Stereoselectivity of Halogenoboronation of Phenylacetylene

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The halogenoboronation of phenylacetylene with boron trihalides (halogen = I, Br, or Cl) proceeds under kinetic control to produce dihalogeno-(Z)- or (E)-2-halogeno-2-phenylvinylboranes and (<10%) dihalogeno-(Z)- or (E)-2-halogeno-1-phenylvinylboranes. Subsequent reactions of these boranes with phenylacetylene produce halogenodivinyl- and trivinyl-boranes with the added acetylene substituting always as an (E)-2-halogeno-2-phenylvinyl ligand. The differences in reactivity of boranes formed by addition of boron at C-1 and -2 of the acetylene are discussed.
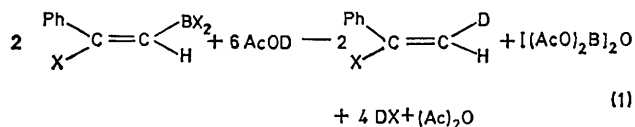
THIS paper describes the reactions and properties of a series of halogenovinylboranes prepared by the addition–substitution reaction known as halogenoboration.[1] The sequence rules of ref. 2 have been used to characterise the geometry of the vinyl substituents by means of the E–Z-nomenclature. The following additional terms are used for brevity: (a) L describes a vinyl ligand attached to boron when the geometry is unimportant or undetermined; and (b) halogenoboration describes the addition of a $>$B–Hal system across a multiple bond and the direction of addition is *trans*[1] if the boron and halogen functions are *trans* to each other in the product.

Halogenoboration.—Lappert and Prokai[1] treated a series of substituted acetylenes with boron Lewis acids. They argued that the most probable course of halogenoboration was that of a thermodynamically controlled process which follows upon an initial *trans*- or *cis*-addition determined by the nature of the reactants.

Some of Lappert and Prokai's methods have been developed to analyse the products of halogenoboration of phenylacetylene. We were able to assign unambiguously the *total* amount of *cis*- or *trans*-addition in dihalogenovinyl-, halogenodivinyl-, and trivinyl-boranes by a suitable degradation process and were also able to decide whether boron was attached to C-1 or -2 of the vinyl ligand. However, the individual isomers of the vinylboranes could not always be observed (or isolated) because their characteristic n.m.r. spectra overlapped, and physical separation techniques were, for the most part, unsatisfactory.

Stereochemistry.—The stereochemical arrangement of the vinyl ligands was determined by treating the vinyl-borane with acetic [²H]acid to produce a trisubstituted ethylene [equation (1)], the configuration of which could be determined independently. We first established that the acetolysis of dihalogenovinylboranes proceeded with complete retention of configuration. The ratio of

$$2 \; \begin{array}{c} Ph \\ X \end{array}\!\!C\!=\!C\!\!\begin{array}{c} BX_2 \\ H \end{array} + 6\,AcOD \longrightarrow 2 \; \begin{array}{c} Ph \\ X \end{array}\!\!C\!=\!C\!\!\begin{array}{c} D \\ H \end{array} + [(AcO)_2B]_2O$$

$$+ \; 4\,DX + (Ac)_2O \qquad\qquad (1)$$

isomers in a mixture of dihalogeno-(Z)- and (E)-2-halogeno-2-phenylvinylboranes may be determined from the ratio of their olefin ¹H n.m.r. signal intensities; after acetolysis with acetic [²H]acid the ratio of the olefinic ¹H n.m.r. signal intensities from the products, (E)- and (Z)-2-deuterio-1-halogeno-1-phenylethylenes, was measured and found to be identical with that of the boranes. (E)-1-Bromo-2-deuterio-1-phenylethylene was prepared by an independent route[3] and the geometry of the acetolysis products thus established from a comparison of n.m.r. spectra. The (E)- and (Z)-1-chloro(or iodo)-2-deuterio-1-phenylethylenes had almost identical n.m.r. spectra with those of their bromo-analogues (Table 2) and so the geometry of the iodo- and chloro-ethylenes could be inferred with some certainty.

