CHLOROBORATION AND ALLIED REACTIONS OF UNSATURATED COMPOUNDS

V*. HALOBORATION AND PHENYLBORATION OF OLEFINS; AND THE PREPARATION OF HEXAPHENYL-1,4-DIBORACYCLOHEXA-2,5-DIENE
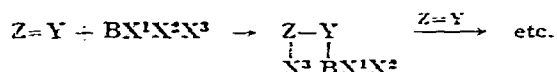
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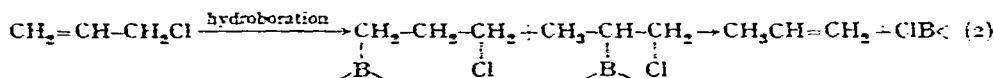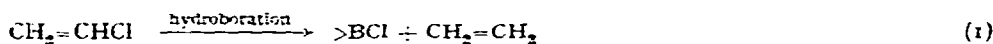
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INTRODUCTION

This series of papers relates to addition reactions of substituted boranes to unsaturated substrates.

$$Z=Y + BX^1X^2X^3 \rightarrow Z-Y \xrightarrow{Z=Y} \text{etc.}$$
$$\underset{X^3 \; BX^1X^2}{| \quad |}$$

In the present contribution, the unsaturated substrate $Z=Y$ is an olefin or polyene and the migrating group X^3 is Cl, Br, or C_6H_5. In some of the reactions to be described, substitution, rather than addition, products were obtained.

We present results on cyclohexene, 1,5-cyclooctadiene, norbornadiene, cyclooctatetraene, cycloheptatriene, and allene, and also on the $C_6H_5C \equiv CC_6H_5/C_6H_5BBr_2/K$ system. Earlier we have briefly communicated on norbornadiene[2,3] and cycloheptatriene[3], and results have now been confirmed and extended (see Figs. 3 and 5, respectively); our previous examination[3] of the C_3H_8/BCl_3 system led us tentatively to propose a bicyclic structure for the compound $C_3H_7BCl_2$, and we now show this to have been in error (see Fig. 4). Some other data on olefins have also appeared in the literature, as summarised below.

Chloroboration and cationic polymerisation appear to be competing processes in BCl_3/olefin systems[2]. Highly relevant also are the facile dechloroborations of 2-chloroalkylboranes, as exemplified by eqns. (1)[4] and (2)[5,6].

$$CH_2=CHCl \xrightarrow{\text{hydroboration}} >BCl + CH_2=CH_2 \tag{1}$$

$$CH_2=CH-CH_2Cl \xrightarrow{\text{hydroboration}} \underset{\diagdown B \diagup}{CH_2-CH_2-CH_2} + \underset{\diagdown B \diagup \;\; Cl}{CH_3-CH-CH_2} \rightarrow CH_3CH=CH_2 + ClB< \tag{2}$$
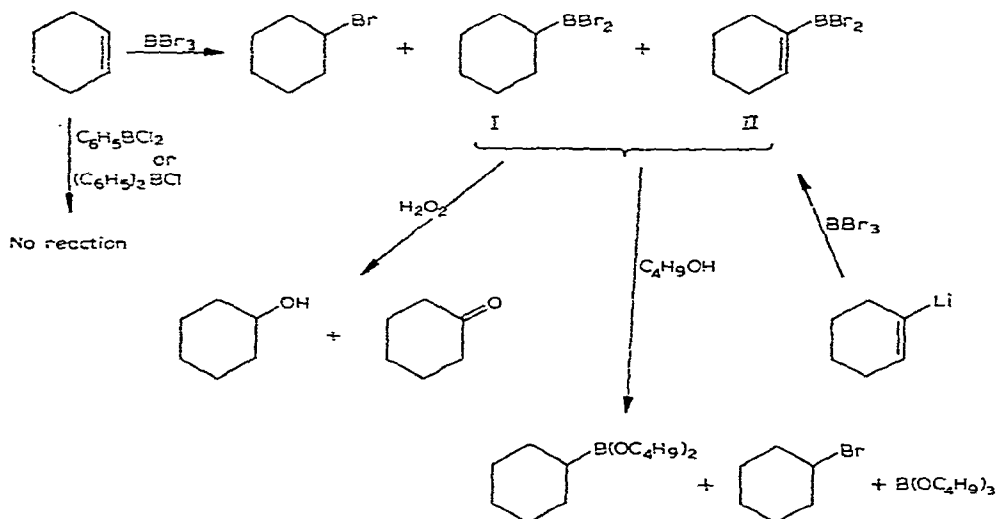

Fig. 1. Reactions based upon cyclohexene.

Of importance to our studies on the C_7H_8/BCl_3 system (Fig. 5) are observations that cycloheptatriene and trihaloboranes yield tropylium salts (*e.g.*, the tetrahaloborates), when mixed at ambient temperature without solvent or in methylene dichloride[7], or in the presence of *tert*-butyl chloride[8]. These experiments differ from our own in that benzyldichloroborane is the product when heating under reflux and then distilling (see Fig. 5).

Results on the cyclohexene/BBr_3 system, with aluminium or mercury(II) halides on activated charcoal as catalysts, have been presented in a patent[9]; two of the three products isolated by us (see Fig. 1) were also there indicated. In another procedure (see eqn. 3), telomeric products were obtained[10]. A free radical-initiated process from 1-$C_4H_8/BCl_3/SnCl_2/(C_6H_5CO)_2O_2$ was said to provide a route to product would be expected readily to dissociate into its factors.
$C_2H_5CHClCH_2BCl_2$ (Ref. 11); however, this claim warrants re-examination, as the product would be expected readily to dissociate into its factors
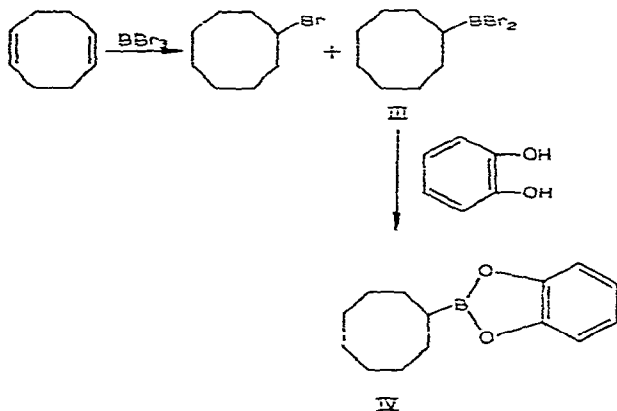

