CHLOROBORATION AND ALLIED REACTIONS OF UNSATURATED COMPOUNDS

II. HALOBORATION AND PHENYLBORATION OF ACETYLENES; AND THE PREPARATION OF SOME ALKYNYLBORANES

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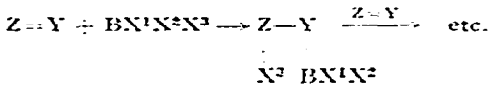
INTRODUCTION

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



$$Z{=}Y + BX^1X^2X^3 \longrightarrow \underset{X^3\quad BX^1X^2}{Z{-}Y} \xrightarrow{Z=Y} \text{etc.} \qquad (1)$$

In the present paper, haloboration and organoboration of acetylenes are described, as well as some other loosely related substitution reactions leading to alkynylboranes.

In Part I (ref. 1), we described the chloroboration and organoboration of aryl iso- and isothio-cyanates:

$$2ArNCQ + BX^1X^2X^3 \longrightarrow X^1B(NAr{-}CQ{-}X^2)(NAr{-}CQ{-}X^3),$$

where Q = O or S, and X^1, X^2, X^3 = Cl or Ar^1; and noted that $Ar^1 > Cl$ in migratory aptitude. Earlier literature on other reactions of type (1) was then reviewed. [We wish to draw attention to an error in that paper; reference 8 should have been to Paetzold, P.I. and not to Opitz, *et al.*] Particularly relevant to the present study are results on olefins[2,3]; with norbornadiene and dichlorophenylborane the product was the (dichloroboryl)phenylnortricyclene[2] (I), thus illustrating that also in this case Ph > Cl in migratory aptitude.

(I)

Whereas addition reactions of Lewis acids to olefins are still rare (except for the much-studied hydroborations[4]), such processes for acetylenes appear to be more common, although the steric course (where decided) depends apparently arbitrarily on the nature of the reagent; it seems useful briefly to review these reactions.

Disubstituted acetylenes afforded alkenylmercury acetates, by reaction with mercury(II) acetate[5]. *Trans*-addition ensued when acetylene was passed through a solution of mercury(II) chloride[6], although the *cis*-product was obtained by using a higher temperature and avoiding solvent[7]. Triethylalane added in a *cisoid* manner across the triple bond[8]. Other examples of chlorometallation of acetylenes are found in the reactions with arsenic(III)[9], antimony(V)[10], sulphur(II)[11], selenium(IV)[12], and tellurium(IV)[13] chlorides, although in many cases the steric course seems still undecided.

Dichlorophenylarsine afforded a number of products, which included (β-chlorovinyl)chlorophenylarsine, bis(β-chlorovinyl)phenylarsine, and (β-chlorovinyl)diphenylarsine as major constituents, by reaction with acetylene in presence of aluminium trichloride, thus showing that in this case $Cl > Ph$ in migratory aptitude[14].

Heterocycles have been obtained from diphenylacetylene in several instances. Thus, triphenylalane afforded 1,2,3-triphenylbenzaluminole[15], selenium(IV) chloride gave 3-chloro-2-phenylbenzoselenophene[16], and germanium(II) iodide, although originally believed to give a 3-membered germanium-containing ring isoelectronic with the cyclopropenyl cation[17], is now known to give the 6-membered dimer[18]. Other heterocycles have been obtained from diphenylacetylene and metal or metalloid halides in the presence of alkali metals; these included 5-membered heteroanalogues of 2,3,4,5-tetraphenylpyrrole (in which the NH group was replaced by Au, Hg, B, Tl, Zr, C, Si, Sn, P, As, Sb, S, Se, and Te)[19], and 6-membered diheteroanalogues of tetraphenylpyran (in which the two oxygen atoms were replaced by GeX_2 or SiX_2)[17,18,20].

A single instance of chloroboration of acetylene has been described, this was with trichloroborane, using a vapour-phase high temperature reaction in the presence of mercury(I) chloride on activated charcoal[21].

Only one type of reaction has previously proved useful for the preparation of acetylenic derivatives of boron; this is by the action of an organometallic compound on a boronic ester or a boron halide. The following such derivatives of boron have been reported: (a) acetyleneboronic acid and dibutoxypropynylborane[22], (b) bis(dialkylboryl)acetylenes[23], (c) dibutoxyethynylborane and dibutoxyhexynylborane[24,25], (d) dibutoxy(vinylethynyl)borane and dibutoxypropynylborane[26], (e) (isopropenylethynyl)dibutylborane[27], and (f) a number of diarylalkynylborane–pyridine complexes[28]. Literature on 4-co-ordinate alkynylboron derivatives has been collected in references 24 and 25.

DISCUSSION

Results on reactions of boranes with acetylenes

Data on the haloboration or phenylboration of three substituted acetylenes and acetylene, and on the acetolytic protodeboration or alcoholysis of the products are indicated in Figures 1–4. From these it will be clear that comment is required upon (a) the establishment of structures of the alkenylboranes, (b) the elucidation of their configuration, and (c) the relative migratory aptitudes (Ph *vs* Cl) of groups originally attached to boron and ultimately to carbon, and the nature and mechanism, more generally, of the chloro- and organoboration reactions.

Reactions of alkylacetylenes with arylboranes (see Fig. 1), and subsequent acetolysis of the products, are noteworthy for providing a novel route to substituted styrenes.

