673. *Boron Hydride Derivatives. Part VIII.*[1] *Some Reactions of Sodium Decaboranate in Relation to Decaboranylmagnesium Iodide.*

By N. J. Blay, R. J. Pace, and R. L. Williams.

Sodium decaboranate, $NaB_{10}H_{13}$, prepared from sodium hydride and decaborane, reacts with methyl and ethyl sulphate and with benzyl chloride to give the same substituted decaboranes as are obtained from decaboranylmagnesium iodide. The ^{11}B nuclear magnetic resonance spectra, and the ultraviolet and infrared spectra, of ethereal solutions of the sodium and Grignard compounds have been measured. Sodium decaboranate prepared in ethereal solution from decaborane and aqueous alkali has physical properties different from those of the salt produced from sodium hydride. The structures of the substances are discussed.

The acidic behaviour of decaborane in aqueous solution was first reported by Schaeffer and his co-workers [2] who subsequently [3] made solutions containing the $B_{10}H_{13}^-$ anion. Hawthorne *et al.*[4] have since described the preparation and characterization of a number of salts containing this anion, including the sodium salt, $NaB_{10}H_{13}$. Hawthorne and Miller [5] also reported the formation of sodium decaboranate by the action of sodium hydride on ethereal decaborane.

In Part VI, it was shown [6] that the reactions of decaboranylmagnesium iodide were consistent with a partially ionic structure, $B_{10}H_{13}^{\delta-}MgI^{\delta+}$. We have now tried the same

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[1] Part VII, Pace, J. Williams, and R. L. Williams, *J.*, 1961, 2196.

[2] Guter and Schaeffer, *J. Amer. Chem. Soc.*, 1956, **78**, 3546.

[3] Schaeffer, Burne, Klingen, Martincheck, and Rozett, Abs. Papers, 135th Meeting, Amer. Chem. Soc., Boston, Mass., 1959, 44M.

[4] Hawthorne, Pitochelli, Strahm, and Miller, *J. Amer. Chem. Soc.*, 1960, **82**, 1825.

[5] Hawthorne and Miller, *J. Amer. Chem. Soc.*, 1959, **81**, 4501.

[6] Dunstan, Blay, and R. L. Williams, *J.*, 1960, 5016.

reactions with sodium decaboranate and, in addition, we have measured a number of physical properties of ethereal solutions of the substances.

EXPERIMENTAL

Physical Methods.—Analytical gas-chromatograms were measured with a Griffin and George mark II apparatus at temperatures between 140° and 160°. Columns, 2 m. long, were filled with Apiezon L grease (20%) on Embacel (80%), and dry hydrogen was used as carrier gas. Preparative separations were carried out with the apparatus described previously,[7] with a column 12 ft. long 1 inch in diameter, under the same conditions as for the analyses. Benzyldecaborane was separated on a 3-ft. column at 160°.

The ^{11}B nuclear magnetic resonance spectra were measured with a Varian Associates V4310 spectrometer at 12 Mc./sec., sample-tubes being 15 mm. in diameter. Decaboranylmagnesium iodide and sodium decaboranate, both in previously filtered ethereal solutions, were measured consecutively under identical instrumental conditions.

Infrared spectra were measured with a Grubb–Parsons GS2 grating spectrometer or a Unicam S.P. 100 grating spectrometer for high-resolution spectra, or with a Grubb–Parsons S3A double-beam spectrometer, fitted with a sodium chloride prism, for low-dispersion spectra. Solutions were measured in 0·1-mm. cells. Methylmagnesium iodide and decaboranylmagnesium iodide were also examined as thin films, obtained by the evaporation of ethereal solutions on rock-salt plates in a nitrogen atmosphere in a dry box. The plates were then mounted inside conventional gas-cells, and the gas-cells were removed from the dry box and evacuated on the vacuum-line. The presence of residual ether in the films was shown by the weak band near 1120 cm.$^{-1}$ in their spectra. However, this is a very intense band in the spectrum of ether so that the rest of its spectrum can make only a negligible contribution to the observed spectrum. The absence of bands in the OH stretching region showed that hydrolytic decomposition was absent. Weak bands were observed near 950 and 860 cm.$^{-1}$ in the decaboranylmagnesium iodide spectrum, which might have been attributed to decaborane. However, the 860 cm.$^{-1}$ band of decaborane is strong, so that the concentration of this compound is too low to have a significant effect on the observed spectrum.