Fig. 2. Reactions based upon 1,5-cyclooctadiene (doubtless other products are formed in the primary reaction, but they were not identified).
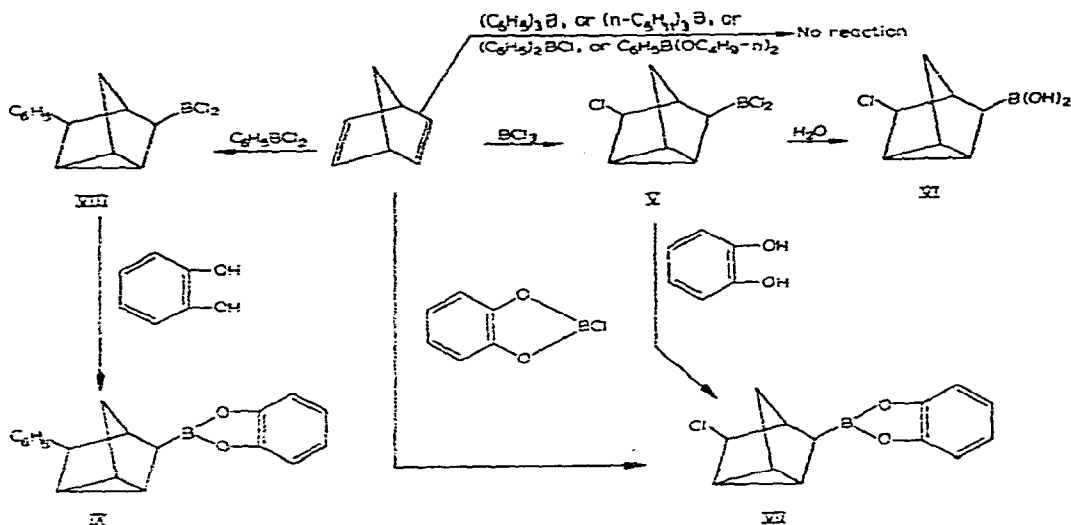
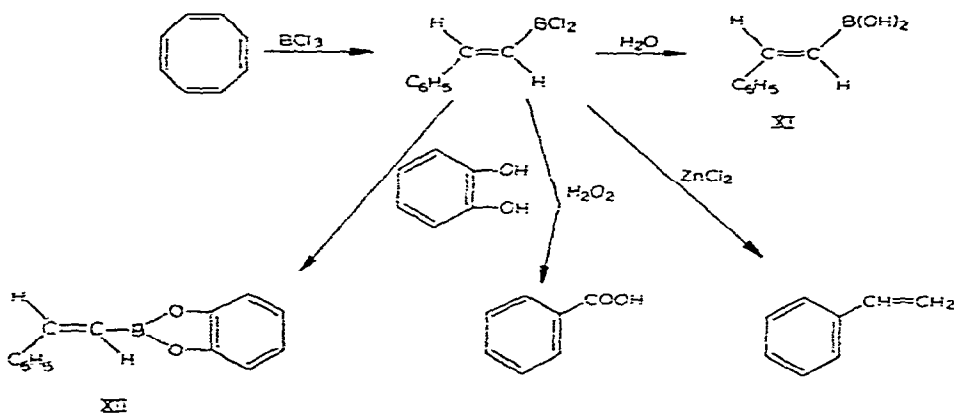Fig. 3. Reactions based upon norbornadiene (Nortricyclene derivatives are probably mixtures of cis- and trans-isomers).
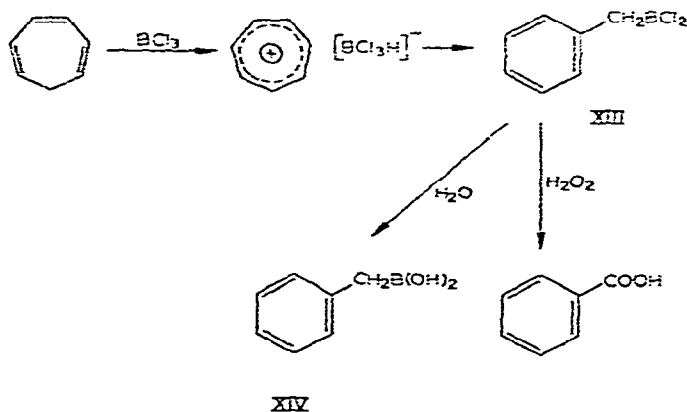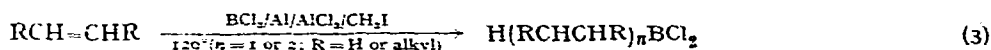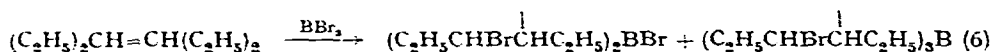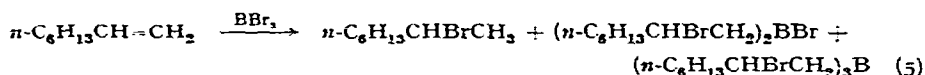

Fig. 4. Reactions based upon cyclooctatetraene.