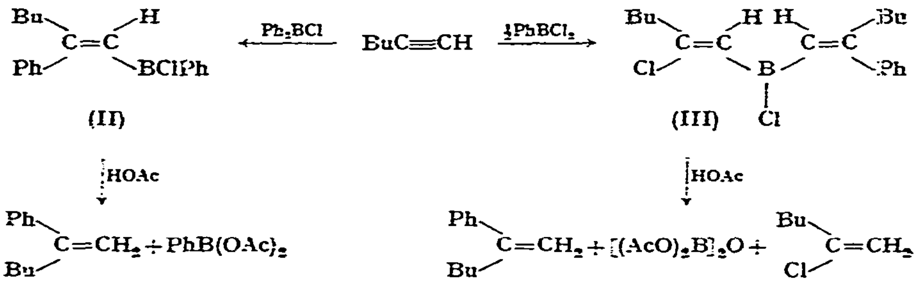


Fig. 1. Reactions of *n*-butylacetylene

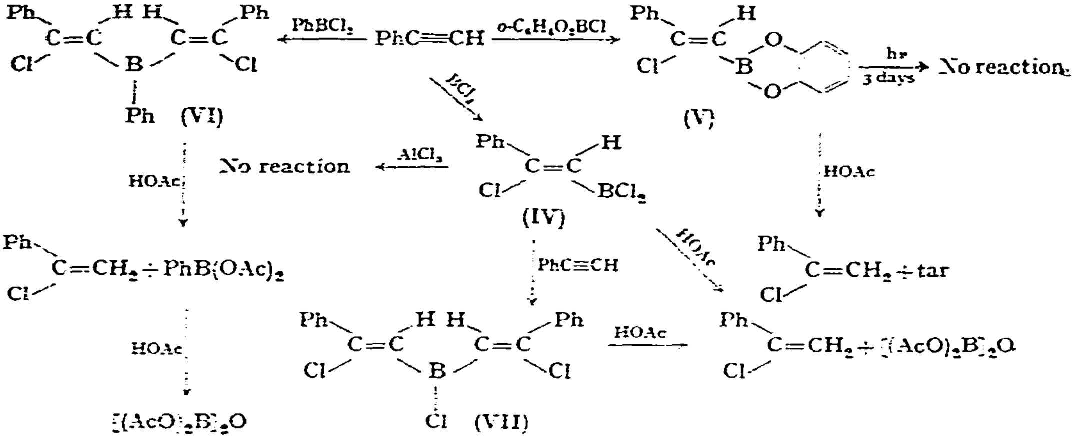


Fig. 2. Reactions of phenylacetylene

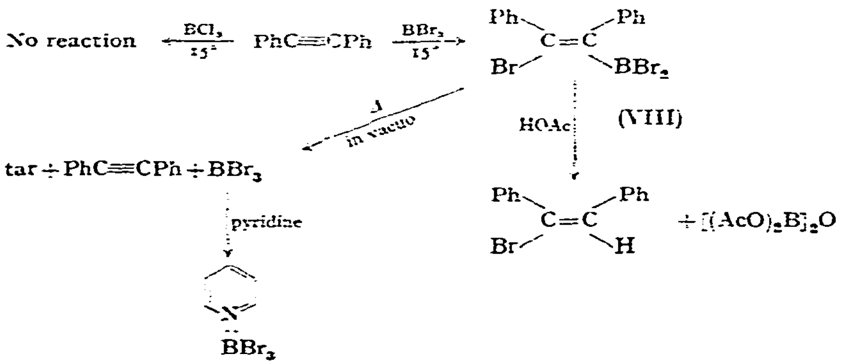


Fig. 3. Reactions of diphenylacetylene

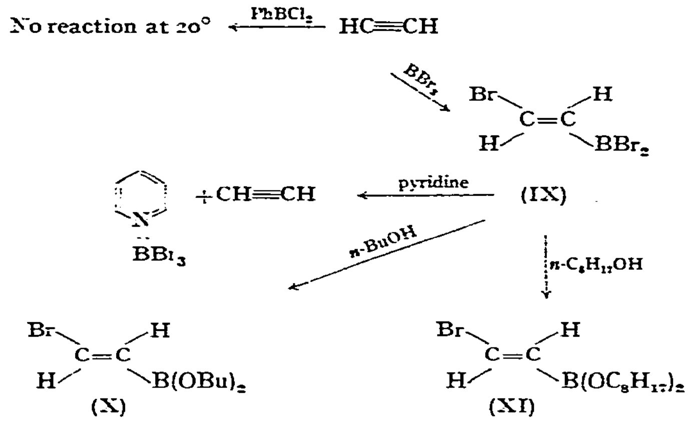


Fig. 4. Reactions of acetylene

The structures of alkenylboranes (II)–(XI)

These were established by full elemental analyses, molecular weight determination (for compound V), degradation with glacial acetic acid (see Figs. 1 to 3), alcoholysis to afford a known derivative, (X), and infrared spectra. The acetolysis of organoboranes is now an established technique of protodeboration[29]. The main features of the infrared spectra of (II)–(XI) are indicated in Table 1, with appropriate assignments, and more details for compounds (IV), (V), (VIII), and (IX) are provided in Fig. 5.

From the aspect of correlation of structure with spectral data, it is clear that a BX_2 group attached to olefinic carbon decreases the C=C stretching frequency. Thus, for example in α-chlorostyrene the C=C stretching frequency lies at ~ 1618 cm^{-1}, but is lowered to 1582 cm^{-1} in (IV), $PhClC{=}CHBCl_2$.

As to the effect of X (in BX_2) upon the C=C stretching frequency, inspection of Table 1 with regard to (IX), (X), and (XI) reveals that the BBr_2 group has a greater frequency-lowering effect than $B(OR)_2$ groups. As boron is less electronegative than carbon, these effects must be due to mesomeric rather than inductive effects.

The steric course of the addition

From Figs. 1–3, it will appear that chloroboration or organoboration proceeds by *cis*-addition for substituted acetylenes. The evidence for this is in fact incomplete. It is based on (i) the establishment of the configuration of the *cis*-bromostilbene obtained by acetolysis of (VIII); (ii) the assumption that acetolysis, under the mild conditions employed, involves retention of configuration; (iii) the assumption that failure to eliminate hydrogen chloride by heating (IV) in presence of aluminium chloride rules out the *trans*-product for (IV); (iv) the failure to isomerise (V) by ultraviolet irradiation and the assumption that there is a large energy difference between it and its stereoisomer; and (v) consistency with the proposed mechanism (see below), especially the interpretation of the reversal of relative migratory aptitude (Ph *vs* Cl) depending on the nature of the acetylene [see (II) and (VI)].