Strong solvent absorptions prevented complete spectra of the ethereal solutions from being obtained. Sufficient detail could be observed to show that there was little difference from the film spectra. Band positions are listed as follows:

$B_{10}H_{13}MgI$, film. 2980s, 2950m, 2910m, 2887m, 2553vs, 2410mw, 1940w, 1888w, 1868w, 1813vw, 1720w, 1660w, 1559mw, 1514mw, 1469ms, 1453ms, 1390s, 1350mw, 1328mw, 1289mw, 1191m, 1148ms, 1115m, 1090ms, 1033vs, 1007w, 968vw, 935w, 923w, 913w, 893s, 860vw, 833ms, 793mw, 774s, 745mw, 722m, 703mw.

MeMgI, film. 2980s, 2950s, 2910s, 2090vw, 1975vw, 1914vw, 1849vw, 1800vw, 1718w, 1653w, 1467ms, 1447ms, 1389s, 1323mw, 1285mw, 1188m, 1147ms, 1085ms, 1033vs, 965mw, 893s, 831ms, 790w, 774s.

$NaB_{10}H_{13}$, from $NaH–B_{10}H_{14}$, compensated ethereal solution. 2532vs, 2477sh, 2440sh, 1953w, 1919w, 1314s, 1004s, 975w, 912s, 876w, 834s, 791s, 739w, 722m, 711ms, 671w. In the solid film, an additional strong band at 1098 cm.$^{-1}$ can be observed which is obscured by ether in the solution.

$Me_4NB_{10}H_{13}$, Nujol and fluorube mulls. 3035w, 2963vw, 2512vvs, 1888w, 1837vw, 1535w, 1470vs, 1406s, 1304w, 1281w, 1185w, 1157mw, 1096mw, 1067m, 1017s, 949vs, 916mw, 878w, 840m, 810mw, 782mw, 746w, 718m.

Ultraviolet spectra were recorded with a Unicam S.P. 500 spectrometer or with a Beckman DK 2 recording spectrometer, and 1-cm. cells. B.D.H. ether, " special for spectroscopy " grade, was used as solvent. Sodium decaboranate prepared from ethereal decaborane and sodium hydride gave a solution with absorption maxima at 220 and 286 mμ. The ratio of extinction coefficients, $\varepsilon_{220}/\varepsilon_{286}$, was 2·46 with $\varepsilon_{286} \approx 2700$. Ethereal decaborane shaken for 1 hr. with anhydrous sodium hydroxide gave an almost identical spectrum with $\varepsilon_{220}/\varepsilon_{286} = 2{\cdot}49$. However, if the decaborane solution was treated with aqueous sodium hydroxide for a few minutes, the aqueous portion separated by centrifugation, and the spectrum of the ethereal portion measured as quickly as possible, maxima at 270 and 336 mμ ($\varepsilon_{270}/\varepsilon_{336} = 1{\cdot}41$;

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[7] R. L. Williams, Dunstan, and Blay, *J.*, 1960, 5006.

Hawthorne *et al.*[4] reported 1·42 for the $B_{10}H_{13}^-$ anion) were observed, which were replaced in a few hours by a single band at 276 mμ. Decaboranylmagnesium iodide has a band at 225 mμ (ε > 1000) for an ethereal solution, as has ethereal methylmagnesium iodide. The latter has a second, weaker, absorption at 261 mμ. Ethereal magnesium iodide prepared from iodine and an excess of magnesium in dry ether has a very strong band at 225 and a weaker one at 290 mμ; the second band is probably due to the I_3^- ion since the absorption increases with time but can be reduced by addition of more magnesium.

Compounds.—Decaboranylmagnesium iodide was prepared in ethereal solution by the method of Siegel *et al.*[8] Tetramethylammonium decaboranate was made according to the directions of Hawthorne *et al.*[4]

Sodium Decaboranate from Sodium Hydride.—The method outlined by Hawthorne and Miller [5] was used. Decaborane (from the American Potash and Chemical Corporation) was recrystallized from hexane before use. Sodium hydride was supplied by L. Light and Co. as a 50% dispersion in mineral oil; analysis by hydrogen evolution showed a sodium hydride content of 52·8%; titration with standard acid indicated in addition 6·0% of alkali as sodium hydroxide. Decaborane (0·24 g., 2 mmoles) in dry ether (20 ml.) was added to sodium hydride covered with ether (5 ml.). The mixture was boiled for 30 min., cooled, and used as soon as possible, since the yellow solution gives a white deposit on storage. Usually 0·2 g. (4 mmoles) of the sodium hydride dispersion was used.

