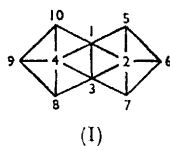


970. *Boron Hydride Derivatives. Part V.¹ Nucleophilic Substitution in Decaborane.*

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Nucleophilic substitution in decaborane ($B_{10}H_{14}$) by the action of methyl- or ethyl-lithium has been studied. The principal product is 6-methyl- or 6-ethyl-decaborane, but in the case of methylation small amounts of 5-methyl-, 6,5(or 8)-dimethyl-, and 6,9-dimethyl-decaborane are also formed. Charge distribution in decaborane is discussed with respect to these compounds.

A STUDY of electrophilic alkylation^{1,2} of decaborane (I) by Friedel-Crafts reaction has indicated that the order of decreasing electron density in the molecule is $2,4 > 1,3 > 5,7,8,10 > 6,9$. It is possible to confirm this result by a study of nucleophilic reactions wherein the attacking species would be expected to substitute positions of low electron density. The reaction of decaborane with methyl- or ethyl-lithium has therefore been examined and a number of alkyl derivatives have been isolated and their structures have been determined by ^{11}B nuclear magnetic resonance spectroscopy.



EXPERIMENTAL

Lithium Alkyls.—A benzene solution of ethyl-lithium was obtained by reaction between lithium and redistilled ethyl bromide in anhydrous isopentane, followed by dilution with benzene and distillation to remove isopentane.³ The reaction is faster in the presence of ether but the resulting solution is unstable since the metal alkyl cleaves diethyl ether, forming lithium ethoxide. Fortunately, ethereal solutions of methyl-lithium are stable if stored under dry

¹ Part IV, preceding paper.

² Blay, Dunstan, and R. L. Williams, *J.*, 1960, 430.

³ Talalaeva and Kocheskov, *J. Gen. Chem. U.S.S.R.*, 1953, 23, 399.

nitrogen, and the reagent was conveniently prepared by treating lithium in ether with methyl iodide.⁴ The concentration of alkyl-lithium solutions was determined by the double-titration method using redistilled benzyl chloride and standard sodium hydroxide solution.⁵

Ethylation of Decaborane.—A 0.188*N*-solution of ethyl-lithium in benzene (53.2 c.c., 0.01 mole) was added dropwise to decaborane (1.22 g., 0.01 mole; recrystallised from *n*-hexane) dissolved in anhydrous benzene (50 c.c.) in a 3-necked, 250 c.c., round-bottomed flask fitted with mercury-sealed stirrer, dropping funnel, condenser, and nitrogen inlet. Heat was evolved, and a bulky white precipitate formed. The mixture was stirred for 30 min., stored at room temperature overnight, then treated with dry hydrogen chloride. Filtration gave a yellow solution from which solvent was removed under diminished pressure, leaving a yellow liquid mixture of ethylated decaboranes (1.52 g.), shown by gas chromatography to consist of 6-ethyl- (89.7%) and two diethyl-decaboranes (7.8 and 2.6%).

Products were identified by gas-chromatographic retention volumes, elemental analysis, and intensity of alkyl absorption in the infrared region, as described in Part IV. In some cases equivalent weights were determined by potentiometric titration in acetonitrile.^{6,7} Structures were assigned after nuclear magnetic resonance spectroscopy.

Methylation of Decaborane.—A 0.75*N*-solution of methyl-lithium in ether (53.3 c.c., 0.04 mole) was added dropwise, with stirring, to recrystallised decaborane (4.88 g., 0.04 mole) in anhydrous benzene (100 c.c.) under nitrogen. A vigorous, exothermic reaction occurred. After 2 hr. the solution was treated with dry hydrogen chloride, giving a precipitate of lithium chloride and a red solution which was separated by filtration and evaporated to yield a mixture of methylated decaboranes as a red, mobile liquid (5.34 g.). Gas chromatography showed this to consist of decaborane (28.2%), 6-methyl- (45.4%), 6,5(or 8)-dimethyl- (17.3%), and 6,9-dimethyl-decaborane (7.6%). In addition, there was 1.5% of 5-methyldecaborane, of smaller retention volume than 6-methyldecaborane, identified by infrared spectrum and retention volume.⁸ The yield of 6-methyldecaborane based on decaborane converted was 65.0%.

Compounds examined.—Retention volumes are at 140° relative to V_R (naphthalene) = 1 and V_R (decaborane) = 0.78.

6-Ethyldecaborane, m. p. -2.5° to -2° (Found: B, 71.0; C, 16.4%; equiv., 150.4. $B_{10}H_{13}C_2H_5$ requires B, 72.0; C, 16.0%; equiv., 150.4), retention volume, 1.77 at 167° (V_R naphthalene = 1, at 167°).