A direct solution to the problem of establishing the configuration of the alkenylboranes (II)–(VIII) is in fact difficult. Such matters are often solved by examination

TABLE 1

ALKENYLBORANES (II)–(XI): PRINCIPAL ABSORPTION MAXIMA (cm^{-1}) AND ASSIGNMENTS

Compound										*Assignment*
II	III	IV	V	VI	VII	VIII	IX[e]	X[e]	XI[e]	
1597 1575	1598	1600 (1) 1576 (3)	1600 (2)	1597 1593	1598 1592	1607 (1) 1575 (3)				C–C ring stretch (skeletal in-plane vibration)
1597[a]	1590 1585	1582 (2)	1618 (1)	1587	1582	1587 (2)	1575 (sh) (1) 1548 (2)	1582	1582	C=C stretch
			1468 (3)							B–O stretch (ring)[b]
								1333	1337	B–O stretch[c]
			1235 (4)							C–O stretch (ring)[b]
909 890	917 892				943 925					B–Cl stretch[d]
		956 (4) 934 (5)								BCl_2 asym. stretch[d]
						833 (4) 800 (5)	840 (3) 800 (4)			BBr_2 asym. stretch[d]

[a] $\nu_{C=C}$ stretching mode is masked by the ν_{C-C} ring skeletal in-plane vibration.

[b] These two bands are characteristic of the benzo-1,3-dioxa-2-boroles, (*cf.* J. A. BLAU, W. GERRARD, M. F. LAPPERT, B. A. MOUNTFIELD AND H. PYSZORA, *J. Chem. Soc.*, (1960) 380).

[c] L. J. BELLAMY, W. GERRARD, M. F. LAPPERT AND R. L. WILLIAMS, *J. Chem. Soc.*, (1958) 2412.

[d] L. P. LINDEMAN AND M. K. WILSON, *J. Chem. Phys.*, 24 (1956) 242.

[e] See also Table 2.

Numbers in parentheses refer to location in Fig. 5.

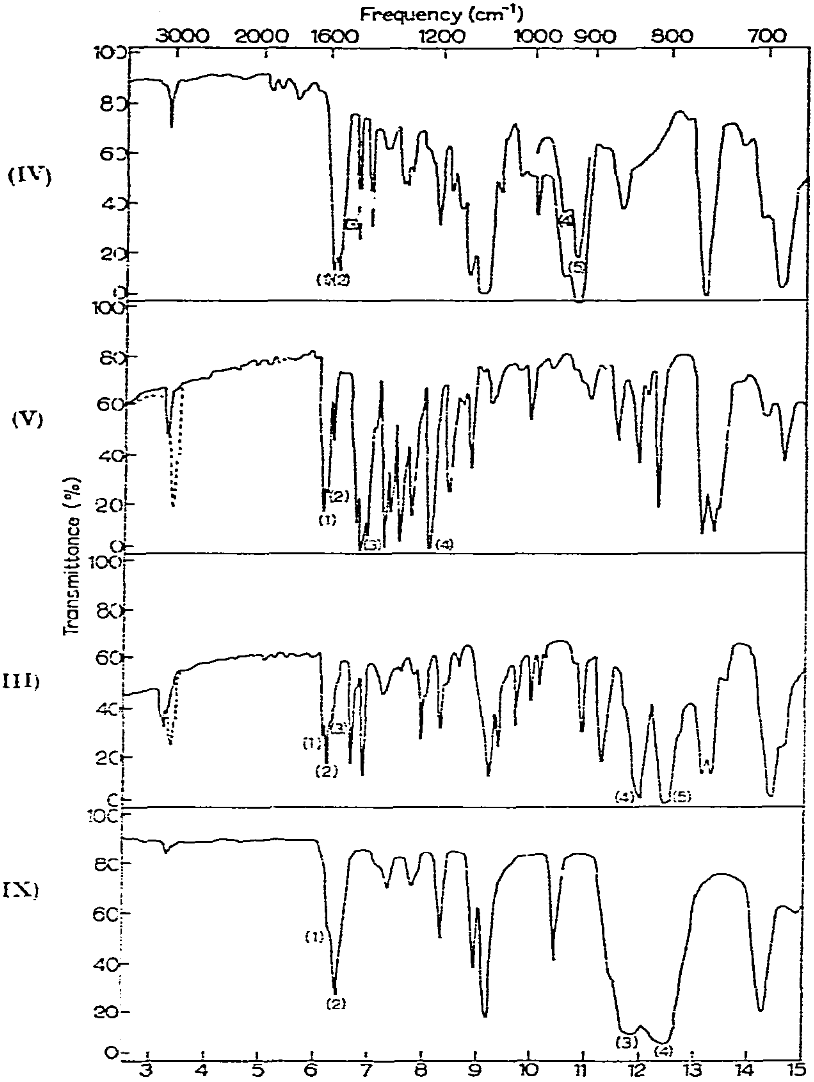


Fig. 5. Infrared spectra of alkenylboranes (see also Table 1).

of infrared and ^1H nuclear magnetic resonance spectra. Unfortunately, these are applicable only if each of the olefinic carbon atoms bears a hydrogen substituent, when the *trans*-isomer is characterised by a particularly strong CH out-of-plane deformation mode in the region 990–965 cm^{-1} (ref. 30) and this may be as low as 935 cm^{-1} if an electronegative substituent (Cl, Br) is attached to carbon[31]; an absorption characteristic of the *cis*-isomer is less well established. The proton spin–spin coupling constants for the $-CH_a{=}CH_b-$ system are of value in deciding stereochemistry, since for *cis*-protons $J_{ab} = 6$–14 c/s, whereas for *trans*-protons $J_{ab} = 11$–18 c/s (ref. 33).

This led us to investigate addition reactions of acetylene itself. Under the conditions used in our other experiments, namely at atmospheric pressure, acetylene failed to react with dichlorophenylborane. On the other hand, bromoboration was readily effected and compounds (IX)–(XI) were examined spectroscopically. Results are shown in Table 2.

TABLE 2

ALKENYLBORANES (IX)–(XI); SPECTROSCOPIC DATA RELEVANT TO STEREOCHEMISTRY

Compound	*Absorption in region 985–935 cm^{-1}*	$J_{H_aH_b}$
(IX)	952	15.2 c/s
(X)	950	14.9 c/s
(XI)	950	14.7 c/s

Compound (X) is identical to the compound prepared[25] by hydrogen bromide addition to di-*n*-butoxyethynylborane.