Reactions of Sodium Decaboranate.—(a) *Methylation.* Redistilled dimethyl sulphate (1 ml.) was added at room temperature to ethereal sodium decaboranate (from decaborane 0·26 g., 2·1 mmoles, and sodium hydride 0·310 g.), and the mixture was refluxed for 30 min. and then filtered. Gas-chromatography with durene as internal standard gave: decaborane 0·105 g., 0·86 mmole, 40·6%; 5-methyldecaborane 0·0378 g., 0·28 mmole; and 6-methyldecaborane 0·006 g., 0·04 mmole, corresponding to a 28·1% conversion of decaborane. The methyldecaboranes were identified by their retention volumes and by their infrared spectra after gas-chromatographic separation.

In a second experiment, the sodium decaboranate solution was evaporated to dryness *in vacuo* and then redissolved in dibutyl ether. Dimethyl sulphate was added and the mixture was refluxed. Analysis showed a 48·5% recovery of unchanged decaborane and a lower yield of methyldecaboranes, corresponding to 14% conversion. When the whole operation was carried out in dibutyl ether, the conversion of decaborane was less than 4%.

(b) *Ethylation.* Experiments were carried out in a similar manner to the methylations, with different $B_{10}H_{14}$: NaH ratios. Analysis with naphthalene as internal standard gave the tabulated results:

				Found				
$B_{10}H_{14}$		50% NaH	Et_2SO_4	$B_{10}H_{14}$		$EtB_{10}H_{13}$		$B_{10}H_{14}$ converted (%)
g.	mmole	g.	ml.	g.	mmole	g.	mmole	
0·246	2·01	0·101	0·9	0·128	1·05	0·022	0·15	15·2
0·226	1·85	0·218	1·2	0·083	0·68	0·058	0·39	33·0
0·251	2·05	0·452	1·8	0·115	0·94	0·048	0·32	31·6

The ethyldecaborane was separated and its infrared spectrum measured. No quantitative analysis was made, but its composition could be estimated as 5-ethyldecaborane 60—70% and 6-ethyldecaborane 40—30% by comparison of the spectrum with those of the pure compounds. A little diethyldecaborane was formed; this had a similar spectrum to that of the mixture of diethyldecaboranes described in Part II.[9] Control tests showed that there was no reaction between decaborane and dimethyl or diethyl sulphate under the conditions of the experiments.

(c) *Benzylation.* Ethereal sodium decaboranate (from 0·47 g. of decaborane and 0·37 g. of sodium hydride dispersion) was evaporated to dryness and redistilled benzyl chloride (2 ml.) added. The mixture was heated on a water-bath for several hours, then extracted with ether, and the extract examined by gas-chromatography. A peak corresponding to benzyldecaborane was observed. The solution was therefore chromatographed on a larger scale and seven fractions, covering equal time-intervals, were collected. The infrared spectra of the first five fractions indicated a mixture of two or more substances containing no boron, but the sixth and

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[8] Siegel, Mack, Lowe, and Gallaghan, *J. Amer. Chem. Soc.*, 1958, **80**, 4523.

[9] Blay, J. Williams, and R. L. Williams, *J.*, **1960**, 424.

the seventh fraction had spectra identical with that of benzyldecaborane, contaminated with traces of the earlier unidentified materials. This was confirmed by analytical gas-chromatography, which showed that each fraction contained two common constituents but that the concentration of these was low in the sixth and the seventh fraction. The seventh contained one major component of the same retention volume as benzyldecaborane. The presence of the same materials in each fraction indicates a reaction on the column. However, gas-chromatography shows that no reaction takes place when benzyl chloride is heated with decaborane at 100° for several hours. The products must therefore arise from decomposition on the column either of benzyldecaborane or of by-products from the sodium decaboranate reaction. Their infrared spectra showed the presence of benzyl groups.

(d) *Reactions with alkyl halides.* Ethereal sodium decaboranate (from $B_{10}H_{14}$ 0·239 g., 1·94 mmoles) was refluxed with redistilled methyl iodide (1·5 ml.) for 3 hr. The product contained $B_{10}H_{14}$ 0·056 g., 0·46 mmole, and 5-methyldecaborane 0·003 g., 0·025 mmole, corresponding to 2% conversion of decaborane. In a similar experiment with ethyl bromide there was no reaction.

Recovery of Decaborane from Sodium Decaboranate.—This was established by three methods.

(*a*) *Infrared spectra.* Comparison of the low-dispersion spectra of ethereal decaborane before and after the addition of sodium hydride shows that complete reaction has occurred since the decaborane absorptions disappear or shift in frequency. On acidification, the decaborane spectrum reappears.

Similarly, with high resolution, the BH stretching band of decaborane at 2586 cm.$^{-1}$, $\Delta\nu_{\frac{1}{2}}$ 36 cm.$^{-1}$, is replaced by a broader band at 2532 cm.$^{-1}$, $\Delta\nu_{\frac{1}{2}}$ 100 cm.$^{-1}$. After acidification, the spectrum reverts to that of decaborane.