Fig. 5. Reactions based upon cycloheptatriene.

$$RCH=CHR \xrightarrow[120°(n=1 \text{ or } 2; R=H \text{ or alkyl})]{BCl_3/Al/AlCl_3/CH_3I} H(RCHCHR)_nBCl_2 \tag{3}$$

Reactions of three acyclic olefins have been studied by Mikhailov and Niko-laeva[12]. Their results are shown in eqns. (4)–(6), but in the light of our experience with cyclohexene (see Fig. 1), it seems probable that bromoalkenylboranes are likely to be formed also.

$$n\text{-}C_4H_9CH=CH_2 \xrightarrow{BBr_3} n\text{-}C_4H_9CHBrCH_3 + n\text{-}C_4H_9CHBrCH_2BBr_2 \tag{4}$$

$$n\text{-}C_6H_{13}CH=CH_2 \xrightarrow{BBr_3} n\text{-}C_6H_{13}CHBrCH_3 + (n\text{-}C_6H_{13}CHBrCH_2)_2BBr +$$
$$(n\text{-}C_6H_{13}CHBrCH_2)_3B \tag{5}$$

$$(C_2H_5)_2CH=CH(C_2H_5)_2 \xrightarrow{BBr_3} (C_2H_5CHBrCHC_2H_5)_2BBr + (C_2H_5CHBrCHC_2H_5)_3B \tag{6}$$

DISCUSSION

Results on reactions of boranes with olefins

Data on the haloboration or phenylboration of cyclohexene and four polyenes, with chemical reactions on the products to help in their identification, are outlined in Figs. 1–5. It was also shown that allene forms a 1:1 adduct with tribromoborane, and the course of this reaction is tentatively proposed to follow eqn. (7). Carbon polymers were obtained from C_3H_6/BCl_3 and $C_6H_5CH=CH_2/C_6H_5BCl_2$, whilst lack of reaction was noticed between C_4Cl_6/BBr_3, and with the weaker Lewis acids and cyclohexene or norbornadiene (see, Figs. 1 and 3).

$$CH_2=C=CH_2 + BBr_3 \longrightarrow CH_2=CHBr-CH_2BBr_2 \tag{7}$$
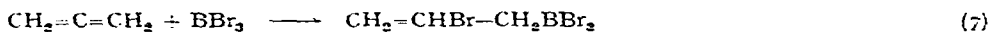
Further comments are required upon (a) the establishment of the structures and stereochemistry of the primary products, (b) the relative migratory aptitudes (C_6H_5 vs. Hal) of the groups originally attached to boron and ultimately to carbon, and the scope, limitation, nature, and mechanism (especially from the standpoint of the molecular rearrangements), more generally, of the halo- and organoboration reactions, including a comparison with hydroboration.

The structures and stereochemistry of the boranes (I)–(XIV)

These were established by full elemental analyses, oxidation [for (I), (II), (X), and (XIII)], hydrolysis [for (V), (X), and (XIII)], alcoholysis or reaction with catechol [for (I)–(III), (V), (VIII), and (X)], protodeboronation [for (X)], and alternative syntheses [for (II) and (VII)]. In addition, considerable support derives from analysis of the infrared (Tables 1 and 2) and ^1H nuclear magnetic resonance spectra (Table 3).

The mechanism of halo- and organo-boration of olefins

It will be clear that the olefin/BX_3 system is much more complex than the olefin/BH_3[13]. For example, hydroboration of norbornadiene reduces the double bonds

TABLE 1

SUBSTITUTED BORANES (I)–(IX): PRINCIPAL ABSORPTION MAXIMA (cm^{-1}) AND ASSIGNMENTS

Compound									Assignment
(I)[a]	(II)[a]	(III)[a]	(IV)[b]	(V)[a,b]	(VI)[b]	(VII)[b]	(VIII)[a]	(IX)[b]	
				3086		3086			CH stretch (cyclopropane)
			3067						CH stretch (aromatic)
	2985								CH stretch (olefinic)
2926	2924	2933	2950	2976					CH_2 stretch (asym.)
				2899					
2846	2849	2849	2874	2865					CH_2 stretch (sym.)
			1968		1938	1965	1968		Overtone and combination
			1940		1887	1934	1942		bands (CH out-of-plane)
			1881		1770	1876	1900		
			1876		1672	1773	1871		
			1818			1754	1810		
	1587								$C=C$ stretch
1445	1447	1439	1460	1464					CH_2 scissor
		1431							
			1610		1613	1605	1609		C–C stretch (ring)
			1587						
			1450		1439			1445	B–O stretch (ring)
				1346					B–O stretch
1259	1252	1247	1274	1261	1289(?)	1267			B–C stretch
					1276				
			1235		1238		1236		C–O stretch (ring)
				917		917			B–Cl stretch
				892		900			
840	844	813							B–Br stretch
818	813	787							
				813	815	821			CH def. (out-of-plane)
734	730	708		712					CH_2 rock
			740		746	739	740		CH ring def. (out-of-plane)

[a] Pure liquid. [b] Nujol mull and HCB.

stepwise, as shown by oxidation of the first-formed product to afford predominantly *exo*-dehydronorborneol[14].

A speculative reaction sequence that will account for most of the data is shown in eqns. (8)–(11). The carbonium ion intermediate of eqns. (1) and (11) may rearrange (see Figs. 3–5). An alternative to eqn. (9) may well be eqns. (12) and (13).

$$RCH{=}CHR' + BX_3 \rightleftharpoons \underset{\overset{|}{X}\quad\overset{|}{BX_2}}{RCH{-}CHR'} \qquad (8)$$

$$\underset{\overset{|}{X}\quad\overset{|}{BX_2}}{RCH{-}CHR'} + RCH{=}CHR' \rightleftharpoons \underset{\overset{|}{BX_2}}{RCH{=}CR'} + \underset{\overset{|}{X}}{RCHCH_2R'} \qquad (9)$$

$$\underset{\overset{|}{X}}{RCH{-}CH_2R'} + BX_3 \rightleftharpoons [RCHCH_2R']^+ [BX_4]^- \qquad (10)$$

$$[RCHCH_2R']^+ [BX_4]^- \rightarrow \underset{\overset{|}{BX_2}}{RCHCH_2R'} + X_2 \qquad (11)$$
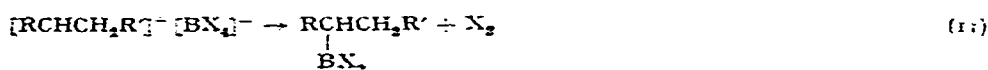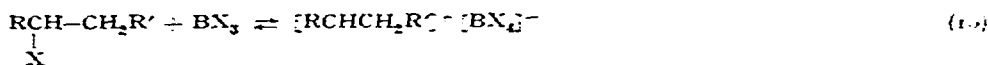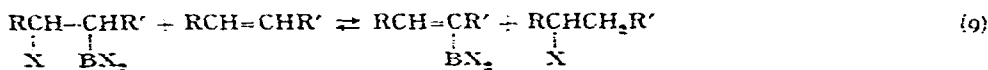
TABLE 2