Another indirect way that we sought to employ was to make a comparison of appropriate products with identical ones, or isomeric partners, obtained from alkynylboranes by addition reactions (this indeed is the reason that in the present paper we report on such compounds). A suitable example appeared to be (XII), the isomer of which was presumably accessible by reaction of phenylacetylene with bromodiphenylborane. This example of bromoboration was in fact not pursued, since reaction (2) was not realised.

$$\mathrm{Ph{-}C{\equiv}CBPh_2} \xrightarrow{\mathrm{HBr}}\!\!\!\!\!\!\!/\quad \mathrm{(Ph)(Br)C{=}C(BPh_2)(H)} \qquad (2)$$

(XIII) (XII)

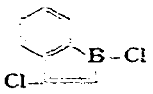
Interaction of (XIII) and hydrogen bromide led instead to preferential B–C cleavage, to give Ph_2BBr and $PhBBr_2$, and α-bromostyrene. Protodeboration, involving Ph–B< fission, by anhydrous hydrogen bromide, had been demonstrated before[34].

In a similar manner, we report the bromodeboration of $PhC{\equiv}CBPh_2$ by tribromoborane; the only identified product was bromodiphenylborane, Ph_2BBr (see also ref. 34). The bromoboration of diphenylacetylene had proved such a facile reaction (see Fig. 3), that there was a possibility of forming a diborylalkene $Ph(Br_2B)C{=}C(BPh_2)Br$. No doubt this would have been sterically difficult.

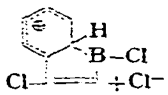
As to (i), the stereochemistry of α-bromostilbene was established by comparison with the authentic product which had been prepared previously[35]. The acetolysis reaction for protodeboration is now well-established[29], and it has been demonstrated in a number of cases of hydroborated olefins[36] and acetylenes[37], that acetolysis leads to retention of configuration. Coupling of (i) and (ii) thus provides evidence for the configuration of (VIII) to be as depicted in Fig. 3.

As to (iii), it was considered probable that the product of *trans*-addition of trichloroborane to phenylacetylene would undergo a Friedel-Crafts reaction (see ref. 38) to afford (XIV). Failure to effect such dehydrochlorination may be taken as some evidence for the configuration of (IV) to be as indicated. However, it may be that

(XIV) could in any case not be formed from the *trans*-isomer, since this would probably require a transition state, (XV), in which the *ortho*-carbon atom is tetrahedral, a condition which could not in those circumstances be achieved.



(XIV)



(XV)

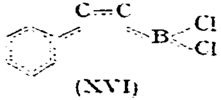
Regarding (iv), the failure to isomerise (V) may be due to an unusually large difference in energy between it and its stereoisomer. This in turn is reasonable, when it is noted that in (V) extended conjugation is possible, but would not be in its stereoisomer because of the steric difficulty of all the atoms in that molecule being coplanar.

The mechanism of halo- and organo-boration of acetylenes

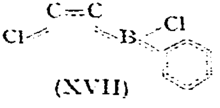
Features, admittedly based on limited data, that require rationalisation are (i) the Markownikoff direction of addition to acetylenes, (ii) the variable steric course, (iii) the dependence of reactivity upon the Lewis acid strength of the borane, (iv) the dependence of reactivity upon the basicity of the acetylene, and (v) the dependence of relative migratory aptitude (Ph *vs* Cl) upon the nature of the acetylene. These are all, except for the *trans*-addition to acetylene itself, reconcilable on the basis of a four-centre transition state, the driving force for the formation of which is the nucleophilic attack of the acetylene (as in acetylenic addition reactions, generally) on the electron-deficient boron atom, and which approaches more closely in structure to that of the products than of the reactants.

The Markownikoff addition to *n*-butylacetylene is explicable by the $+I$-effect of the *n*-butyl group, and to phenylacetylene by noting the possibility of delocalisation of the partial positive charge on the 1- but not the 2-carbon atom.

Points (ii) and (v) are conveniently considered together. It is a striking fact that the relative migratory aptitude, Ph > Cl, for *n*-butylacetylene is reversed for phenylacetylene. These data fall into place if it be recognised that control is thermodynamic, in terms of a transition state which closely resembles in structure that of the products. In this event, the stabilisation of the developing product depends upon maximum conjugation being effected. Thus, considering addition of dichlorophenylborane to



(XVI)



(XVII)

n-butyl- and phenylacetylenes, phenyl- (XVI) or chloro- (XVII) boration is possible. If R = Bu, the more effective conjugation is represented by (XVI), whilst if R = Ph, it is (XVII), since in this case the π-type molecular orbital also of course encompasses the group R.

The evidence that reactivity is related to the acceptor strength of the borane is based upon the following observations: (a) whereas mixing of phenylacetylene and boron trichloride at —78° was highly exothermal, heating was necessary in order to effect chloroboration with dichlorophenylborane, and even this proved of no avail when the reagent was chlorodiphenylborane; (b) whereas trichloroborane did not react with diphenylacetylene at room temperature, bromoboration with tribromoborane was readily achieved; and (c) tribromoborane was more reactive than dichlorophenylborane with respect to acetylene. It is established, with respect to tertiary amines or ethyl acetate as ligands, that relative acceptor strengths decrease in the series (a) $BCl_3 > PhBCl_2 > Ph_2BCl$ (ref. 39), and (b) $BBr_3 > BCl_3$ (ref. 40).

The influence of the basicity of the acetylene is shown by the greater reactivity of *n*-butylacetylene than of acetylene. Ionisation potential data on these hydrocarbons support the interpretation and are relevant since the energy of removal of an electron is related to electron-availability. The first ionisation potential for acetylene is 11.41 ± 0.01 ev, whilst for monoalkylacetylenes[41] this is decreased to ~ 10.3 ev. Our results also show reactivities decreasing in the order $BuC{\equiv}CH > PhC{\equiv}CH > PhC{\equiv}CPh$. Thus, under stated conditions (see Table 4), chlorodiphenylborane added to *n*-butylacetylene but not to phenylacetylene and trichloroborane added to phenylacetylene but not to diphenylacetylene. This order is more difficult to rationalise; ionisation potentials are not helpful, because aromatic π-electrons are preferentially removed.