The olefinic ¹H n.m.r. signals of halogenodivinyl- and trivinyl-boranes are partially obscured by the aromatic signals and so it is *assumed* that retention of configuration occurs when these boranes undergo acetolysis; this seems quite reasonable and it is certainly true for acetolysis of alkylvinylhalogenoboranes where no signal overlap is

[1] N. F. Lappert and B. Prokai, *J. Organometallic Chem.*, 1964, **1**, 384.

[2] R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem. Internat. Edn.*, 1966, **5**, 385.

[3] C. Dufraisse, *Compt. rend.*, 1920, **171**, 961.

encountered.[4] We can thus assign the stereochemistry of all substituted vinyl ligands where attack by boron of phenylacetylene occurs at C-1. The geometry of substituted vinyl ligands arising from C-2 attack cannot be established in a similar way because the boron–carbon bond does not break on acetolysis.

Preparation and Reactions of Halogenovinylboranes from Attack on C-1.—Table 1 contains a breakdown of the

and *all* other halogenoborations proceed almost 100% by addition of boron at C-1. The nature of the boron trihalide does not appear particularly important in determining the direction of C-1 addition.

Once a vinyl ligand has been introduced into a halogenoborane all subsequent halogenoborations convert phenylacetylene into the (*E*)-2-halogeno-2-phenylvinyl ligand *exclusively*. In addition, the reaction can

TABLE 1

Isomer ratios of trisubstituted ethylenes from acetolysis of halogenovinylboranes with acetic [^{2}H]acid [a]

Borane	$\begin{array}{c}C_6H_5\\ \diagdown C{=}C\diagup H\\ X\diagup \quad \diagdown D\end{array}$	$\begin{array}{c}C_6H_5\\ \diagdown C{=}C\diagup D\\ X\diagup \quad \diagdown H\end{array}$	$\begin{array}{c}C_6H_5\\ \diagdown C{=}C\diagup X\\ D\diagup \quad \diagdown H\end{array}$	$\begin{array}{c}C_6H_5\\ \diagdown C{=}C\diagup H\\ D\diagup \quad \diagdown X\end{array}$
LBI$_2$	50 (d)*	50 (d)*	~0.5)	(~0.5)
L$_2$BI (X = I)	20	80		
L$_3$B	8	91		
LBBr$_2$	40 (30)*	60 (70)*	(~0.5)	(~0·5)
L$_2$BBr (X = Br)	15	85		
L$_3$B	7	92		
LBCl$_2$	31 (0)*	49 (100)*	10	10
L$_2$BCl (X = Cl)	26	66	(~4)	(~4)
L$_3$B	Does not form			

* Thermodynamic product ratio, d = decomposition.

[a] Halogenoborations carried out in light petroleum at − 70° C.

