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THE HALOBORATION OF n-HEXYNE-1

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Summary

The assignment of configurations to isomers of 2-halo-2-phenylvinylboranes and 1-halo-1-phenyl-2-deuteroethylenes described in a previous paper has been revised. The mechanism of haloboration of n-hexyne-1 is discussed in the light of the geometrical isomer ratios of 2-halohex-1-ene-1-ylboranes obtained as products.

Introduction

Assignment of the NMR spectra of trisubstituted ethylenes

The assignment of the ^{1}H NMR spectra of 1-halo-1-phenyl-2-deuteroethylenes described previously [1] was based on the assumption that deuterium bromide added specifically *trans* to phenylacetylene in acetic acid.

The tabulations of Dyer [2] for the expected values of *cis*- and *trans*-coupling constants between C-1 and C-3 protons of alkenes-1 were used to assign the NMR spectra of the isomers of 2-bromo-1-deuterohexene-1. These assignments were used to show that haloboration of phenylacetylene [1] and n-alkyne-1 species proceed under kinetic control with a predominance of *trans* addition. We now believe these assignments to be incorrect. A variety of evidence based on kinetic isotope effects for hydrogen halide elimination [3], complete NMR spectral analysis [4] and stereospecific addition of hydrogen halides to similar alkynes [5] and the substituent effects on NMR spectra described by Tobey [6] has led us to reverse the *Z*,*E* labels of all 2-halo-substituted ethylenes mentioned in Tables 1 and 2 of ref. 1. The result of this revised labelling for those not familiar with the nomenclature [7] is that *cis* addition of a boron—halogen bond to phenylacetylene is increasingly favoured as the reactivity of the boron halide decreases. (Reverse columns 1 and 2 of Table 1, ref. 1). The configuration of tris(2-halovinyl)boranes produced by treatment of triiodoborane or tribromoborane with

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TABLE 1

ANALYSES OF 2-HALO-SUBSTITUTED ETHYLENES

Compound (mixed isomers)	Found (calcd.) (%)			B.p. (°C/mmHg)
	C	H	Hal	
n-BuCBr=CHBBr$_2$ (*Z*,*E*-I)	20.1 (21.7)	3.0 (3.03)	71.3 (72.1)	48/0.1
n-BuCCl=CHBCl$_2$ (*Z*,*E*-I)	36.0 (36.1)	5.2 (5.06)	52.5 (53.3)	70/5.0
(n-BuCBr=CH)$_2$BBr (*Z*,*Z*-II, *E*,*Z*-II)	35.1 (34.7)	4.9 (4.86)	56.0 (57.8)	100—110/0.1
(n-BuCCl=CH)$_2$BCl	51.2 (51.2)	7.0 (7.16)	51.2 (37.8)	Decomp.
(n-BuCBr=CH)$_3$B (*Z*,*Z*,*Z*-III, *E*,*Z*,*Z*-III)	44.0 (43.5)	6.2 (6.08)	47.7 (48.2)	Decomp.
n-BuCBr=CH$_2$	44.0 (44.2)	6.9 (6.80)		134/760
n-BuCBr=CHB(NEt$_2$)$_2$	52.0 (53.0)	9.1 (9.54)		Decomp.
n-BuCCl=CHB(NEt$_2$)$_2$	61.7 (61.6)	11.2 (11.1)		Decomp.
(n-BuCCl=CH)$_2$BNEt$_2$	61.0 (60.4)	9.3 (9.51)		130/2.0

phenylacetylene are therefore found to over 90% *cis* (*Z*). We now present a similar study of the haloboration of n-hexyne-1.

The purpose of this study was to investigate the kinetic or thermodynamic factors which control the product isomer distribution. This was not possible in the study of haloboration of phenylacetylene because the ^{1}H NMR spectra of phenyl- and vinyl-hydrogens overlapped.

Results

Bromoboration of n-hexyne-1

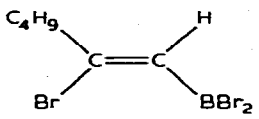
Z- or *E*-2-bromohex-1-ene-1-yldibromoborane (I), *Z*,*E*- and *Z*,*Z*-bis(2-bromohex-1-ene-1-yl)bromoborane (II) (Fig. 1) and *Z*,*Z*,*Z*- and *Z*,*Z*,*E*-tris(2-bromohex-1-ene-

TABLE 2

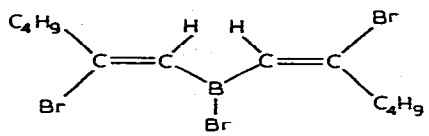
^{1}H NMR SPECTRA OF 2-HALO-SUBSTITUTED ETHYLENES