In the above terms, the result on the bromoboration of acetylene appears anomalous. There are two possible explanations. Either the mechanism for addition to acetylene is different (and clearly cannot involve a 4-centre transition state) from that of substituted acetylenes. Alternatively, a unifying feature is that in every case products appear to be those that are thermodynamically favoured. This would imply that, unlike for hydroboration where control is kinetic, haloboration and organoboration reactions are thermodynamically controlled processes, which follow upon initial *cis*- or *trans*-addition. A consequence of this hypothesis is that reactions be reversible. In support for this, we observe (a) that addition of pyridine to (IX) effects elimination of $py \cdot BBr_3$ and regeneration of acetylene, and (b) that compound (VIII) upon heating under reflux in a partial vacuum reversibly dissociates.

Alkynylboranes

Two new alkynylboranes, (XVIII) and (XIX), were prepared as shown below.

$$\underset{\text{(XVIII)}}{PhC{\equiv}CBPh_2} \xleftarrow{Ph_2BCl} PhC{\equiv}\bar{C}Li^{+} \xrightarrow{PhBCl_2} \underset{\text{(XIX)}}{(PhC{\equiv}C)_2BPh}$$

TABLE 3

ALKYNYLBORANES (XVIII) AND (XIX): PRINCIPAL ABSORPTION MAXIMA (cm^{-1}) AND ASSIGNMENTS

Compound (XVIII)	(XIX)	*Assignment*
2165	2160 (1)	$C{\equiv}C$ stretch
1590	1592 (2)	C–C ring stretch (A_1)
1261	1256 (3)	B–C stretch
757	758 (4)	C–H out-of-plane deformation (B_2)
746 sh		

Numbers in parentheses refer to location in Fig. 6.

These were characterised by analysis and by their infrared spectra (see Table 3 and Fig. 6).

(XIX)

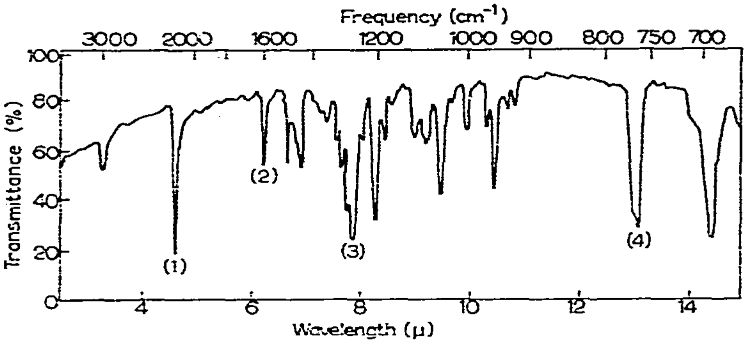


Fig. 6. Infrared spectra of alkynylborane (XIX) (see also Table 3).

Reactions of (XVIII) with hydrogen bromide and tribromoborane have already been commented upon.

EXPERIMENTAL

General procedures

Hydrocarbon solvents were dried over sodium wire. 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 and some also by the microanalytical laboratory of this department, and we offer our thanks to Mr. B. MANOHIN and his staff. Infrared spectra were recorded on a Perkin-Elmer 21 spectrophotometer, with sodium chloride optics, and ^{1}H nuclear magnetic resonance spectra on the Varian V4300B instrument at 40 Mc/s. Substituted boranes were prepared by standard methods[42]. The lithium reagents were prepared by known routes[43]. 1-Hexyne was prepared by addition of *n*-butyl bromide to monosodium acetylide in liquid ammonia[44]. Authentic samples of α-chlorostyrene[45] and α-bromostilbene[35] were prepared for purposes of comparison with reaction products.

Boration of acetylenes

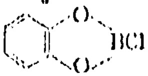
The general procedures for the preparation of alkenylboranes may be illustrated by the examples cited below, and other details are found in Table 4. All operations for the preparation of alkenylboranes were carried out under nitrogen atmosphere.

Preparation of (2-chloro-2-phenylvinyl)dichloroborane

Phenylacetylene (5.75 g, 1 mol.) was added dropwise to trichloroborane (6.6 g, 1 mol.) at —78°. The apparatus comprised a three-necked flask, fitted with a dropping funnel, a cold finger (—78°) condenser, and a nitrogen inlet. Drying tubes were employed to prevent incursion of atmospheric moisture. The reaction was very vigorous and much heat was evolved during mixing. At the completion of the addition (50 min), a heavy, dark-coloured liquid was obtained. The reaction mixture was allowed to warm up,

TABLE 4

ORGANOBORATION AND HALOBORATION OF ACETYLENES

Reactants		*Product*	*Experimental conditions*	*Yield %*	*B.P. °C/mm*	*Analysis*							
Substituted Borane	*Acetylene*					*Found (%)*				*Required (%)*			
						C	*H*	*B*	*Hal*	*C*	*H*	*B*	*Hal*
Ph_2BCl	BuC≡CH	(II)	130–140°; 4 h	37·4	138–40/0.01	75·5	7·4	3·75	12·5	76·5	7·1	3·8	12·5
$PhBCl_2$	BuC≡CH	(III)	130–140°; 5 h	39·2	160/0.07	67·5	7·8	3·2	21·1	67·0	7·75	3·3	21·8
BCl_3	PhC≡CH	(IV)	−78°; 1 h	38·8	92/0.3	44·0	2·8	4·9	48·2	43·7	2·7	4·9	48·5
	PhC≡CH	(V)	130–150°; 4 h	75·0	136/0.03 m.p. 78°	65·9	4·2	4·2	13·7	65·5	3·9	4·2	13·8
$PhBCl_2$	PhC≡CH	(VI)	0°; 3 h	36·2	170/0.2	73·4	3·5	2·9	19·1	73·0	3·3	3	19·5
BCl_3	PhC≡CH	(VII)	−78°; 2 h	41·1	99/0.1	58·0	3·9	3·3	32·4	59·9	3·7	3·4	33·0
BBr_3	PhC≡CPh	(VIII)	20°; 1 h	74·5	m.p. 53–54	39·0	3·6	2·6	55·8	39·3	2·3	2·5	56·0
BBr_3	HC≡CH	(IX)	20–45°; 5 h	70·0	104–106/100	8·8	0·5	3·8	87·0	87·0	0·7	3·9	87·0

and all matter volatile was removed at 20°/12 mm, and was trapped at —78°, whilst the residue upon distillation afforded (2-chloro-2-phenylvinyl)dichloroborane (4.8 g, 38.8%), b.p. 92°/0.3 mm, (Found: C, 44.0; H, 2.8; B, 4.9; Cl, 48.2. $C_8H_6BCl_3$ calcd.: C, 43.7; H, 2.7; B, 4.9; Cl, 48.5%), leaving an undistillable residue (6.34 g). The volatile material, collected at —78°, afforded the benzonitrile–trichloroborane complex [2.26 g, 18.2% (this figure is calculated on the quantity of trichloroborane originally used)], m.p. 140–42° (Found: B, 4.91; Cl, 48.1. $C_7H_5BCl_3N$ calcd.: B, 4.91; Cl, 48.3%), upon the addition of benzonitrile (1.06 g, 1 mol.).