(*b*) *Ultraviolet spectra.* Ethereal decaborane has a single maximum at 268 mμ. Addition of sodium hydride shifts this to 286 mμ with a minimum at 268 mμ. Ethereal hydrogen chloride restores the maximum to 268 mμ, but there is now a minimum at 244 mμ with increasing absorption at shorter wavelengths which can be shown to be due to decomposition products.

(*c*) *Gas-chromatography.* Decaborane (0·1356 g.), with naphthalene as internal standard, was treated with a two-fold excess of sodium hydride in ether (5 ml.). The infrared spectrum showed that reaction was complete. After an hour, two portions of the solution were analysed (column at 160° and sample vaporizer on) and found to contain 0·0157 and 0·0167 g., severally, of decaborane per ml. (initial concentration 0·0271 g./ml.). A third portion was mixed with ethereal hydrogen chloride and then had an increased concentration of decaborane equivalent to 0·0212 g./ml.

Repetition of the analysis at lower column-temperatures and with the sample vaporizer off gave lower decaborane concentrations from the unacidified decaboranate solutions. This observation in conjunction with the broadness of the decaborane peak on the chromatogram indicates decomposition of sodium decaboranate when injected on to the column.

DISCUSSION

The experimental results show that sodium decaboranate almost completely parallels decaboranylmagnesium iodide in its chemical behaviour. Reactions take place with those substances which possess markedly polar structures, *e.g.*, alkyl sulphates, while less polar reagents have little or no effect. Moreover, it has been reported recently [10] that sodium decaboranate does not give Grignard-type reactions with acetaldehyde, acetone, or carbon dioxide. It might therefore be inferred that both the sodium and magnesium compounds possess the same ionic structures and that the latter is not a true Grignard reagent. However, this view is not confirmed from the physical properties of their ethereal solutions. The similarity of reaction products must therefore arise from reaction intermediates which have very similar structures.

Decaboranylmagnesium Iodide.—The infrared spectra of ethereal solutions of a number of Grignard compounds and also of the magnesium halides have been examined by several

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[10] Palchak, Norman, and R. E. Williams, *J. Amer. Chem. Soc.*, 1961, **83**, 3380.

workers,[11] whose results have been confined to the 1000—650 cm.$^{-1}$ region because of solvent absorptions. Spectra of films of methyl- and decaboranyl-magnesium iodide (Fig. 1) confirm these earlier results but extend the range of observation. The similarity of the two spectra is very marked and any differences can be ascribed to the methyl and decaboranyl groups. The boron compound must have the same structure, therefore, as other Grignard reagents and its isolation [8] as a solid monoether solvate, $B_{10}H_{13}MgI,Et_2O$, is in keeping with this. Additional confirmation follows from an assignment of the spectrum. With diethyl ether, the CH stretching modes are very intense and lie at 2981 (antisymm.) and 2869 cm.$^{-1}$ (symm.) for the CH_3 group. The corresponding deformation vibrations occur in the 1400 cm.$^{-1}$ region and can be allocated by analogy to the assignments given by Francis,[12] *viz.*, 1457, 1445 (w, antisymm. CH_3), 1416 (w, CH_2–O), 1383 (m, sym. CH_3), and 1351 cm.$^{-1}$ (mw, CH_2–O). The weak doublet at 1297, 1280 cm.$^{-1}$ is probably a CH_2 twisting or wagging mode, while the weak bands between 1182 and 1029 cm.$^{-1}$ represent C–C stretching or CH_3 rocking vibrations. The medium band at 847 cm.$^{-1}$ is assigned to a C–C stretching vibration by analogy with n-alkanes.[13] The remaining bands (1120vs and 938w cm.$^{-1}$) represent the C–O–C antisymmetric and symmetric stretching modes, which occur at 1122 and 940 cm.$^{-1}$ in dimethyl ether.[14]