TABLE 2

	^{1}H N.m.r. data (τ)	
(a) Boranes	ArH	=CH
Dichloro-2-chloro-2-phenylvinylborane (Z,E)	3·00	3·73 (Z), 3·56 (E)
Chlorobis-(2-chloro-2-phenylvinyl)borane	3·00	Components 3·43, 3·94
Diacetoxy-2-chloro-1-phenylvinylborane	2·65	3·77 (E), 4·00 (Z)
Dibromo-2-bromo-2-phenylvinylborane (Z,E)	2·8	3·09 (E), 3·20 (Z)
Bromobis-(2-bromo-2-phenylvinyl)borane	2·8	Component 3·5
Di-iodo-2-iodo-2-phenylvinylborane (Z,E)	2·8	3·1 (Z), 2·23 (E)
Di-iodo-2-iodo-1-phenylvinylborane (Z,E)	2·8	3·90, 3·51
Diacetoxy-2-iodo-2-phenylvinylborane (Z,E)	2·8	3·44 (Z), 3·36 (E)
(b) Ethylenes		
1-Chloro-1-phenylethylene	2·7	4·6611, 4·6789, 4·4789, 4·4611 ($^2J_{HH}$ 1·6 Hz
(Z) and (E)-1-chloro-2-deuterio-1-phenylethylene	2·7	4·68 (Z), (+ 0·01) *, 4·48 (E) (+ 0·01) *
(E)-1-Chloro-2-phenylethylene [6]	2·6	3·11, 3·34, 3·46, 3·69 ($^3J_{HH}$ 13·95 Hz)
(Z)-1-Chloro-2-phenylethylene [6]	2·6	3·46, 3·61, 3·85, 4·00 ($^3J_{HH}$ 8·7 Hz)
1-Bromo-1-phenylethylene [3,5]	2·8	4·093, 4·115, 4·40, 4·42 ($^2J_{HH}$ 1·8 Hz)
(Z)- and (E)-1-bromo-2-deuterio-1-phenylethylene	2·8	4·42 (Z) (+ 0·012) * 4·12 (E) (+ 0·155) *
(E)-1-Bromo-2-phenylethylene [7]	2·72	3·43, 3·19, 3·00, 2·76 ($^3J_{HH}$ 14·4 Hz)
(Z)-1-Bromo-2-phenylethylene [7]	2·5	3·67, 3·53, 3·0, 2·86 ($^3J_{HH}$ 8·4 Hz)
1-Iodo-1-phenylethylene	2·8	3·7856, 3·8045, 4·119, 4·138 ($^2J_{HH}$ 1·9 Hz)
(Z)- and (E)-1-iodo-2-deuterio-1-phenylethylene	2·8	4·1385 (Z) (0·01),* 3·80905 (E) (0·014) *

Solvent: light petroleum (b.p. 40—60° C) except for the acetoxy-compounds (water) pH *ca.* 3.

* Isotopic shift upfield measured from the centre of either the A or the B doublet of the protio-compound.

total amounts of (*E*)- and (*Z*)-1-deuterio-2-halogeno-2-phenylethylenes produced by acetolysis. The monovinyl compound is the precursor of the divinyl product which in turn is the precursor of the trivinylborane so the results in Table 1 represent ethylenes from a sequence of stepwise halogenoborations with each particular boron trihalide.

Halogenoboration of phenylethyne with boron trichloride produces up to 20% addition of boron at C-2

produce isomerisation of the first vinyl ligand only in the $Z \longrightarrow E$ sense so that for example in the halogenoboration of phenylacetylene with a 1 : 1 mixture of dibromo(*E*)- and (*Z*)-2-bromo-2-phenylvinylboranes the *E* : *Z* ratio in the divinyl product is >3 : 1. This isomerisation does not occur by intermolecular vinyl ligand exchange in the course of the reaction.

Equations (2)—(4) illustrate the possible vinyl ligand scrambling reactions and *all* are slow on the n.m.r. time
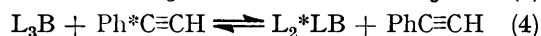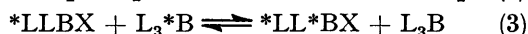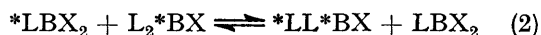
[4] J. R. Blackborow, unpublished results.
[5] C. Dufraisse and J. E. Viel, *Bull. Soc. chim. France*, 1925, 4(37), 877.

[6] R. W. L. Clark, *J. Chem. Soc.*, 1910, 97, 894.
[7] E. Grovenstein, jun., and D. E. Lee, *J. Amer. Chem. Soc.*, 1953, 75, 2639; S. J. Cristol and W. P. Norris, *ibid.*, p. 2645.

scale at 30 °C. (Isomerisation of individual boranes is also slow at 30 °C.) Boron–halogen scrambling is however rapid under these conditions.

$$*LBX_2 + L_2*BX \rightleftharpoons *LL*BX + LBX_2 \quad (2)$$

$$*LLBX + L_3*B \rightleftharpoons *LL*BX + L_3B \quad (3)$$

$$L_3B + Ph*C\equiv CH \rightleftharpoons L_2*LB + PhC\equiv CH \quad (4)$$

$$X = \text{halogen}$$

The production of dihalogenovinyl-, halogenodivinyl-, and trivinyl-boranes is exothermic and essentially complete within 3—4 s. The $Z : E$ ratios of dihalogenovinylboranes depend on temperature and concentration of solvent (see Discussion section) and all products

tities. This hydrolysis appears to involve the selective *trans*-deoxyboration of the diacetoxy-(Z)-vinylborane (Scheme). We defer discussion of this novel reaction until the reasons for the stability of the C-2–B bond towards acetolysis are understood.