SUBSTITUTED BORANES (X)–(XIV): PRINCIPAL ABSORPTION MAXIMA (cm^{-1}) AND ASSIGNMENTS

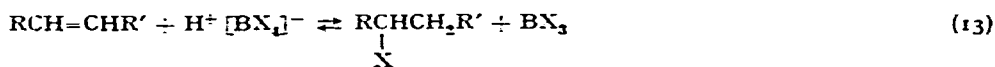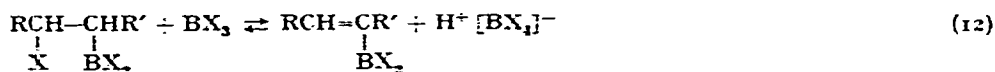| Compound					Assignment
(X)[a]	(XI)[a,c]	(XII)[a,c]	(XIII)[a]	(XIV)[b]	
3058	3021	3030	3040	3028	CH stretch (aromatic)
			3021	3010	
3021	2967	3021			CH stretch (olefinic)
			2924	2918	CH$_2$ stretch (asym.)
			2849	2842	CH$_2$ stretch (sym.)
1969	1964	1967	1961	1960	Overtone and combination
1949	1942	1938	1946	1942	bands (CH out-of-plane)
1898	1891	1883	1870	1878	
1883	1880	1878	1855	1851	
1821	1816	1815	1802	1800	
1799			1755		
1603	1623	1629			C=C stretch
1572	1575	1582	1603	1596	C–C stretch (ring)
1472	1490	1475	1493	1487	
1451	1449	1451	1449	1445	C–C stretch (ring), (skeletal in-plane)
		1445			B–O stretch (ring)
	1360			1358	B–O stretch
		1238			C–O stretch (ring)
1261			1266		B–C stretch
1230			1235		
994	992	995			CH def. (out-of-plane)
949			952		B–Cl stretch
917			930		
			775	773	CH$_2$ rock
744	754	747	754	751	CH ring def. (out-of-plane)
686	690	742	699	694	
		692			

[a] Pure liquid. [b] Nujol mull and HCB. [c] Solution (CS$_2$).

TABLE 3

^{1}H NMR DATA ON SUBSTITUTED BORANES

NMR spectra were recorded in CCl$_4$ solution using TMS as internal standard.

Compound	τ	Assignment
(II)	2.58	=CH–
	8.38[a]	–CH$_2$–
(III)	7.48	>CH–
	8.46[a]	–CH$_2$–
(V)	6.09, 7.82[b]	>CH–
	8.43[b]	–CH$_2$–
(X)[c]	2.8	C$_6$H$_5$CH–
	2.5[b], 3.6[b]	–CH=CH–

[a] Midpoint of a broad doublet. [b] Midpoint of a sharp doublet. [c] Proton spin–spin coupling constant J = 17.85 cps.

$$\underset{\substack{|\\ X \quad BX_2}}{RCH\!-\!CHR'} + BX_3 \rightleftharpoons \underset{\substack{|\\ BX_2}}{RCH\!=\!CR'} + H^+ [BX_4]^- \tag{12}$$

$$RCH\!=\!CHR' + H^+ [BX_4]^- \rightleftharpoons \underset{\substack{|\\ X}}{RCHCH_2R'} + BX_3 \tag{13}$$

Eqn. 8 describes the reaction path observed for norbornadiene (see Fig. 3). The most contentious of the foregoing equations is eqn. (11), because the entity X_2 has never been isolated. However, in most instances $X_2 = Br_2$, and the substantial residues invariably obtained in our experiments may have contained brominated hydrocarbons. Eqn. (9) has previously been demonstrated with especially reactive halides, such as trityl chloride[15], and tropylium halides[7].
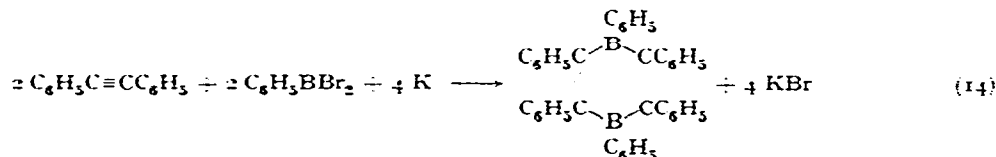
The norbornadiene → nortricyclene rearrangement has previously been demonstrated with other reagents, such as halogens[16]. The nearest previous approach to the cycloheptatriene → benzyl transformation is the tropylium bromide/bromine reaction, the product of which gave benzaldehyde upon hydrolysis[17]. There are numerous precedents for a cyclooctatetraene → styrene rearrangement; for example, halocyclooctatetraenes isomerise into the thermodynamically more stable β-halostyrenes upon heating[18].

The question of relative migratory aptitudes of groups originally attached to boron in the borane reagent and ultimately to carbon in the adduct is $C_6H_5 > Cl$ in the norbornadiene system (Fig. 3). This problem, in the wider context of boration reactions with a large selection of unsaturated substrates, has been considered in Part IV[8]. For the present, suffice it to say that, while the result was unexpected by us, dichlorophenylborane $C_6H_5BCl_2$ is here behaving like an organometallic reagent such as C_6H_5MgCl.

The most severe limitation upon the generality of haloboration for olefins and polyenes is the reverse reaction [see eqn. (8)]. However, for bromoboration, unlike chloroboration, this appears not to be too significant, because the first-formed product readily reacts further. It is likely, therefore, that hydroboration of vinyl and allyl bromides and iodides will prove to proceed differently from the chlorides (Eqs. 1 and 2); such experiments have not yet been carried out. A further restriction is that olefins, in contrast to many other substrates[1], require the strongest of the Lewis acids ($BBr_3 > BCl_3 > C_6H_5BBr_2 > C_6H_5BCl_2$) in order for reaction to occur. Finally, competing polymerisation, especially of reactive monomers such as styrene, presents a problem.