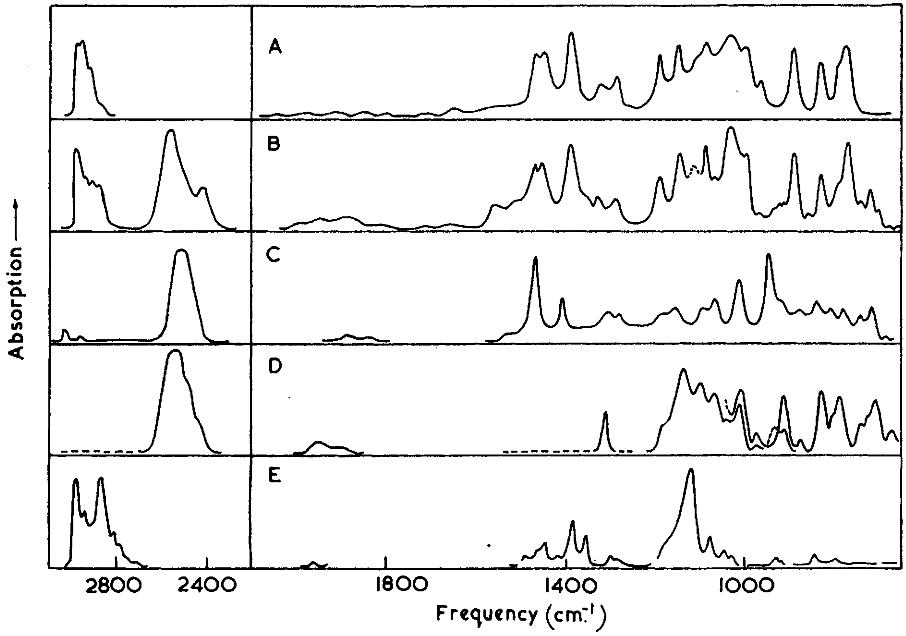

FIG. 1. The infrared spectra of: (A) MeMgI, film; (B) $B_{10}H_{13}MgI$, film; (C) $B_{10}H_{13}NMe_4$, Nujol and Fluorube mulls; (D) $B_{10}H_{13}Na$, ethereal solution; broken line, solid film; (E) Et_2O, film.

The spectra of the two Grignard compounds are nearly identical and their bands lie in similar regions of the spectrum to those of diethyl ether but are often displaced in frequency and usually differ in intensity, showing that the spectra are mainly those of a co-ordinated

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[11] Plum, *J. Chem. Phys.*, 1936, **5**, 172; Zeil, *Z. Elektrochem.*, 1952, **56**, 789; Hamelin and Hayes, *Compt. rend.*, 1961, **252**, 1616.

[12] Francis, *J. Chem. Phys.*, 1951, **19**, 942.

[13] Sheppard and Simpson, *Quart. Rev.*, 1953, **7**, 19.

[14] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand Co., New York, 1945, p. 353.

diethyl ether group. The CH stretching modes are least altered and lie at the same frequencies as in ether but with different intensities, which in the case of the methylmagnesium iodide can be attributed to the methyl group. The CH deformational modes are characterized by an extra band near 1470 cm.$^{-1}$ and disappearance of the ether absorption at 1416 cm.$^{-1}$. The latter was assigned to the CH_2 deformation mode, whose frequency was lowered by the presence of the adjacent ether–oxygen atom. On co-ordination of this oxygen in the Grignard compound, its influence on the CH_2 group is removed and the CH_2 absorption reappears at its normal frequency near 1470 cm.$^{-1}$. The disappearance of the 1351 cm.$^{-1}$ band, also assigned to CH_2–O–, supports this deduction. The CH_2 twisting or wagging modes are raised in frequency by comparison with ether to 1323, 1285 cm.$^{-1}$, while the bands between 1188 and 995 cm.$^{-1}$ are enhanced in intensity. The C–O–C stretching vibrations are both reduced in intensity and lowered in frequency to 1033 and 893 cm.$^{-1}$, showing that the oxygen is the site of the association. The C–C stretching band occurs at 830 cm.$^{-1}$ but the assignment of the band at 774 cm.$^{-1}$ is uncertain.

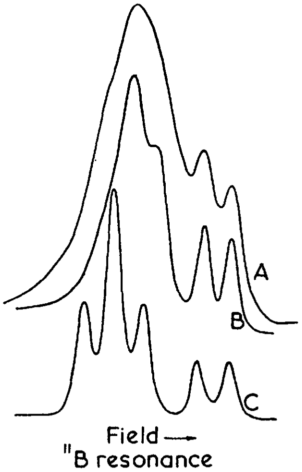

FIG. 2. The ^{11}B nuclear magnetic resonance spectra of: (A) $B_{10}H_{13}MgI$; (B) $B_{10}H_{13}Na$; (C) $B_{10}H_{14}$.

The weak band at 965 cm.$^{-1}$ in the spectrum of methylmagnesium iodide has been observed by Hamelin and Hayes[11] for other Grignard compounds and has been assigned by them to the alkyl group.