Compound	Aliphatic ^{1}H[a]	Olefinic ^{1}H (scale TMS = 10 ppm)
n-BuCBr=CHBBr$_2$	8 ~ 9 7.4 t (*Z*), 6.9 t (*E*)	3.33(*Z*), 3.03(*E*)
n-BuCCl=CHBCl$_2$	8 ~ 9 7.6 t (*Z*), 7.1 t (*E*)	3.93(*Z*), 3.80(*E*)
(n-BuCBr=CH)$_2$BBr	8 ~ 9 7.4 t (*Z*,*Z*), 6.9 t (*E*,*Z*)	3.33(*Z*,*Z*), 3.42(*E*,*Z*), 2.96(*E*,*Z*)
(n-BuCCl=CH)$_2$BCl	8 ~ 9 7.6 t (*Z*,*Z*), 7.1 t (*E*,*Z*)?	3.82(*Z*,*Z*), 4.00, 3.57
(n-BuCBr=CH)$_3$B	8 ~ 9 7.4 t (*Z*,*Z*,*Z*)	3.22(*Z*,*Z*,*Z*), 3.38(*Z*,*Z*,*E*), 3.22(*Z*,*Z*,*E*)
n-BuCBr=CH$_2$	8 ~ 9	5.58, 5.60(*Z*)[b], ^{4}*J*(HCCCH < 0.25 Hz, ^{2}*J*(HCH) 1.25 Hz; 5.43(3), 5.41(9), 5.40(5), 5.39(1) (*E*)[b], ^{4}*J*(HCCH) 1.25 Hz, ^{2}*J*(HCH) 1.25 Hz
n-BuCBr=CHD (*Z*)	8 ~ 9	5.40
n-BuCBr=CHD (*E*)	8 ~ 9	5.36

[a] t = triplet. [b] Hydrogen under observation is considered, in the nomenclature of ref. 7, artifically to have a higher molecular weight than the other C-1 hydrogen.



Z-2-bromohex-1-ene-1-yldibromoborane



Z,E-bis(2-bromohex-1-ene-1-yl)bromoborane

Fig. 1.

1-yl)borane (III) can be prepared by the addition of the stoichiometric amounts of n-hexyne-1 to tribromoborane. Intermolecular exchange of hexenyl substituents of I, II or III is slow but scrambling of halogen attached to boron is fast (on the NMR time scale at 33°C). We were able to measure the total amount of *Z*- or *E*-hexenyl substituents in any compound [1] and estimate the amounts of the geometrical isomers of II and III obtained from a set of preparations (n-hexyne-1 → I → II → III) within an estimated error of ±5% (see next section). Table 3 illustrates the experimental conditions and isomer ratios obtained. The addition of boron to C-2 of n-hexenyl-1 was certainly less than 5%.

Substituent stereochemistry

The acetolysis of I, II and III with acetic acid-d_1 occurs with retention of configuration [1] therefore it is possible to equate the configuration of the acetolysis product, *Z*- or *E*-1-deutero-2-bromohex-1-ene which is already known [4], to

TABLE 3

BROMOBORATION OF n-HEXYNE-1

Preparation Sequences I → II → III: Isomer Distribution

Reaction conditions for preparation	(2-Bromohex-1-ene-1-yl)dibromoborane (I)		Bis(2-bromohex-1-ene-1-yl)bromoborane (II)		Tris(1-bromohex-1-ene-1-yl)borane (III)	
	Total *E/Z* ratio [b]	Isomer ratios [c] *E/Z*	Total *E/Z* ratio [b]	Isomer ratios [c] *Z,Z/Z,E*	Total *E/Z* ratio [b]	Isomer ratios [c] *Z,Z,Z/Z,Z,E*
1 Petroleum spirit [a]						
I, II, III; −40°C	64/30	64/30	50/150	1/1	1/5	1/1
I, II, III; −20°C	54/40	54/40	30/110	7/6	12/65	7/6
2 Petroleum spirit [a]						
I, II, III; −80°C	2/98	2/98	0/100	100/0	0/100	100/0
3 Dichloromethane						
I, II, III; −80°C	2/98	2/98	0/100	100/0	0/100	100/0
4 Petroleum spirit [a]						
I: −60°C						
II, III: −80°C	30/70	30/70	22/180	4/1	10/140	4/1
5 Neat liquid (from prep. 3)						
I + BBr_3, 20°C (3 days)	75/25	75/25				
6 I heated to 120°C (5 min)	60/40	60/40 [d]				
7 Neat liquid, 33°C (4 days)	No change		No change		All isomers? [d]	
I, II and III from prep. 3						

[a] B.p. 40–60°C. [b] From acetolysis with AcOH-*d*. [c] From ^{1}H NMR (I, II, III). [d] 20% decomposition.

that existing in the compounds I, II and III. Each hexenyl substituent gives rise to an individual ^{1}H olefinic NMR signal so that the amounts and configurations of all isomers prepared in stoichiometric reactions may be determined.