DISCUSSION

The mechanism of halogenoboration can only be superficially investigated by the preparative experiments described in this paper. Some of the relevant points are (a) the direction of addition, (b) the variation of direction of addition with halogen substitution, (c) whether Z- and E-C-1 boron additions occur by different

SCHEME   Stereospecific deoxyboration
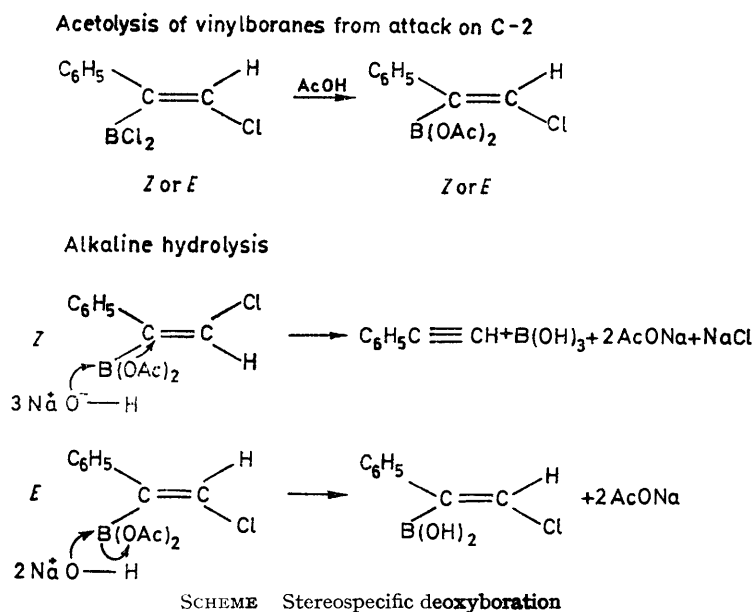
decompose above 120 °C, usually by dissociation and a further unidentified reaction.

We were able to establish the thermodynamic $Z : E$ ratios for dihalogenovinylboranes (halogen = Cl or Br) by heating the products of low temperature reactions (−70 °C) to 100 °C (Table 1) so that isomerisation occurred without appreciable decomposition. The E-configuration is more thermodynamically stable.

Reactions of Halogenovinylboranes from Attack on C-2. —The chloroboration of phenylethyne with boron trichloride produces up to 20% dichloro-(Z)- or (E)-2-chloro-1-phenylvinylborane in a 1 : 1 ratio.

Halogenoboration with tri-iodo- or tribromo-borane produces tiny quantities (n.m.r.) of products from C-2 attack also with $Z : E$ ratios of 1 : 1 (Table 1). Acetolysis of the mixtures of dichlorovinylboranes from both C-1 and -2 attack produces the deuterio-olefins (see above) and equal quantities of diacetoxy-(Z)- and -(E)-2-chloro-1-phenylvinylboranes which may be extracted in aqueous acetic acid. Alkaline hydrolysis of the diacetoxyboranes produces phenylacetylene and (E)-2-chloro-1-phenylvinyldihydroxyborane in equal quan-

mechanisms, and (d) the possible occurrence of a mesomeric interaction of vinyl and halogenoborane substituents causing intramolecular isomerisation as a plausible method of obtaining the $Z : E$ ratios for halogenodivinylboranes in Table 1.

Information relevant to these points was obtained from the following general qualitative experimental results which refer only to the preparation of dihalogenovinylboranes. (1) The ratio of C-1 : C-2 boron addition increases with solvent dilution. (2) The ratio of $E : Z$-C-1-boron addition increase with dilution and temperature and when a more polar solvent is used. (3) The ratio of C-1 : C-2 boron addition decreases when a more polar solvent is used but C-2 boron addition still occurs with an $E : Z$ ratio of 1 : 1. (4) ' Thermodynamic products ' do not isomerise in different solvents.