The $C_6H_5C\!\equiv\!CC_6H_5/C_6H_5BBr_2/K$ system

The reaction is represented by eqn. (14).

$$2\,C_6H_5C\!\equiv\!CC_6H_5 + 2\,C_6H_5BBr_2 + 4\,K \longrightarrow \underset{\underset{C_6H_5}{}}{\overset{\overset{C_6H_5}{}}{\underset{C_6H_5C\diagdown_B\diagup CC_6H_5}{C_6H_5C\diagup^B\diagdown CC_6H_5}}} + 4\,KBr \tag{14}$$

Our original objective was to attempt the preparation of the cyclopropenyl cation analogue $(C_6H_5)_3C_2B$. (There is a suggestion[19] that this has been made by another

route from cis-C_6H_5BBr–$C(C_6H_5)$=$C(C_6H_5)Br$ and Li in THF.) We have not yet had the opportunity to examine the product in detail. Its high melting point, and experience with related silicon[20] and germanium[21] systems, convinced us that a dimeric formula, as the diboracyclohexadiene structure shown in eqn. (14) was more plausible. However, two features are curious. Firstly, high apparent stability in air, and secondly absence of infrared spectral absorptions to be expected from a compound having C=C bonds. A suggestion, therefore, is that the compound may be an organocarborane of type (XV). Although a number of organocarboranes have recently been prepared[22], a

XV   XVI
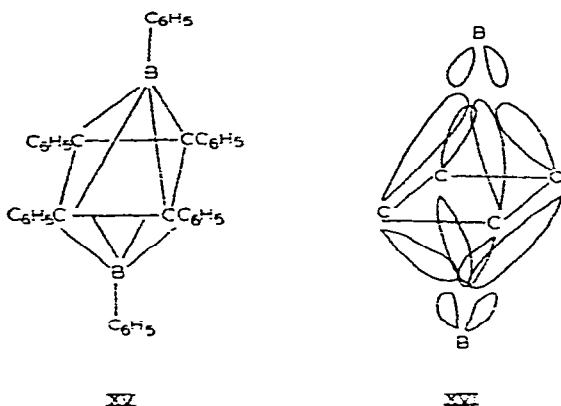
C_4B_2 skeleton would be novel. A description of the bonding in such an octahedral compound of D_{4h} symmetry, involves multicentre orbitals, as shown in (XVI). The bonding picture would thus be very similar to that in pentaborane-9.

EXPERIMENTAL

General procedures

Substituted boranes were prepared by standard methods[23]. 1-Chlorocyclohexene was prepared from cyclohexanone and phosphorus pentachloride[24]. Chlorine and bromine were estimated by Volhard's method, after hydrolysis with ethanolic sodium hydroxide at reflux temperature (30–40 min). Boron was estimated by aqueous hydrolysis and subsequent titration (NaOH) in the presence of mannitol. Microanalyses (C and H) were carried out by us, but some also by the microanalytical laboratory of this department, and for these we thank Mr. B. MANOHIN and his staff.

Infrared spectra were recorded on a Perkin–Elmer 21 spectrophotometer, with sodium chloride optics, and ^1H nuclear magnetic resonance spectra at 60 Mc/s on a Perkin–Elmer R 10 or an A.E.I. RS.2. instrument.

All manipulative operations were carried out under a nitrogen atmosphere.

The chloroboration of cyclohexene, and related reactions

Preparation of a mixture of dibromocyclohexyl- and dibromocyclohexenyl-boranes, (I) and (II). Cyclohexene (14.9 g, 2 mol.) was added slowly to tribromoborane (22.9 g, 1 mol.) at 20°. There was a very vigorous reaction, and a dark brown colour appeared almost immediately. The reaction mixture was kept at 50–60° for 7 h and then at 20°

for 24 h. The heavy viscous liquid, upon two successive fractional distillations, afforded the following fractions: (a) tribromoborane (3.2 g), b.p. $63°/245$ mm (Found: B, 4.0; Br, 94.8. BBr_3 calcd.: B, 4.3; Br, 95.5%.); (b) 1-bromocyclohexane (4.2 g), b.p. $58-60°/15$ mm (Found: Br, 53.4. $C_6H_{11}Br$ calcd.: Br, 52.7 %.); (c) a third fraction (4.1 g), b.p. $85-97°/11$ mm, which appeared to be a mixture of (b) and (d) (from its infrared spectrum); and (d) a mixture of dibromocyclohexylborane and 1-dibromo-cyclohexenylborane, (I) and (II), (12.2 g), b.p. $128-136°/11$ mm (Found: C, 28.8; H, 4.6; B, 4.3; Br, 62.7. $C_6H_{11}BBr_2$ calcd.: C, 28.4; H, 4.34; B, 4.26; Br, 62.8. $C_6H_9BBr_2$ calcd.: C, 28.6; H, 3.56; B, 4.28; Br, 63.1 %.). The infrared spectrum of (d) showed a weak intensity band at 1587 cm^{-1}, which was assigned to the C=C stretching frequency adjacent to $-BBr_2$ in the dibromocyclohexenylborane. This stretching frequency was identical in position to that found in an authentic sample, obtained by a different procedure (see below); however, the intensity was three times enhanced in the latter. There was a solid residue (12.7 g), which appeared to be polymeric, and contained boron.

The above experiment was repeated, using 1:1 and 3:1 stoichiometries, but in both instances the same products were obtained although in different proportions.