6-Methyldecaborane, m. p. 27–28° (Found: B, 77.9; C, 9.3%; equiv., 138.7. $B_{10}H_{13}CH_3$ requires B, 79.4; C, 8.8%; equiv., 136.3), retention volume 1.18.

6,5(or 8)-Dimethyldecaborane, m. p. 26.5–28.5° [Found: H, 11.9, 12.3; C, 17.3%; equiv., 153.4. $B_{10}H_{12}(CH_3)_2$ requires H, 12.1; C, 16.0%; equiv., 150.4], retention volume 1.60.

6,9-Dimethyldecaborane, m. p. 64–66°, retention volume 1.86. Only a very small amount of material was recovered after nuclear magnetic resonance examination and no satisfactory analysis could be carried out.

Methods.—The same experimental methods for gas chromatography, infrared spectroscopy, and nuclear magnetic resonance spectroscopy were used as in the previous paper.

¹¹B Nuclear Magnetic Resonance Spectra.—The spectra of the three methyl compounds, together with that of decaborane, are shown in the Figure. The spectrum of 6-ethyldecaborane (not shown) is almost identical with that of the 6-methyl compound.

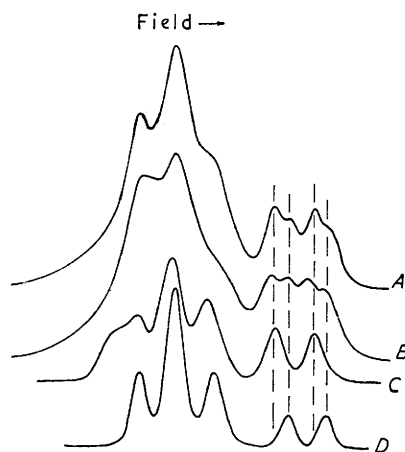
⁴ Gilman, Zoellner, and Selby, *J. Amer. Chem. Soc.*, 1933, **55**, 1252.

⁵ Wittig, "Newer Methods of Preparative Organic Chemistry," Interscience Publ. Inc., New York, 1948, p. 575.

⁶ Atteberry, *J. Phys. Chem.*, 1958, **62**, 1458.

⁷ Griffiths and R. L. Williams, *Chem. and Ind.*, 1959, 655.

⁸ Unpublished work.



The ¹¹B nuclear magnetic resonance spectra of (A) 6-methyldecaborane; (B) 6,6-dimethyldecaborane; (C) 6,9-dimethyldecaborane; (D) decaborane.

Comparing the spectrum of the monomethyl compound with that of decaborane shows that the high-field doublet has been split into two doublets of the same spacing as that of decaborane, but with one of them displaced towards lower field. The half-band width of the latter doublet must be smaller than that of the higher-field doublet to account for the observed intensities. With the low-field triplet, the low-field component is enhanced, and the centre- and high-field components reduced relative to decaborane.

The splitting of the high-field doublet implies that the shielding at the 2-position is different from that at the 4-position. This is only possible for substitution at the 6(9)- or the 5(7),8(10)-positions, since the 1- and the 3-position are symmetrically placed relative to the 2,4-positions. However, the ethyldecaborane described in Part II ^{9,8} is one with 5-substitution, and this substance shows no splitting in the high-field doublet of its spectrum. Accordingly, the present isomer must be the 6-derivative.

It is not possible to carry out a graphical analysis of the low-field triplet, but the relative peak heights are 5.0 : 7.0 : 3.8. If it is assumed that the 6(9)-doublet partially collapses on top of its low-field component, then the theoretical ratio is 5 : 7 : 4. The loss in resolution of the peaks may be due to slight changes in the half-band widths, similar to those observed in the high-field doublet.

The spectrum of the first dimethyl derivative shows a similar splitting of the high-field doublet into four components. Their intensities, however, are almost identical with those calculated theoretically for the superposition of two doublets of the same half widths. The splitting requires that one of the methyl groups is in the 6-position. The location of the second methyl group follows from the intensities of the low-field triplet. In this, there has been a pronounced diminution of both the mid- and high-field components, so that the observed peak heights are approximately 6.2 : 7.0 : 3, the last figure being for the point of inflexion. If it is assumed that the 6(9)-doublet collapses in a similar fashion to that in the monomethyl derivative and that the other position substituted is either the 5- or the 8-, the theoretical heights are 5 : 6 : 3, to which has to be added the collapsed peak from the 5-position. The latter peak will probably lie somewhere on the low-field side of its parent doublet in a similar way to that found for the doublets of the other alkyldecaboranes, and consequently will distribute its intensity to the low- and mid-field components of the triplet. The overall expected ratio will therefore be near 6 : 7 : 3. It is not possible to decide directly from the spectrum whether the substance is the 5,6- or the 6,8-dimethyl compound or a mixture of the two. The sharp m. p. suggests that it is a single compound and it is possible that it is the 5,6-dimethyl derivative, since reduced splitting in the high-field spectrum of the 6,8-compound might be expected on the basis that the environments of the 2- and the 4-position are very similar in this compound.