Several bands occur in the spectrum of decaboranylmagnesium iodide which are unique to the compound. The very strong band at 2553 cm.$^{-1}$ is due to the BH stretching vibration. However, the presence of a weaker satellite at 2416 cm.$^{-1}$ implies that either some of the BH bands are in a very different environment from the remainder, or else that the band is the symmetric mode of a BH_2 group whose antisymmetric vibration underlies the main peak. The first possibility can be discounted since even in the $B_{10}H_{13}^-$ anion of tetramethylammonium decaboranate the BH frequency has only dropped to 2514 cm.$^{-1}$. The doublet separation of a BH_2 group is usually 100 cm.$^{-1}$ compared with the observed separation of 137 cm.$^{-1}$. However, the asymmetry of the main band on its low-frequency side indicates that the antisymmetric BH_2 vibration could lie at a lower frequency than 2553 cm.$^{-1}$ with a correspondingly more normal doublet separation. It is not possible to observe the BH_2 deformation and wagging modes, which should fall in the ranges[15] 1205—1140 and 975—945 cm.$^{-1}$ because of the strong ether bands.

The moderately weak absorption near 1900 cm.$^{-1}$ could be assigned to combination frequencies, as is possible with the corresponding bands in methylmagnesium iodide. The

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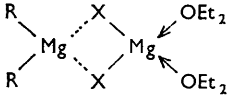
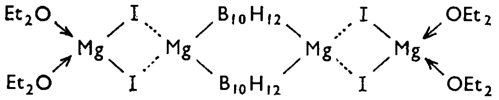
[15] Bellamy, Gerrard, Lappert, and R. L. Williams, *J.*, 1958, 2412.

latter are, however, much sharper and well resolved and lie throughout the region 2100—1650 cm.$^{-1}$. A more satisfactory assignment is to B–H–B vibrations in which the bridges are in a similar environment to those in decaborane.[5] Such bands occur for ethereal decaborane at 1980, 1941, and 1900 cm.$^{-1}$ but their diagnostic value is limited to compounds having the decaborane structure. Other bands which can be attributed with certainty to the $B_{10}H_{12}$ group lie at 745, 720, and 703 cm.$^{-1}$.

The ultraviolet spectra also serve to emphasize the similarity of methyl- and decaboranyl-magnesium iodide, but in a more restricted way. Both have strong bands at 225 mμ, as has also ethereal magnesium iodide. Since an absorption is found at this point for ethylmagnesium iodide but not for the bromide,[16] the band must originate in the MgI part of the system. The I^- ion itself absorbs near 226 mμ in aqueous or alcoholic solution [17] and it is probable, therefore, that the MgI bond has a high degree of ionicity.

It has been established that Grignard compounds consist of an equilibrium mixture: [18] $R_2Mg,MgX_2 \rightleftharpoons R_2Mg + MgX_2$, and on the basis of this, in conjunction with the spectroscopic results, Kirmann and Hamelin [19] proposed structure (I) for the Grignard complex. Decaboranylmagnesium iodide can therefore be represented by structure (I) where R is $B_{10}H_{13}$, and the double Grignard compound $B_{10}H_{12}(MgI)_2,2Et_2O$ reported by Siegel *et al.*[8] can be formulated as (II). The structure of the $B_{10}H_{13}$ unit will be considered in conjunction with that of sodium decaboranate.


(I)


(II)

Sodium Decaboranate.—The studies by Schaeffer and his co-workers [2,3] and later by Hawthorne *et al.*[4] have shown that, in aqueous solution, two anions are produced from decaborane, $B_{10}H_{13}^-$, having absorption maxima at 267 and 335 mμ, and $B_{10}H_{13},H_2O^-$ with a single maximum at 249 mμ. A number of salts of the unsolvated anion have been isolated,[4] *e.g.*, $Et_2NH_2^+,B_{10}H_{13}^-$, which dissolve in 2,2′-dimethoxydiethyl ether or acetonitrile, to give solutions with absorption maxima at 267 and 335 mμ. These are therefore still unsolvated.

Ethereal decaborane reacts with anhydrous sodium hydroxide or sodium hydride to form a salt (A) which has absorption maxima at 220 and 286 mμ. This is not a disodium derivative $Na_2B_{10}H_{12}$, since Palchak *et al.*[10] showed that a monosodium derivative is the major product even when a high base : decaborane ratio is used. If, however, aqueous sodium hydroxide is used as reagent, then ethereal decaborane forms a solution with the normal $B_{10}H_{13}^-$ absorptions at 267 and 335 mμ (salt B).

The ^{11}B nuclear magnetic resonance spectra of decaboranylmagnesium iodide, sodium decaboranate (A), and decaborane are given in Fig. 2. The presence of the high-field doublet shows that the 2,4-positions of the $B_{10}H_{14}$ molecule are unaffected by the formation of either the sodium or the magnesium compound, while the loss of structure in the low-field triplet, indicates that in both derivatives hydrogen abstraction has taken place from amongst the basal borons. However, the considerable difference between the spectra of the magnesium and sodium derivatives confirms the finding from the ultraviolet spectra that the $B_{10}H_{13}$ unit in each must be different. The spectrum of sodium decaboronate (A) is nearly identical in contour with that reported by Knoth and Muetterties [20] for tetramethylammonium decaboranate in acetonitrile. Moreover, though no chemical shifts were measured for the sodium salt, the peak positions relative to that at highest field are

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[16] Hamelin, personal communication.