Oxidation of fraction (d). Fraction (d) (9.1 g) in light petroleum (b.p. $30-40°$) (20 ml) was treated with excess hydrogen peroxide (15 ml, 20 vol.) at $20°$. There was an exothermal reaction, and the mixture was kept at $20°$ for 5 h. Water (20 ml), and ether (40 ml) were then added to the reaction mixture. The organic layer was separated, dried over anhydrous magnesium sulphate, and was then distilled, using an efficient column. Cyclohexanone (1.1 g, 31.2%), b.p. $154-155°$, and cyclohexanol (2.1 g, 58.2%), b.p. $159-160°$ (both compounds were identified also by their infrared spectra; complete separation was not achieved), were obtained.

Alcoholysis of fraction (d). n-Butanol (6.0 g) was added to fraction (d) at $10°$. The reaction was vigorous, and hydrogen bromide was evolved. The mixture was held at $20-30°$ for 3 h, with manual agitation, and was then freed from all volatile matter at $20°/20$ mm. The residue, upon fractional distillation afforded 1-bromocyclohexane (1.36 g), b.p. $48-49°/8$ mm; tri-n-butoxyborane (1.9 g), b.p. $98-100°/8$ mm, n_D^{20} 1.4082 (Found: B, 4.6. $C_{12}H_{27}BO_3$ calcd.: B, 4.7%.); and di-n-butoxycyclohexylborane (2.4 g), b.p. $129-133°/8$ mm (Found: B, 4.43. $C_{14}H_{29}BO_2$ calcd.: B, 4.5%.).

Preparation of dibromocyclohexenylborane (II). Cyclohexenyllithium (1 mol.) [prepared from 1-chlorocyclohexene (10.3 g) and lithium (3 g) in light petroleum (b.p. $30-40°$) (180 ml)] was added to tribromoborane (20.4 g, 1 mol.) with vigorous stirring at $20°$. The reaction was exothermal, and the temperature was maintained between $20-30°$. After completion of the addition, the reaction mixture was stirred for an additional 4 h. The insoluble precipitate was filtered off and was identified as lithium bromide. The filtrate was freed from solvent at $20°/15$ mm, and upon fractional distillation, the residue afforded 1-dibromocyclohexenylborane (11.8 g, 57.4 %), b.p. $90-94°/5$ mm (Found: C, 28.4; H, 3.7; B, 4.3; Br, 63.4%.).

The bromoboration of 1,5-cyclooctadiene, and related reactions

Preparation of dibromocyclooctylborane, (III). 1,5-Cyclooctadiene (9.75 g, 1 mol.) was added dropwise to tribromoborane (22.6 g, 1 mol.) at $10°$. The reaction mixture was kept at $40-60°$ for 6 h, and then at $20°$ for 18 h. Upon distillation, the identified products were: (a) 1-bromocyclooctane (5.2 g, 30.1 %), b.p. $92°/15$ mm (Found: Br,

41.5. $C_8H_{15}Br$ calcd.: Br, 41.8%.); and (b) dibromocyclooctylborane, (III), (6.2 g, 24.4%), b.p. 108–110°/10 mm (Found: C, 35.1; H, 4.1; B, 3.9; Br, 57.0. $C_8H_{15}BBr_2$ calcd.: C, 34.1; H, 5.3; B, 3.84; Br, 56.9%.).

Interaction of dibromocyclooctylborane and catechol. Dibromocyclooctylborane (5.1 g, 1 mol.) in methylene chloride (15 ml) was added slowly to catechol (1.99 g, 1 mol.) in the same solvent (15 ml), and the mixture was stirred at 40–50° for 3 h. All matter, volatile at 20°/20 mm, was removed. The residue afforded 2-cyclooctyl-1,3,2-benzodioxaborole, (IV), (3.58 g, 86.1%), b.p. 109–110°/0.09 mm (Found: C, 74.4; H, 6.9; B, 4.9. $C_{14}H_{19}BO_2$ calcd.: C, 73.3; H, 8.3; B, 4.7%.).

The chloroboration of norbornadiene, and related reactions

Preparation of (cis- and trans-6-chloro-2-nortricyclyl)dichloroboranes, (V). Norbornadiene (5.8 g, 1 mol.) was slowly added to trichloroborane (7.4 g, 1 mol.) at —80°. There was a highly exothermal reaction, the reaction mixture assumed a purple colour, and a precipitate formed. After the completion of the addition, the mixture was set aside at 20° for 2 h, whilst it gradually solidified. Distillation afforded a mixture of (cis- and trans-6-chloro-2-nortricyclyl)dichloroboranes, (V), (5.5 g, 83.2%), b.p. 60°/0.85 mm (Found: B, 5.1; Cl, 51.2. $C_7H_8BCl_3$ calcd.: B, 5.2; Cl, 50.9%.).

Preparation of (cis- and trans-6-phenyl-2-nortricyclyl)dichloroboranes, (VIII). Norbornadiene (6.11 g, 1.07 mol.) was added to dichlorophenylborane (9.85 g, 1 mol.) at —78°. The mixture was heated at 100° for 5 h, whereafter separation into two phases – a white solid and a green liquid – occurred. Material (0.18 g), trapped at —78°, volatile at 24°/0.5 mm was removed. Distillation afforded a mixture of (cis- and trans-6-phenyl-2-nortricyclyl)dichloroboranes, (VIII), (11.3 g, 72%), as a white crystalline solid which rapidly turned blue in air, b.p. 84°/0.03 mm (Found: C, 60.8; H, 5.2; B, 4.2; Cl, 27.8. $C_{13}H_{13}BCl_2$ calcd.: C, 62.2; H, 5.2; B, 4.3; Cl, 28.2%.)

In another experiment, distillation directly after mixing the components resulted in a yield of only 18% of the nortricyclyl derivatives; whereas if the mixture was first set aside at 20° for 5 h prior to distillation the yield was 59.8%.

Preparation of 2-(cis- and trans-6'-chloro-2'-nortricyclyl)benzo-1,3,2-dioxaborole, (VII). Norbornadiene (4.07 g, 1.3 mol.) was added to 2-chloro-1,3,2-benzodioxaborole (5.24 g, 1 mol.) at 25°. Addition was endothermal. The mixture was heated under reflux at 100° for 7 h. Distillation afforded a forerun (1.52 g), and then the viscous 2-(cis- and trans-6'-chloro-2'-nortricyclyl)benzo-1,3,2-dioxaborole, (VII), (5.51 g, 65.9%), b.p. 102°/0.05 mm (Found: C, 62.6; H, 4.9; B, 4.3; Cl, 14.3. $C_{13}H_{12}BClO_2$ calcd.: C, 63.3; H, 4.9; B, 4.4; Cl, 14.4%.), which slowly crystallised.