The second dimethyl derivative has a spectrum in which the multiplet structure on the high-field side has reverted to a single doublet. This doublet, however, lies at a lower field than that of decaborane, at a position which is the same as that of the low-field components in 6-methyldecaborane. The low-field triplet also shows considerable changes, with the emergence of a new peak, just on the low-field side of the triplet.

Since the high-field spectrum is a doublet, the 2- and the 4-position must be in an identical environment. This condition is satisfied by the substance's being 6,9-dimethyldecaborane. The new peak on the low-field side of the triplet is that resulting from the collapse of the 6,9-doublet on complete substitution.

DISCUSSION

The behaviour of decaborane with lithium alkyls is the converse of that with Friedel-Crafts reagents.^{1,2} The active species is R^- and this will be expected to attack points of low charge density. Accordingly, a different methyl isomer, 6-methyldecaborane, is the main product and shows that the 6-position is the most electropositive in decaborane.

A number of other reactions confirm this deduction. For example, acetonitrile reacts with decaborane with the elimination of hydrogen to form decaborane-bisacetonitrile,¹⁰

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

¹⁰ Schaeffer, *J. Amer. Chem. Soc.*, 1957, **79**, 1006.

$B_{10}H_{12}(CH_3 \cdot CN)_2$. In this molecule, the nitrogen is attached at the 6,9-positions,¹¹ and presumably the reaction proceeds by the donation of the nitrogen lone-pair of electrons to the most electropositive points in decaborane. Similar reactions occur between decaborane and triphenylphosphine,¹² diethylcyanamide,¹³ and pyridine.¹³

The deuterium exchange of decaborane with D_2O in dioxan¹⁴ is also accounted for by a mechanism involving donation of a lone-pair of electrons from the solvent to the 6(9)-position.

The production of a small amount of 5-methyldecaborane during the methylation indicates that this is the second most electropositive point in the molecule, though much less so than the 6-position. The disubstituted products, *viz.*, 6,9- and 6,5(or 8)-dimethyldecaborane confirm these deductions.

The Friedel-Crafts and alkyl-lithium products therefore both lead to the result that the order of decreasing electron density in decaborane is 2- > 1- > 5- > 6-. This result does not agree very well with the predictions of Eberhardt *et al.*,¹⁵ who calculated a charge distribution of $+2e/3$ for the 2,4-positions, $-e/3$ for positions 5, 7, 8, and 10 and zero charge for the remainder, using simple L.C.A.O. wave functions. However, in an appendix, they report that with a self-consistent L.C.A.O. approximation, a charge distribution of $-0.19e$ for the 2(4)-, $-0.03e$ for the 1(3)-, 0 for the 6(9)-, and $+0.11e$ for the 5(7),8(10)-positions is obtained. Moreover, Lipscomb¹⁶ has since modified this result to take account of two factors. First, negative charge tends to concentrate in the innermost parts of the molecule, since the wave functions vanish toward the exposed regions. Secondly, the bridge hydrogens carry a charge of -0.1 to $-0.2e$. Both these effects tend to increase the positive charge at position 6(9) and they may therefore become more electro-positive than the 5(7)8(10)-positions. The theoretical charge distribution is then in tolerably good accord with experiment.

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¹¹ Reddy and Lipscomb, *J. Chem. Phys.*, 1959, **31**, 610.

¹² Hawthorne and Pitochelli, *J. Amer. Chem. Soc.*, 1958, **80**, 6685.

¹³ Burkardt and Fetter, *Chem. and Ind.*, 1959, 1191.

¹⁴ Shapiro, Lustig, and R. E. Williams, *J. Amer. Chem. Soc.*, 1959, **81**, 840.

¹⁵ Eberhardt, Crawford, and Lipscomb, *J. Chem. Phys.*, 1954, **22**, 989.

¹⁶ Lipscomb, in "Advances in Inorganic Chemistry and Radiochemistry," ed. Emeléus and Sharpe, Academic Press, New York, Vol. I, 1959, p. 118.