It is probable therefore that: (1) Z- and E-C-1 boron additions occur by different mechanisms under kinetic control, with E-products favoured by solvents more readily supporting polar transition states. (2) The $Z : E$ ratio or C-1 boron additions are little affected by variation of the trihalogenoborane but boron trichloride

is anomalous as a halogenoboration agent because reactions take longer to proceed to completion (LBCl$_2$ *ca.* 20 s, L$_2$BCl *ca.* 5 min at room temperature) and a large amount of C-2 boron substitution occurs. (3) The fact that C-2 boron addition products form in 1 : 1 *Z* : *E* ratios may be due to the presence of an ionic transition state so that halogen may add *E* or *Z* with equal probability to give the final product. (4) The mesomeric interaction of vinyl and halogenoborane substituents is difficult to prove. However, in other systems (hex-1-yne for example) where the olefinic [1]H n.m.r. spectra of halogenodivinylboranes and trivinyl-boranes are clearly observable we noticed that the addition of an acetylene to halogeno-(*Z*)-vinylboranes is accompanied by isomerisation but not where addition occurs to the *E*-isomer. The mechanism of this isomerisation is complex and we cannot yet define the steps satisfactorily.

In conclusion this limited preparative study has shown that for dihalogeno-2-halogeno-2-phenylvinylboranes *E* geometries are more thermodynamically stable than *Z* but the isomer product ratios of kinetically controlled reactions are determined by a variety of factors.

EXPERIMENTAL

All reactions were performed using Schlenk techniques under dry nitrogen. Solvents and phenylacetylene were

phenylvinylborane at 0·5 mmHg proceeds with almost complete decomposition. B.p.s for other compounds are given in Table 3. Distillation data for dichloro-(*Z*) and -(*E*)-2-chloro-2-phenylvinylborane are in complete agreement with those of Lappert and Prokai,[1] but slow distillation results in a co-distillate of thermodynamic products. N.m.r. spectra of all products were in agreement with assigned structures and are given in Table 2. Analytical data are given in Table 3.

Stereoconformation.—DBr was produced *in situ* by reaction of CH$_3$CN,BBr$_3$ with [^{2}H$_4$]MeOH. The gas was dried over P$_2$O$_5$ and bubbled through a 20% solution of phenylacetylene in glacial acetic [^{2}H]acid at 0 °C; after 30 min the n.m.r. spectrum of the solution showed the presence of (*E*)-1-bromo-2-deuterio-1-phenylethylene. Purification is described elsewhere.[3]

No attempt has been made to relate the isomer product ratios of dihalogenovinylboranes to temperature or concentration of reactants except on a qualitative basis (see Discussion section).

Sample Preparation.—Phenylacetylene (5 g, 0·05 mol) in light petroleum (b.p. 40—60 °C) (30 ml) was added to a stirred solution of boron trichloride (8·0 g, 0·0685 mol) in light petroleum (50 ml) at −70 °C over 5 min. Solvent and excess of reactants were removed under vacuum. A product (a) C$_8$H$_6$BCl$_3$ (Table 1) remained. The n.m.r. spectrum of (a) indicated a 1 : 1 ratio of dichloro-(*E*) and -(*Z*)-2-chloro-2-phenylvinylborane and traces (*ca.* 2%) of dichloro-2-chloro-1-phenylvinylboranes. Distillation of (a) (0·3 mmHg) yield a first fraction of the 2-chloro-2-phenyl