[17] Mason, *Quart. Rev.*, 1961, **15**, 287.

[18] Coates, " Organo-Metallic Compounds," Methuen and Co. Ltd., London, 1960, p. 52.

[19] Kirmann and Hamelin, *Compt. rend.*, 1960, **251**, 2990.

[20] Knoth and Muetterties, *J. Inorg. Nuclear Chem.*, 1961, **20**, 66.

the same within experimental error as those given by Knoth and Muetterties [20] (1 : 2·8 : 3·7 compared with 1 : 2·6 : 3·8). Tetramethylammonium decaboranate has an ultraviolet spectrum identical with that of the normal sodium decaboranate (B), with absorption bands characteristic of $B_{10}H_{13}^-$ at 267 and 336 mμ. The situation therefore arises that though salts (A) and (B) must have nearly identical structures because of their nuclear magnetic resonance spectra, their ultraviolet spectra differ considerably.

This apparent paradox can be resolved by a consideration of the infrared spectrum of salt (A) (Fig. 1). The spectrum of an ethereal solution, although incomplete because of strong solvent absorptions, has bands at 1004, 912, 834, and 791 cm.$^{-1}$, which provide good evidence for the presence of co-ordinated ether. Attempts to make films of the substance free from ether in a manner similar to that used for the magnesium compounds, were less successful since the co-ordinated ether seemed much less tightly bound. However, a number of spectra were obtained in which sufficient solvent had been removed to show that the solid retained all the spectral features of the solution but with extra bands in regions previously made inaccessible by solvent absorption. The band positions below 1100 cm.$^{-1}$ are compared in the Table with those of ether, ethereal hydrogen chloride, Grignard compounds, and boron trifluoride–ether complex. There is a smooth change in most band positions as the co-ordinate link becomes stronger. The ether bonding in sodium decaboranate is weak and similar to that between ether and hydrogen chloride.

	Antisym. C–O–C			Sym. C–O–C			
Et_2O *	1120	1071	1044	1022	935	845	794
Et_2O,HCl †	1100	1082	1040	1020	925	840	798
$NaB_{10}H_{13}$ (A) ‡	1098	1070	—	1004	912	834	791
$B_{10}H_{13}MgI$ ‡	1033	1089	—	996	893	833	774
Et_2O,BF_3 §	1020	1094, 1077, 1065	—	959	878	829	761

* Liquid film. † Et_2O saturated with dry HCl. ‡ Solid film. § E. F. Mooney, personal communication, liquid film.

Only a few bands can be associated with the $B_{10}H_{13}$ unit. The B–H stretching band at 2532 cm.$^{-1}$ is intense with slight shoulders at 2477 and 2470 cm.$^{-1}$. The latter might be taken as indicative of BH_2 groups, but the bands are very much more indefinite than with decaboranylmagnesium iodide and the separation from the main peak would be too small for a BH_2 doublet. The bridge BHB band at 1953, 1919 cm.$^{-1}$ is definite though weak.

The spectrum of tetramethylammonium decaboranate, which from the ultraviolet evidence contains the same anion as sodium decaboranate (B), is shown in Fig. 1. The frequencies of the tetramethylammonium ion are well known [21] and occur at 3035, 2963 (CH stretch), 1470 and 1403 (CH_3 deformations), 1281 (CH_3 rock), and 949 cm.$^{-1}$ (CN stretch). The main features of interest in the $B_{10}H_{13}^-$ absorptions are the very intense BH stretching band at 2513 cm.$^{-1}$, which is symmetric, with no sign of any lower-frequency component, and the bridge BHB band which absorbs weakly at 1888, 1837 cm.$^{-1}$. The remainder of the spectrum is similar to that of decaborane except for the absence of the strong band of the latter at 1514 cm.$^{-1}$.

The structures of the various $B_{10}H_{12}$ residues can now be considered in the light of Lipscomb's topological structural theory for boron hydrides.[22] In decaboranylmagnesium iodide, the evidence for a BH_2 group is strong and that for decaborane type B–H–B bonds is good. If the Mg–$B_{10}H_{13}$ link is covalent, Lipscomb's theory [23] permits two possible structures, 2802 or 3711 but both of these are of low symmetry and the BHB links are not in positions equivalent to those of decaborane. If, on the other hand, the bond is largely ionic, then the observed facts are accounted for by formula (III), which could easily go over to a symmetric 0822 $B_{10}H_{12}^{2-}$ ion in the $B_{10}H_{12}(MgI)_2$ compound.

