	15.3	61.1	11.8	15.1

[a] Kovats indices (Silicone oil M.F.C. (Hopkin and Williams)) at 146°: I, 1420; II, 1580; III, 1535; IV, 1680; V, 1665; VI, 1595; VII, 1830; VIII, 1510; IX, 1635; X, 1600; XI, 1725; XII, 1720; XIII, 1665; XIV, 1855.

Compounds I and VIII were chosen as starting materials for the following reasons. First, on account of wide boiling point differences, they are readily separated pure by distillation from the other products ($B_3H_3N_3R_3$, $B_3H_3N_3RCy_2$, and $B_3H_3N_3Cy_3$) with which they are formed in their syntheses. Second, tri- and tetrasubstituted borazines, especially those bearing large substituents such as cyclohexyl, are much less susceptible to hydrolysis than the mono- and disubstituted compounds studied by Beachley.[2] Consequently conventional bench procedures could be used in this work, and, moreover, a commercial preparative gas chromatograph could be used without modification for the separation of products.

Very approximate proportions of products formed in these reactions, estimated by gas chromatography, show that while compound I is substituted largely in the 2 position (*ca.* 80% 2 isomer, 20% 4 isomer) by methylmagnesium iodide or ethylmagnesium bromide, compound VIII is attacked less selectively (*ca.* 60% 2 isomer, 40% 4 isomer). This is in agreement with the suggestion[7] that steric effects are important in determining the reactivity of 1,3,5-trialkylborazines toward Grignard reagents. In compound I substitution in the 2 position between the two *N*-methyl groups is favored, whereas in compound VIII the more similar steric requirements of ethyl and cyclohexyl groups lead to less discrimination between the 2 and 4 positions.

Characterization of the Borazines. The product mixtures obtained from the Grignard reactions were analyzed by gas-liquid chromatography on silicone oil columns. Kovats indices for the borazines are quoted in Table I. Individual

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(1) Part V: P. Powell, P. J. Sherwood, M. Stephens, and E. F. H. Brittain, *J. Chem. Soc. A*, 2951 (1971).

(2) O. T. Beachley, Jr., *J. Amer. Chem. Soc.*, 94, 4223 (1972).

(3) C. S. G. Phillips, P. Powell, J. A. Semlyen, and P. L. Timms, *Z. Anal. Chem.*, 197, 202 (1963).

(4) P. Powell, D.Phil. Thesis, Oxford, 1963.

(5) C. S. G. Phillips, P. Powell, and J. A. Semlyen, *J. Chem. Soc.*, 1202 (1963).

(6) O. T. Beachley, Jr., *Inorg. Chem.*, 8, 981 (1969).

(7) A. Grace and P. Powell, *J. Chem. Soc. A*, 673 (1966).

Table II. Major Ions in the Mass Spectra of the Borazines and Relative Intensities (in Parentheses) [m/e values of ^{11}B-Containing Species Only in Clusters of Ions Containing Three Boron Atoms]

	Species					
Compd	a molecular ion[a]	b $[a - C_3H_7]^+$	$[a - C_5H_9]^+$	$[a - CH_3]^{+\,b}$	$[a - C_2H_5]^+$	$[b - C_2H_4]^+$
I	191 (24)	148 (100)	122 (11)			
II	205 (26)	162 (100)	136 (10)	190 (1)		
III	205 (27)	162 (100)	136 (9)	190 (2)		
IV	219 (26)	176 (100)	150 (7)	204 (3)		
V	219 (27)	176 (100)	150 (5)		190 (4)	148 (13)
VI	219 (30)	176 (100)	150 (5)		190 (6)	148 (33)
VII	247 (36)	204 (100)	178 (3)		218 (9)	176 (28)
VIII	219 (24)	176 (100)	150 (7)			
IX	233 (25)	190 (100)	164 (6)	218 (13)		
X	233 (27)	190 (100)	164 (7)	218 (9)		
XI	247 (27)	204 (100)	178 (6)	232 (15)		
XII	247 (31)	204 (100)	178 (3)	232 (10)	218 (3)	176 (11)
XIII	247 (33)	204 (100)	178(4)	232 (4)	218 (6)	176 (31)
XIV	275 (40)	232 (100)	206(3)	260 (11)	246 (9)	204 (28)