Interaction of (cis- and trans-6-chloro-2-nortricyclyl)dichloroboranes and catechol. Catechol (6.12 g, 1.06 mol.) in ether (12 ml) was added (mildly exothermic) to the boranes (10.62 g, 1 mol.) at 0°. The mixture was thoroughly agitated (40 min), whereafter material volatile at 23°/17 mm was removed to leave a residue of crude 2-(cis- and trans-6'-chloro-2'-nortricyclyl)benzo-1,3,2-dioxaborole, (VII), (12.49 g, 97.8%), which was purified by distillation, b.p. 110°/0.1 mm (Found: C, 62.4; H, 4.9; B, 4.3; Cl, 13.5%.), and had an infrared spectrum virtually identical to that obtained from the compound when prepared as in the preceding experiment.

Interaction of (cis- and trans-6-phenyl-2-nortricyclyl)dichloroboranes and catechol. Catechol (1.14 g, 1 mol.) in ether (7 ml) was added to a mixture of cis- and trans-(6-phenyl-2-nortricyclyl)dichloroboranes, (VIII), (2.60 g, 1 mol.) in ether (10 ml) at

o°; a slight heat of reaction was noted. After vigorous shaking (30 min), all matter volatile at 20°/20 mm was removed, to leave as a white solid 2-(cis- and trans-6-phenyl-2-nortricyclyl)benzo-1,3,2-dioxaborole (3.00 g, 100%). Distillation afforded the pure borole, m.p. 75°, b.p. 130°/0.2 mm (Found: C, 77.9; H, 5.7; B, 3.6. $C_{19}H_{17}BO_2$ calcd.: C, 79.2; H, 6.0; B, 3.7%.).

Interaction of (cis- and trans-6-chloro-2-nortricyclyl)dichloroboranes and water. Water (3.82 g, 2 mol.) in ether (30 ml) was added dropwise with shaking to the boranes (19.06 g, 1 mol.) at o°; there was heat of addition. Volatile matter at 25°/18 mm was removed to leave the white solid residue of (cis- and trans-6-chloro-2-nortricyclyl)-dihydroxyborane, (VI), (15.08 g, 96%), m.p. 110-1° (Found: C, 48.6; H, 6.1; B, 6.2; Cl, 20.5. $C_7H_{10}BClO_2$ calcd.: C, 48.7; H, 5.9; B, 6.3; Cl, 20.6%.). The borane could be recrystallised from diethyl ether.

The chloroboration of cyclooctatetraene and related reactions

Preparation of trans-β-styryldichloroborane. (X). Cyclooctatetraene (8.16 g, 1 mol.) was added dropwise to trichloroborane (9.2 g, 1 mol.) at −78°. The reaction was exothermal. At the completion of the addition, a white solid was obtained. The reaction mixture was allowed to warm up and all matter volatile at 20°/12 mm was removed and was trapped at −78°. The residue afforded trans-β-styryldichloro-borane, (X), (5.2 g, 34.4%), b.p. 57-60°/0.17 mm (Found: C, 52.3; H, 4.0; B, 5.8; Cl, 38.1. $C_8H_7BCl_2$ calcd.: C, 52.0; H, 3.8; B, 5.85; Cl, 38.5%.), leaving an undistillable residue (10.7 g). The volatile material, collected at −78°, was mainly trichloroborane (characterised as its pyridine complex).

Interaction of trans-β-styryldichloroborane and catechol. Catechol (1.75 g, 1 mol.) was added in suspension in methylene dichloride (~ 10 ml) to trans-β-styryldichloro-borane (3.1 g, 1 mol.) at −10°. The mixture was warmed to 20°, hydrogen chloride was evolved, and the residue, after being freed from solvent at 20°/12 mm, afforded 2-(trans-β-styryl)-1,3,2-benzodioxaborole, (XII), (2.64 g, 71.0%), b.p. 111-113°/0.1 mm (Found: C, 75.7; H, 5.2; B, 4.7. $C_{14}H_{11}BO_2$ calcd.: C, 76.0; H, 5.0; B, 4.9%.).

Hydrolysis of trans-β-styryldichloroborane. Water (0.98 g, 2 mol.) was added slowly to trans-β-styryldichloroborane (4.2 g, 1 mol.) suspended in light petroleum (b.p. 30-40°) (30 ml) at o°. The reaction was highly exothermal and hydrogen chloride was evolved. The system was warmed to 20°, and the white precipitate, trans-β-styryldihydroxyborane, (XI), (3.0 g, 89.4%), m.p. 143-146° (Found: C, 64.7; H, 6.3; B, 7.2. $C_8H_9BO_2$ calcd.: C, 65.0; H, 6.1; B, 7.3%.), was filtered off and washed with light petroleum (b.p. 30-40°) (2 × 10 ml).

Oxidation of trans-β-styryldichloroborane. Hydrogen peroxide (12 ml, 100 vol.) in water (50 ml) was added slowly to trans-β-styryldichloroborane (3.0 g) at 25°. After 12 h at 20°, the mixture was extracted with ether (2 × 50 ml). The ethereal extract was dried (Na_2SO_4) and, after removal of ether at 20°/12 mm, there was a residual white solid and a yellow liquid. Separation of this mixture by filtration afforded a solid, identified as benzoic acid, m.p. 121-122°. The filtrate, upon distillation, gave trans-β-chlorostyrene, b.p. 56-60°/3 mm, n_D^{25} 1.5731.