Another experiment was carried out, using an identical procedure to the above, except that chloroform was the solvent and the reaction was carried out in the presence of aluminium trichloride (1.6 mol.). There was no evolution of hydrogen chloride, and the yield of (2-chloro-2-phenylvinyl)dichloroborane was considerably less (30.2%).

Preparation of (2-chloro-2-phenylvinyl)(o-phenylenedioxy)borane

Phenylacetylene (2.58 g, 1 mol.) was added to (*o*-phenylenedioxy)chloroborane (3.9 g, 1 mol.). The reaction mixture was heated for 4 h at 130–150°. Upon distillation, the reaction mixture afforded (2-chloro-2-phenylvinyl)(*o*-phenylenedioxy)borane (4.86 g, 75%), b.p. 136°/0.03 mm, m.p. 78° (Found: C, 65.9; H, 4.2; B, 4.2; Cl, 13.7. $C_{14}H_{10}BClO_2$ calcd.: C, 65.5; H, 3.9; B, 4.2; Cl, 13.8%), leaving a solid residue (0.6 g).

Preparation of (2-chloro-2-phenylvinyl)(o-phenylenedioxy)borane by interaction of catechol and (2-chloro-2-phenylvinyl)dichloroborane

Catechol (1.16 g, 1 mol.) was added in suspension in methylene dichloride (~ 8 ml) to (2-chloro-2-phenylvinyl)dichloroborane (2.3 g, 1 mol.) at —10°. The system was warmed to 20°, when hydrogen chloride was evolved, and the residue, after being freed from solvent at 20°/12 mm, afforded (2-chloro-2-phenylvinyl)(*o*-phenylenedioxy)borane (2.1 g, 78%), b.p. 148°/0.06 mm (Found: B, 4.18; Cl, 13.8%) on distillation. There was a residue (0.5 g).

(2-Chloro-2-phenylvinyl)(*o*-phenylenedioxy)borane (5.8 g) was subjected to ultraviolet irradiation in a quartz flask for 3 days. There appeared to be some decomposition. The material was distilled, and gave the unchanged starting material (5.1 g, 88%), b.p. 156°/0.1 mm, mixed m.p. 76–78°, (Found: B, 4.2; Cl, 13.7%). The infrared spectrum of the compound was identical with that of the original sample.

Preparation of (2-bromo-1,2-diphenylvinyl)dibromoborane

Tribromoborane (5.3 g, 1 mol.) was added slowly to diphenylacetylene (3.76 g, 1 mol.). The reaction was exothermal and almost at once a dark purple solution was formed. The reaction mixture was allowed to cool, whereupon (2-bromo-1,2-diphenylvinyl)-dibromoborane (6.7 g, 74.5%), m.p. 53–54° (Found: C, 39.0; H, 3.6; B, 2.6; Br, 55.8. $C_{14}H_{10}BBr_3$ calcd.: C, 39.3; H, 2.34; B, 2.52; Br, 56.0%), crystallized out, and was recrystallized from benzene.

Interaction of acetic acid and vinylboranes

The results are given in (*a*)–(*g*), and summarised in Table 5.

TABLE 5

ACETOLYSIS OF BORANE

Reactants *$HOOCCH_3$ and vinylborane*	*Derivative of hydrocarbon formed*	*Boron compound formed*
$PhCCl{=}CHBCl_2$	$PhCCl{=}CH_2$	$[(CH_3COO)_2B]_2O$
$(PhCCl{=}CH)_2BCl$	$PhCCl{=}CH_2$	$[(CH_3COO)_2B]_2O$
$(PhCCl{=}CH)_2BPh$	$PhCCl{=}CH_2$, C_6H_6	$[(CH_3COO)_2B]_2O$
	$PhCCl{=}CH_2$	tar
$BuCPh{=}CHBClPh$	$BuCPh{=}CH_2$	$PhB(OOCCH_3)_2$
$BuCPh{=}CH\text{-}BCl\text{-}CH{=}CClBu$	$BuCPh{=}CH_2$, $BuCCl{=}CH_2$	$[(CH_3COO)_2B]_2O$
$PhCBr{=}C(BBr_2)Ph$	$PhCBr{=}CHPh$	$[(CH_3COO)_2B]_2O$

(*a*) *(2-Chloro-2-phenylvinyl)dichloroborane.* Acetic acid (4.3 g, 3.3 mol.) in light petroleum (b.p. 30–40°) (10 ml) was added dropwise with shaking to (2-chloro-2-phenylvinyl)dichloroborane (4.8 g, 1 mol.) in the same solvent (12 ml) at 20°. The reaction was exothermal and hydrogen chloride was evolved. The reaction mixture was allowed to reflux at 30–40° for 1.5 h and after cooling, it was filtered. The filtrate, upon fractional distillation, afforded α-chlorostyrene (2.8 g, 92.5 %), b.p. 69°/12 mm (Found: C, 70.0; H, 5.1; Cl, 25.6. C_8H_7Cl calcd.: C, 69.5; H, 5.05; Cl, 25.6 %). The precipitate was identified as tetra-acetyl diborate (2.7 g, 90 %), m.p. 150° (Found: B, 7.9. $C_8H_{12}B_2O_9$ calcd.: B, 7.9 %).