[a] Some loss of H from molecular ion group observed (*cf.* ref 1). [b] For compounds IX–XIV, presumably loss of CH_3 from *N*-ethyl substituent.

components of the mixtures were separated by preparative gas chromatography and investigated by chemical analysis and nmr and ir spectroscopy.

Combined gas chromatography-mass spectrometry provided a useful method of establishing the composition of the borazines, although it did not distinguish between isomers. The mass spectra are entirely consistent with our previous observations on B- and N-substituted borazines.[1,8] In no case does the molecular ion form the base peak of the spectrum at 80 eV. The principal fragmentation pathway, which leads to the set of ions containing the base peak, involves loss of $C_3H_7\cdot$ or of $CH_3\cdot$ + ethylene from the cyclohexyl group of the molecular ion. This mode of cleavage is also characteristic of cyclohexylamines.[9]

For the *B*-ethyl compounds V, VI, VII, XII, XIII, and XIV this is followed by elimination of ethylene. Other significant losses from the molecular ions are (a) 69 mass units ($-C_5H_9$?), also characteristic of *N*-cyclohexylborazines, (b) 15 mass units ($-CH_3$ from *B*-CH_3 or *N*-CH_2CH_3 substituents), (c) 29 mass units ($-C_2H_5$ from *B*-C_2H_5 substituents). (See Table II.)

The mass spectra of pairs of isomers are similar; for compounds II and III they are essentially identical. Cleavages of *B*-ethyl substituents and ethylene loss, however, seem favored for the unsymmetrical isomers C.

The structures of the isomers follow, in three of the four examples, directly from the proton magnetic resonance spectra (Table III). Those of compounds V and VI are assigned mainly on the basis of gas chromatographic data by analogy with the other isomer pairs, compound VI eluting before compound V. In isomers of type B, the *N*-methyl or *N*-ethyl substituents are equivalent, whereas in those of type C, they are in slightly different environments, leading to observable chemical shift differences in the spectra of compounds III, X, and XIII.

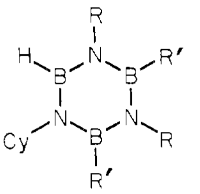
The α-carbon protons of *N*-cyclohexyl substituents show a broad resonance at $\tau \sim 6.9$, often largely obscured by the resonances from other *N*-alkyl substituents. The remaining ten protons of the cyclohexyl groups give rise to broad features in the region τ 8–9. The positions of the main maxima of these features only are noted in Table III. An empirical correlation between the shapes of these maxima and the environment of the cyclohexyl group seems to emerge. Where this substituent is flanked by two *B*-H atoms (as in compounds I, II, V, VIII, IX, and XII), the main cyclohexyl resonance shows only one main maximum at $\tau \sim 8.3$, while for the other compounds in which the substituent is flanked by one *B*-H atom and one *B*-alkyl group, the main band shows two close maxima in this region.