TABLE 3

Analyses

Compound (mixed isomers)	Found (%)			Calc. (%)			B.p. [°C (mmHg)]
	C	H	Hal	C	H	Hal	
PhClC:CHBCl$_2$	42·4	2·8	48·3	43·8	2·76	48·5	93 (0·3)
PhBrC:CHBBr$_2$	28·0	1·81	68·0	27·3	1·71	68·0	92 (2)
PhIC:CHBI$_2$	18·6	1·3	75·0	19·5	1·23	77·1	Decomp.
(PhClC:CH)$_2$BCl	57·2	3·86	33·4	59·8	3·86	33·1	100 (0·1)*
(PhBrC:CH)$_2$BBr	42·0	3·04	52·2	42·2	2·66	52·7	100 (0·1)*
(PhIC:CH)$_2$BI	32·2	2·21	61·0	32·2	2·03	63·9	Decomp.
(PhBrC:CH)$_3$B	50·6	3·22	42·6	51·8	3·25	43·0	Dissociation
(PhIC:CH)$_3$B	41·0	2·67	53·6	41·3	2·60	54·6	Decomp.
PhCCl:CH$_2$	69·2	5·00		69·3	5·09	25·6	70 (10)
PhCBr:CH$_2$	53·2	3·39		52·5	3·86	43·6	70 (7)
PhCI:CH$_2$	40·8	2·2		41·8	3·07	55·2	Photo-sensitive decomp.
(*Z*)-PhC[B(OH)$_2$]CHCl	51·8	4·1	18·0	52·69	4·42	19·4	

* Decomposition of compounds of *ca.* 50% by weight was observed.

purified by standard procedures. Acetic [^{2}H]acid was prepared by reaction of D$_2$O (Norsk Hydro 99·7%) with AnalaR acetic anhydride. Trihalogenoboranes [B.D.H. (BCl$_3$, BBr$_3$) and Koch–Light (BI$_3$)] were used without further purification.

Reactions were run in light petroleum (b.p. 40—60 °C) or CH$_2$Cl$_2$. Dihalogenovinylboranes were prepared by adding phenylacetylene to the trihalogenoborane in slight excess. Halogenodivinylboranes were prepared directly from dihalogenovinylboranes and phenylacetylene. Trivinyl-boranes were prepared from halogenodivinylboranes similarly.

Acetolysis was conducted at room temperature and isomer ratios were found to be independent of solvent, but the reaction is not always qualitative.[1]

Distillation of iodo-compounds and tris-(*E*)-2-bromo-2-

isomer with a *Z* : *E* ratio of 1 : 1 (b.p. 93 °C) and a second fraction with a *Z* : *E* ratio of 0·9 : 1·0 (b.p. 96 °C). A residue (black tar, 65%) was left.

Deoxyboration.—Phenylacetylene (5 g, 0·05 mol) in light petroleum (b.p. 40—60 °C) (20 ml) was added to a stirred solution of boron trichloride (8·0 g, 0·0685 mol) in light petroleum (20 ml) at −40 °C over 5 min. Solvent and excess of boron trichloride were removed under vacuum. Light petroleum (50 ml) was added to the crude product and acetic [^{2}H]acid (9·15 g, 0·15 mol) in light petroleum (20 ml) added from a side-tube over 3 min, the DCl produced in the reaction being continuously removed by application of a vacuum. The acetic acid solution was homogenised with the minimum quantity of CH$_2$Cl$_2$ and immediately extracted with water (2 × 10 ml). The [1]H n.m.r. spectrum showed the presence of aromatic protons

and two equally intense peaks in the olefinic proton region. Phenylacetylene (evidenced from n.m.r.) formed in small globules in the solution when sodium hydroxide was added (pH > 12). The homogenised solution (30% acetone) showed ^{1}H n.m.r. signals of equivalent intensity for the suspected ' (E)-2-chloro-1-phenylvinyldihydroxyborane ' and phenylacetylene. The solution was evaporated to 10% of its original value and the crystals [B(OH)$_3$, NaOAc] which had formed were filtered off. The filtrate and crystals were shaken separately with light petroleum, the ether solution was dried, and the ether and volatiles removed under vacuum; a white-yellow powder remained which gave an analysis and mass spectrum consistent with (E)-2-chloro-1-phenylvinyldihydroxyborane.

Mass spectra of all vinylboranes were obtained and identified by isotope patterns of the parent ions, but scrambling of ligands occurs in the mass spectrometer.

N.m.r. spectra were run on a Bruker Spectrospin instrument and mass spectra were recorded on a A.E.I. MS9 spectrometer.