(*b*) *Bis(2-chloro-2-phenylvinyl)chloroborane.* A mixture of acetic acid (3.0 g, 3.8 mol.) and bis(2-chloro-2-phenylvinyl)-chloroborane (4.2 g, 1 mol.) in a total volume of light petroleum (b.p. 30–40°) (20 ml) was treated substantially as described above. The reaction was exothermal and hydrogen chloride evolution was noted. The filtrate was fractionally distilled to yield α-chlorostyrene (3.2 g, 87.5 %), b.p. 73°/15 mm, (Found: Cl, 25.6 %). The precipitate was found to be tetra-acetyl diborate (1.6 g, 89.5 %), m.p. 148° (Found: B, 7.8 %).

(*c*) *Bis(2-chloro-2-phenylvinyl)phenylborane.* Acetic acid (2.4 g, 3.84 mol.) in light petroleum (b.p. 30–40°) (8 ml) was slowly added with shaking to bis(2-chloro-2-phenylvinyl)phenylborane (3.8 g, 1 mol.) in the same solvent (10 ml)at 20°. The reaction mixture was refluxed for 5 h. At the completion of the reaction, the precipitate of tetra-acetyl diborate, (1.1 g, 75 %), m.p. 147–148° (Found: B, 7.7 %) was filtered off and was washed with light petroleum (b.p. 30–40°) (10 ml). The filtrate was carefully fractionally distilled; the products, as well as acetic acid and acetic anhydride, included benzene (0.6 g, 74 %) b.p. 80° (also identified by its infrared spectrum) and α-chlorostyrene (3.6 g, 90 %), b.p. 12°/14 mm, (Found: Cl, 25.4 %). There was an undistillable residue.

(*d*) *(2-Chloro-2-phenylvinyl)(o-phenylenedioxy)borane.* Acetic acid (2.02 g, 1.7 mol.) in light petroleum (b.p. 30–40°) (5 ml) was added to (2-chloro-2-phenylvinyl)(*o*-phenylenedioxy)borane (5.1 g, 1 mol.) suspended in the same solvent (20 ml) at 20°. The reaction was allowed to proceed at reflux temperature for 1 h. Fractional distillation of the reaction mixture afforded α-chlorostyrene (2.1 g, 76.5 %), b.p. 80°/20 mm, (Found: Cl, 25.5 %) (also identified by its infrared spectrum). There was a tarry residue which was not identified.

(*e*) *(2-Phenyl-2-n-butylvinyl)chlorophenylborane.* Acetic acid (1.61 g, 2 mol.) in *n*-pentane (5 ml) was added dropwise with shaking to (2-phenyl-2-*n*-butylvinyl)-chlorophenylborane (3.8 g, 1 mol.) in the same solvent (10 ml) at 20°. Considerable heat was evolved, and hydrogen chloride was formed. At the completion of the reaction, the precipitate, diacetoxyphenylborane, (2.2 g, 81 %), m.p. 170–176° (decomp.) (Found: B, 5.5. $C_{10}H_{11}BO_4$ calcd.: B, 5.3 %) was filtered off. The filtrate, upon fractional distillation, afforded α-butylstyrene (1.68 g, 78%), b.p. 94°/14 mm (Found: C, 89.1; H, 10.7. $C_{12}H_{16}$ calcd.: C, 90; H, 10 %).

(*f*) *(2-n-Butyl-2-phenylvinyl)(2-n-butyl-2-chlorovinyl)chloroborane.* Acetic acid (2.7 g, 3 mol.) and (2-*n*-butyl-2-phenylvinyl)(2-*n*-butyl-2-chlorovinyl)chloroborane (4.9 g, 1 mol.) in a total volume of *n*-pentane (20 ml) were reacted together as described in (*e*). Hydrogen chloride evolution and heat of reaction were noted. The precipitate, tetra-acetyl diborate, (1.7 g, 82 %), m.p. 144–147° (Found: B, 7.8 %), which formed during the course of reaction, was filtered off. The filtrate was subjected to fractional distillation, which afforded 2-chloro-1-hexene (1.49 g., 82.8 %), b.p. 118° (Found: Cl, 29.0. $C_6H_{11}Cl$ calcd.: Cl, 29.5%), acetic anhydride (0.6 g, 77.5 %), b.p. 138° (identified by its infrared spectrum), and α-butylstyrene (2.1 g, 86.5 %) b.p. 90°/12 mm, (Found: C, 89.0; H, 10.6 %).

(*g*) *(2-Bromo-1,2-diphenylvinyl)dibromoborane.* Acetic acid (4.06 g, 3.2 mol.) in *n*-pentane (10 ml) was added to (2-bromo-1,2-diphenylvinyl)dibromoborane (9.05 g., 1 mol.) in the same solvent (20 ml) at 20°. There was a considerable heat of reaction and hydrogen bromide was evolved. The reaction was allowed to proceed for 1 h, whereafter the precipitate of tetra-acetyl diborate (2.2 g, 78 %), m.p. 147–148° (Found: B, 7.82 %) was filtered off. The filtrate afforded α-bromostilbene (4.65 g, 85 %), b.p. 138°/0.4 mm, m.p. 19–20° (Found: C, 65.3; H, 4.7; Br, 31.0. $C_{14}H_{11}Br$ calcd.: C, 65.0; H, 4.25; Br, 30.9%).

Alcoholysis of vinylboranes

a. Preparation of (2-bromovinyl)dibutoxyborane. 1-Butanol (3.46 g, 2 mol.) was added slowly to (2-bromovinyl)dibromoborane (6.47 g, 1 mol.) at 0°. The reaction was highly exothermal and hydrogen bromide was evolved. The system was warmed to 20° and freed from hydrogen bromide at 20°/40 mm. The residue upon distillation afforded (2-bromovinyl)dibutoxyborane (4.9 g, 80%), b.p. 60–61°/0.1 mm, (Found: 4.1; Br, 30.0. $C_{10}H_{20}BBrO_2$ calcd.: B, 4.1; Br, 30.4%).

b. Preparation of (2-bromovinyl)di(octyloxy)borane. 1-Octanol (4.25 g, 2 mol.) was treated, substantially as described above, with (2-bromovinyl)dibromoborane (4.45 g, 1 mol.). The residue upon distillation afforded (2-bromovinyl)di(octyloxy)borane (4.7 g, 78%), b.p. 190–195°/0.05 mm (Found: C, 58.0; H, 9.8; B, 2.9; Br, 21.4. $C_{18}H_{36}BBrO_2$ calcd.: C, 57.5; H, 9.6; B, 3.0; Br, 21.4%).