Table III. Proton Magnetic Resonance Spectra of the Borazines

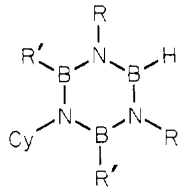
	N-Substituent resonances, τ		B-Substituent resonances, τ
Compd	*N*-R	*N*-Cy[a]	
I	6.95 (s)	8.33	
II	7.03 (s)	8.34	9.58 (s)
III	6.97 (s) 7.03 (s)	8.30, 8.35	9.57 (s)
IV	7.03 (s) 7.13 (s)	8.30, 8.35	9.57 (s)
V	7.00 (s)	8.32	9.01 (s)
VI	6.96 (s)	8.30, 8.36	9.01 (s)
VII	6.96 (s) 7.02 (s)	8.30, 8.37	9.02 (s) 9.04 (s)
VIII	6.70 (q), 8.88 (t)	8.32	
IX	6.68 (q), 8.88 (t)	8.34	9.50 (s)
X	6.68 (q), 8.84 (t) 6.72 (q), 8.89 (t)	8.28, 8.32	9.52 (s)
XI	6.71 (q), 8.91 (t) 8.94 (t)	8.30, 8.35	9.52 (s)
XII	6.68 (q), 8.87 (t)	8.30	9.01 (s)
XIII	6.69 (q), 8.84 (t) 6.73 (q), 8.86 (t)	8.30, 8.34	9.01 (s)
XIV	6.72 (q), 8.84 (t)[b]	8.28, 8.34	9.01 (s)

[a] See text. [b] Another closely overlapping triplet could also be present (J_{HH} for *N*-CH_2CH_3 is ~7 Hz).

In each of the four reactions studied, only one peak corresponding to a di-B-substituted compound was observed by gas chromatography. The ^1H nmr spectra of IV and VII were consistent with the presence of only one isomer, of type E, in these fractions. The disubstituted derivatives XI and XIV however, while consisting mainly of isomer E, could



E



F

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(8) E. F. H. Brittain and P. Powell, unpublished work.

(9) D. Goldsmith, D. Becher, S. Sample, and C. Djerassi, *Tetrahedron, Suppl.*, No. 7, 145 (1966).

on the basis of their nmr spectra contain a minor proportion of the symmetrical isomer F. This would mean that the two isomers are not resolved by gas chromatography under the conditions tried.

Noticeable differences in the infrared spectra of isomers were observed. These differences, however, cannot be interpreted on the basis of the limited evidence available at present. The spectra are consistent with the proposed structures.[10]

It has been reported recently[11] that unsymmetrically substituted borazines such as *B*-phenylpentamethylborazine undergo exchange of B substituents on distillation. No evidence of such exchange of *B*-alkyl and *B*-H substituents during distillation, gas chromatography or on standing at room temperature was obtained for the compounds described here. The purity of nmr samples was always checked by gas chromatography and was at least 96% and usually 99%. Exchange of substituents under more forcing conditions than those described here, however, was not investigated.

Experimental Section

All preparations were carried out under dry nitrogen. Solvents were dried by standard methods.

Preparation of the B-Substituted Borazines. In a typical reaction, 1,3-dimethyl-5-cyclohexylborazine[8] (6.5 g, 0.025 mol) in diethyl ether (75 ml) was treated dropwise with stirring with Grignard reagent [from magnesium (0.72 g, 0.03 mg-atom) and methyl iodide (4.2 g, 0.03 mol) in ether (75 ml)]. The reaction mixture was stirred at room temperature for 24 hr. Ether was removed under reduced pressure and the residue extracted with petroleum ether (bp 40–60°) (three 50-ml portions). The insoluble magnesium compounds were filtered off and washed with petroleum ether. The filtrate was evaporated and the residue was distilled to give a fraction, bp 66–72° (0.25 mm) (4.65 g), consisting mainly (*ca.* 80%) of compound II but also containing I, III, and IV. Yields in general were of the order of 65–75%.

Gas Chromatographic Apparatus. Analytical Apparatus. A Pye Unicam 104 Model 24 gas chromatograph with flame ionization detectors (nitrogen carrier gas) was fitted with columns (1.5 m long and 4 mm in internal diameter) packed with 10% silicone oil M.F.C. (Hopkin and Williams) on Celite, treated with hexamethyldisilazane.