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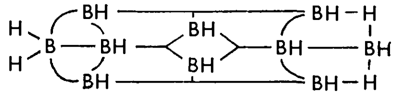
[21] Lorenzelli and Möller, *Compt. rend.*, 1960, **251**, 1483.

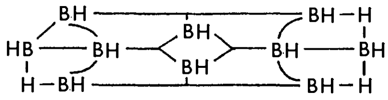
[22] Lipscomb, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 117.

[23] Reddy and Lipscomb, *J. Chem. Phys.*, 1959, **31**, 610.

The normal $B_{10}H_{13}^-$ anion, as found in the tetramethylammonium and sodium salts with ultraviolet maxima at 267 and 326 mμ, has no BH_2 group but has B–H–B bridges. This requirement is met by formula (IV). Structures (III) and (IV) are in fact the tautomeric forms of the $B_{10}H_{13}^-$ ion proposed by Lipscomb.[22]

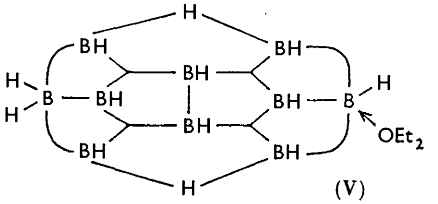


(III)

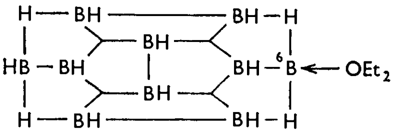


(IV)

The second sodium decaboranate contains co-ordinated ether and the most obvious choice of structure is the 2632 form (V) of $B_{10}H_{14}^{2-}$ found in the $B_{10}H_{12}(CH_3{\cdot}CN)_2$ derivatives.[23] However, this possibility appears to be ruled out by the absence of BH_2 groups and the presence of decaborane type B–H–B links from the infrared spectrum. Furthermore, structure (V) would not be expected to have a nuclear magnetic resonance spectrum similar to that of (IV). An arrangement which seems to satisfy the requirements is derived from the 4450 form (VI) of $B_{10}H_{14}^{2-}$.



(V)



(VI)

These structures are based on localized three-centre bonds and though structures (IV) and (VI) differ considerably in the distribution of these, it is probable that such differences would be smoothed out in a molecular orbital treatment.[24] Intramolecular hydrogen exchange will also minimize differences.[25] The 6-position for co-ordination in (VI) is not proved but seems reasonable in view of the structure of bisacetonitriledecaborane [23] and the mechanism of deuterium exchange of decaborane in the presence of donor solvents.[26] The reaction of ethereal sodium decaboranate with iodine,[27] to give ethoxydecaborane, is also best interpreted on the basis of specific solvation of the sodium decaboranate.[28]

The existence of a solvated and an unsolvated anion in ethereal solution is analogous to the behaviour in aqueous solution. In the latter the hydration of the $B_{10}H_{13}^-$ ion proceeds at a measurable rate,[4] and since the $Et_2O \longrightarrow B_{10}H_{13}^-$ link is weak, it might be expected that the solvation of $B_{10}H_{13}^-$ in ether would proceed more slowly, so that there would be ample time for the observation of the $B_{10}H_{13}^-$ ultraviolet spectrum. Decaborane is also probably solvated in ethereal solution, so that the formation of $B_{10}H_{13}^-,Et_2O$ under anhydrous conditions is to be expected. On the other hand, reaction of ethereal decaborane with aqueous sodium hydroxide will take place either in the aqueous layer or at the interface and an unsolvated ion would be formed.

The co-operation of Dr. B. N. Figgis in obtaining the nuclear magnetic resonance spectra is gratefully acknowledged, as is that of Dr. E. F. Mooney for the infrared spectrum of the boron trifluoride–ether complex.

MINISTRY OF AVIATION, E.R.D.E.,
WALTHAM ABBEY, ESSEX.

[*Received, March 5th*, 1962.]

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[24] Moore, Lohr, and Lipscomb, *J. Chem. Phys.*, 1961, **35**, 1329.

[25] R. E. Williams, *J. Inorg. Nuclear Chem.*, 1961, **20**, 198.

[26] Shapiro, Lustig, and R. E. Williams, *J. Amer. Chem. Soc.*, 1959, **81**, 838.

[27] Hawthorne and Miller, *J. Amer. Chem. Soc.*, 1960, **82**, 500.

[28] Hawthorne, personal communication.