Preparation of bis(phenylethynyl)phenylborane

Dichlorophenylborane (7.9 g, 1 mol.) was added to lithium phenylacetylide (2 mol.) [prepared from a light petroleum (b.p. 30–40°) solution of *n*-butyllithium (116 ml) and phenylacetylene (10.2 g, 1 mol.)] with vigorous stirring, at such a rate as to maintain a steady reflux of the solvent. The reaction was exothermal and mixing was continued for 50 min. After completion of the addition, the reaction mixture was stirred for an additional 3 h, whereafter ether was added in order to dissolve the organic material. The insoluble precipitate was filtered off and identified as lithium chloride (4.25 g, 100%). The filtrate was freed from solvent at 20°/12 mm, and the residue afforded bis(phenylethynyl)phenylborane (15.4 g, 78%), m.p. 84–85° (Found: C, 91.1; H, 5.4; B, 3.7. $C_{22}H_{15}B$ calcd.: C, 91.4; H, 5.18; B, 3.74%), which was recrystallised from benzene.

Preparation of (phenylethynyl)diphenylborane

Chlorodiphenylborane (3.39 g, 1 mol.) was added to lithium phenylacetylide (1 mol.), in light petroleum (b.p. 30–40°) (30 ml) with vigorous stirring. The reaction was exothermal and mixing took 30 min. After the completion of the addition, the reaction mixture was stirred for an additional 3 h. Ether (100 ml) was added to the reaction mixture, which was stirred for a further 30 min. The insoluble material was filtered off and identified as lithium chloride (0.7 g, 100%). The solvent was removed from the filtrate at 20°/13 mm and the residue afforded (phenylethyl)diphenylborane (3.35 g, 74.5%), m.p. 108–110° (Found: C, 90.9; H, 5.72; B, 4.01. $C_{20}H_{15}B$ calcd.: C, 90.5; H, 5.65; B, 4.07%), after recrystallisation from benzene.

Interaction of hydrogen bromide and diphenyl(phenylethynyl)borane

Diphenyl(phenylethynyl)borane (10.2 g) was suspended in *n*-pentane (40 ml) and cooled to −78°. Hydrogen bromide was slowly passed into the reaction vessel. There was an exothermal reaction. The reaction was continued for 3 h, whereafter the temperature was allowed to rise and upon reaching 0° there was vigorous hydrogen bromide evolution. At the completion of the reaction, all matter volatile at 20°/20 mm was removed, and the residue was subjected to careful fractional distillation, which afforded α-bromostyrene (1.4 g, 18.8%), b.p. 76°/10 mm, n_D^{20} 1.5881 (Found: Br, 43.1. C_8H_7Br calcd.: Br, 43.6%); dibromophenylborane (2.5 g, 26.5%), b.p. 85°/10 mm, (Found: B, 4.3; Br, 64.2. $C_6H_5BBr_2$ calcd.: B, 4.37; Br, 64.7%), and bromodiphenylborane (3.5 g, 37.2%), b.p. 165–170°/10 mm (Found: B, 4.5; Br, 32.3. $C_{12}H_{10}BBr$ calcd.: B, 4.4; Br, 32.6%). There was a residue (2.1 g).

Interaction of tribromoborane and diphenyl(phenylethynyl)borane

Tribromoborane (6.1 g, 1 mol.) was added to diphenyl(phenylethynyl)borane (6.4 g, 1 mol.). There was an exothermal reaction At the completion of the reaction (4 h) the mixture was fractionally distilled. The only product identified was bromodiphenylborane (3.3 g, 58.5%), b.p. 105–110°/0.4 mm, (Found: B, 4.3; Br, 32.2%). There was a residue (6.8 g).

Interaction of pyridine and (2-bromovinyl)dibromoborane

Pyridine (0.65 g, 1 mol.) in *n*-pentane (8 ml) was added to (2-bromovinyl)dibromoborane (2.28 g, 1 mol.) in the same solvent (10 ml) at 20°. The reaction was exothermal, and was allowed to proceed at the reflux temperature of the solvent for 3 h, whereafter the precipitate, of tribromoborane–pyridine complex (2.2 g, 81.3%), m.p. 128–130° (Found: B, 3.3. $C_5H_5BBr_3N$ calcd.: B, 3.28%) was filtered off. It was also identified by its infrared spectrum (taken in chloroform solution), which showed characteristic bands at 1629, 1609 sh., 1490, 1462, 1357, 1161, 1094, and 1025 cm^{-1}.

Dissociation of (2-bromo-1,2-diphenylvinyl)dibromoborane

(2-Bromo-1,2-diphenylvinyl)dibromoborane (6.2 g) was slowly heated under partial vacuum (2 mm) for 6 h. All matter volatile was trapped at —78°. The volatile material so collected, afforded the tribromoborane–pyridine complex (3.8 g, 79.8%), m.p. 129° (Found: B, 3.2 %), upon the addition of pyridine. The complex was also identified by its infrared spectrum. The residual matter appeared to be polymeric.

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SUMMARY

Selected haloboranes, $BX^1X^2X^3$ (X^1 = Cl or Br, and X^2 and X^3 are either = X^1 or Ph), generally reacted with acetylenes ($HC\equiv CH$, $BuC\equiv CH$, $PhC\equiv CH$, or $PhC\equiv CPh$) to afford (2-halo- or 2-phenylalkenyl)boranes, depending on the nature of the acetylene. The products were characterised by acetolytic protodeboration, alcoholysis, and by their infrared spectra. For unsymmetrical acetylenes, Markownikoff addition was demonstrated; the steric course of reactions is *trans* for acetylene but is believed to be *cis* for at least some of the substituted acetylenes. Reactivity increases with high acceptor strength of borane and high nucleophilicity of the acetylene. Chloro- and organoboration of acetylenes is evidently a thermodynamically-controlled process, in contrast to hydroboration.

Some of the reactions are of potential application for synthesis of α-substituted styrenes and their derivatives.

Two alkynylboranes have been obtained from haloboranes and lithioacetylenes.

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