Preparative Apparatus. A Pye Unicam 105 gas chromatograph was used, fitted with a column (3 m long and 1 cm in internal diameter) packed with 15% silicone oil on treated Celite. The column temperature was 190° and the nitrogen flow rate was about 180 ml/min. Solutions (50% v/v) of the distilled reaction mixtures were made up in petroleum ether (bp 40–60°). Several injections were required to obtain sufficient material for the various measurements. Only small quantities of compounds III, IV, VI, VII, and XI were obtained even after repeated injection and collection cycles, as these components were present only in low proportion (<10%) in the reaction mixtures. Chemical analyses for these compounds were thus not obtained, although they were well characterized by other methods. As the separation of compounds IX and X was especially tedious on account of their rather similar retention times, analyses for a mixture of these isomers are presented (Table I).

Combined Gas Chromatography–Mass Spectrometry. Mass spectra were recorded on a Hitachi Perkin-Elmer RMS4 mass spectrometer at 80 eV, chamber temperature 170°. Samples were introduced *via* a gas chromatograph (Perkin-Elmer F11) containing a column (1.5 m × 1-mm i.d.) packed with 10% silicone oil on Celite (80–120 mesh) at 150°. The temperature of the molecular separator (Watson-Biemann type) was 165°.

Nuclear Magnetic Resonance Spectra. Proton resonance spectra were obtained using a Varian HA-100 spectrometer at 100 MHz. Borazines were dissolved in carbon tetrachloride and chemical shifts were measured relative to internal tetramethylsilane.

Chemical Analyses. These were carried out by Dr. A. Bernhardt, Elbach uber Engelskirchen, West Germany.

Registry No. MeMgI, 917-64-6; EtMgBr, 925-90-6; I, 38126-09-9; II, 38126-11-3; III, 38126-12-4; IV, 38126-05-5; V, 38126-13-5; VI, 38126-14-6; VII, 38126-06-6; VIII, 38126-10-2; IX, 38126-15-7; X, 38126-16-8; XI, 38126-32-8; XII, 38126-17-9; XIII, 38126-04-4; XIV, 38126-33-9.

Acknowledgments. I am grateful to Dr. D. Gillies for recording the nmr spectra. A grant from the Central Research Fund, University of London, to purchase the analytical gas chromatograph used in this work is acknowledged with thanks.

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[10] A. Meller, *Organometal. Chem. Rev.*, **2**, 1 (1967).

[11] L. A. Melcher, J. L. Adcock, and J. J. Lagowski, *Inorg. Chem.*, **11**, 1247 (1972).

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Optimized Self-Consistent-Field and Localized Molecular Orbital Studies of Tetraborane(4)

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The wave function for B_4H_4 has been computed in the SCF-LCAO-MO approximation. Slater-type orbital exponents and the boron–boron distance have been optimized. The calculation shows that B_4H_4 should be stable by 316.9 kcal/mol with respect to dissociation to form BH units. The Mulliken charges are +0.0046 e on the borons and −0.0046 on the hydrogens. Calculation of localized molecular orbitals for B_4H_4 using the *ab initio* Edmiston–Ruedenberg procedure yields four central three-center B–B–B bonds localized in the faces of the tetrahedron. These bonds are, surprisingly, nonsymmetric and unequivalent. Possible reasons for this result and for the apparent instability of B_4H_4 are discussed.

Introduction

The structures of the boron hydrides have been traditionally divided into two broad categories:[1] open and closed (polyhedral)[2] or, more picturesquely, basket and cage molecules.[3] The open boranes usually, but not always, have molecular formulas B_nH_{n+4} or B_nH_{n+6}, while the polyhedral boranes possess molecular formulas $B_nH_n^{2-}$. The ionic poly-

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[1] See R. E. Williams, *Inorg. Chem.*, **10**, 210 (1971), for the names arachno, nido, and closo for B_nH_{n+6}, B_nH_{n+4}, and B_nH_{n+2}, respectively, or for their charged equivalents upon formal loss of one or more protons.

[2] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

[3] S. F. A. Kettle and V. Tomlinson, *J. Chem. Soc. A*, 2002, 2007 (1969).