Deboronation of trans-β-styryldichloroborane. Zinc chloride (3.44 g, 1.5 mol.) in water (20 ml) was shaken with trans-β-styryldichloroborane (3.11 g, 1 mol.) for 4 h. The oily organic layer was separated and dried (Na_2SO_4). Fractional distillation af-

forded styrene (0.86 g, 49.2 %), b.p. 47°/20 mm (lit. b.p. 48°/20 mm), n_D^{19} 1.5469 (lit. n_D^{20} 1.5462) (identified also by its infrared spectrum).

The chloroboration of cycloheptatriene, and related reactions

Preparation of benzyldichloroborane. Cycloheptatriene (3.53 g, 1 mol.) was slowly added to trichloroborane (4.5 g, 1 mol.) at —78°. There was a white precipitate. The reaction mixture was allowed to warm up to 25°, and was then heated at 60–80° for 8 h. Upon distillation, benzyldichloroborane, (XIII), (2.1 g, 31.6 %), was obtained, b.p. 79–83°/12 mm (Found: C, 48.6; H, 4.2; B, 6.2; Cl, 41.0. C$_7$H$_7$BCl$_2$ calcd.: C, 48.6; H, 4.05; B, 6.25; Cl, 41.2%.).

Oxidation of benzyldichloroborane. Benzyldichloroborane (1.83 g) was reacted with hydrogen peroxide (10 ml, 100 vol.) in water (25 ml) at 25° for 16 h. Ether (50 ml) was added to the reaction mixture with stirring for 1 h. The organic layer was separated and dried over anhydrous Na$_2$SO$_4$. All matter volatile at 20°/13 mm was removed, leaving a white crystalline residue of benzoic acid (1.05 g, 82 %), m.p. 122° (identified also by its infrared spectrum).

Hydrolysis of benzyldichloroborane. Water (0.43 g, 2 mol.) in ether (8 ml) was added slowly to benzyldichloroborane (2.07 g, 1 mol.) in ether (10 ml), with vigorous stirring. The mixture was set aside for 1 h at 25°. Hydrogen chloride and ether were removed at 20°/13 mm, leaving a white residue of benzyldihydroxyborane, (XIV), (1.51 g, 93 %), m.p. 161° (Found: B, 8.1. C$_8$H$_9$BO$_2$ calcd.: B, 7.95 %.), which was recrystallised from benzene.

Interaction of allene and tribromoborane (eqn. 7)

Allene was allowed to pass into tribromoborane (15.8 g) at —20°. The apparatus comprised a three-necked flask, fitted with a cold finger (—78°) condenser and nitrogen- and allene-inlets. The input of allene was regulated by pre-solidification at —180°, and subsequent evaporation at such a rate as to maintain a steady flow during 2 h. There was an exothermal reaction. At the completion of the reaction, the mixture was fractionally distilled into: (*a*) (8.7 g), b.p. 40–50°/270 mm (infrared spectra indicated that this fraction was a mixture of tribromoborane and a brominated hydrocarbon.); and (*b*) (6.4 g), b.p. 79–85°/20 mm of a 1/1 adduct (Found: B, 3.6; Br, 82.4. C$_3$H$_4$BBr$_2$ calcd.: B, 3.72; Br, 82.6%.). The infrared spectrum of fraction (*b*) showed a medium intensity C=C stretching frequency at 1613 cm^{-1} and also the presence of a —BBr$_2$ group at ~ 800 cm^{-1}.

Preparation of hexaphenyl 1,4-diboracyclohexa-2,5-diene (eqn. 14)

Dibromophenylborane (8.0 g, 1 mol.) in light petroleum (b.p. 80–100°) (20 ml) and potassium (2.53 g, 2 mol.) were added to diphenylacetylene (5.76 g, 1 mol.) also in the same solvent (100 ml), almost simultaneously. The reaction mixture was refluxed for 4 h, then filtered. The solid obtained was crude potassium bromide. The filtrate, after being freed from solvent at 20°/10 mm, was suspended in light petroleum (b.p. 30–40°) (50 ml), and (mechanically) shaken for 2 h (this operation was carried out in order to dissolve the unreacted dibromophenylborane), then filtered. The precipitate, hexaphenyl 1,4-diboracyclohexa-2,5-diene (4.0 g, 46.6 %), m.p. 146–149° (Found: C, 87.9; H, 6.1; B, 3.9. C$_{40}$H$_{30}$B$_2$ calcd.: C, 90.04; H, 5.6; B, 4.06%.) was recrystallised from benzene.

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SUMMARY

The reactions of boron halides (Cl, Br) and of some organoboron chlorides with olefins have been investigated. Detailed results are presented on cyclohexene, allene, 1,5-cyclooctadiene, norbornadiene, cyclooctatetraene, and cycloheptatriene. It is clear that boron trichloride reacts only with the most reactive of olefins (the last three), so that the first-formed product may react further and prevent the reversible dechloroboration. Similar debromoborations appear to be less facile, and the general reaction pattern is for olefins to yield corresponding alkenyldibromoboranes, alkyldibromoboranes, and alkyl bromides.

Cyclohexene afforded cyclohexenyl- and cyclohexyldibromoboranes and cyclohexyl bromide. Allene and tribromoborane gave a 1:1 adduct. The only products isolated from the C_3H_{12}/BBr_3 ssytem were cyclooctyldibromoborane and cyclooctyl bromide. From norbornadiene with severally BCl_3, $o-C_6H_4O_2BCl$, and $PhBCl_2$ there was obtained a mixture of (cis- and trans-6-chloro-2-nortricyclyl)dichloroborane, 2-(6'-chloro-2'-nortricyclyl)benzo-1,3,2-dioxaborole, and (6-phenyl-2-nortricyclyl)-dichloroborane, respectively. From C_8H_8/BCl_3, trans-β-styryldichloroborane was produced. Cycloheptatriene and boron trichloride yielded benzyldichloroborane on distillation.

The structures and stereochemistry of the new organoboron halides were established by chemical reactions, infrared and NMR spectra, and syntheses.

From diphenylacetylene, dibromophenylborane, and potassium, there was obtained a compound of empirical formula $(C_6H_5)_3C_2B$. This is believed to be dimeric and may be a diboracyclohexadiene or an organocarborane.

The mechanisms of these reactions are discussed.

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