Observations on the reactivity of the tribromoborane-n-hexenyl-1 system

Small amounts of n-hexyne-1 were added to a sample of tribromoborane and the ^{1}H NMR spectrum recorded after each addition. It was therefore possible to observe the appearance and disappearance of all isomers of I and II and the ratio of isomers in the final product III in the reaction sequence: n-hexyne-1 → I → II → III.

The order in which the products form at room temperature is *Z*-I ~ *E*-I >> *Z,Z*-II > *Z,E*-II >> *Z,Z,Z*-III > *Z,Z,E*-III. Such a series implies that the production of III from n-hexyne-1 and tribromoborane proceeds sequentially via I and II and that isomers with *Z* configurations form preferencially as the reaction proceeds toward III.

Similarly the reaction of tribromoborane with a solution of *Z,Z,E*- and *Z,Z,Z*-isomers of III at room temperature proceeds via II to yield I. The order in which the reactants and intermediates dissappear is *Z,Z,Z*-III > *Z,Z,E*-III >> *Z,Z*-II. > *Z,E*-II. This, again, is an interesting series because since the ratio of total amounts of *Z*- and *E*-hexenyl substituents remains the same throughout, it implies the reaction is an alkyl-redistribution reaction in which compounds with *Z*-alkyl substituents redistribute faster than those with *E*-alkyl substituents.

Aminolysis of I (*Z* or *E*) with diethylamine or tertiary amine-adduct formation (with phenyldimethylamine) proceeds with retention of configuration of the hexenyl substituent.

Chloroboration

Chloroboration is generally slower and less exothermic [1] than either iodo- or bromo-boration and the possibility of a kinetic investigation seemed attractive, however the analysis of the products of acetolysis, the reaction necessary to determine the configuration of the hexenylboranes, was so difficult that little quantitative data could be obtained. In all known chloroborations boron adds to C-1 of the alkyne-1 molecule [1,8].

The chloroboration of n-hexyne-1 produces the two isomeric forms of chlorohexenyldichloroborane; subsequent addition of n-hexyne-1 produces at least two isomers of bis(chlorohexenyl)chloroborane with one isomer always a major component. The production of tris(chlorohexenyl)borane from bis(chlorohexenyl)-chloroborane and n-hexyne-1 occurs in a significantly different way to the analogous bromoboration; at least 5 of the possible 6 olefinic proton resonances of the four tris(2-chlorohex-1-ene-1-yl)borane isomers are observed initially but after a period of two days at room temperature only three significant olefinic resonances remain. Reaction of tris(chlorohexenyl)borane with diethylamine yields bis(chlorohexenyl)diethylaminoborane and n-hexyne-1. An analogous aminolysis reaction occurs with tris(bromohexenyl)borane and diethylamine but more slowly.

Chlorohexenyldichloroborane and bis(chlorohexenyl)chloroborane rearrange in the gas phase (experimental, to give polymeric materials. The reaction of n-hexyne-1 with tris(chlorohexenyl)borane appears not to be a simple exchange reaction, hexyne polymerisation also takes place.

Discussion

Successive substitution of hexenyl for halogen on the boron atom increases the lability of the hexenyl substitutent towards reaction with both acids and bases. Thus at room temperature diethylamine displaces one hexyne molecule from tris(halohexenyl)boranes but not from bis(halohexenyl)haloboranes. Similarly tris(halohexenyl)boranes react more rapidly with trihaloboranes than do bis(halohexenyl)haloboranes.

The choice of simple haloborating agents does not give quantitative kinetic evidence for a mechanism of haloboration. However, bromoboration with tribromoborane appears to be a kinetically controlled process favouring *cis* addition, whereas the thermodynamic stability favours the *trans* isomer (Table 3). When the haloborating agents become progressively weaker as Lewis acids, *cis* addition is increasingly favoured. Thus haloboration of n-hexyne-1 with II leads to 100% *cis* addition.

Experimental

n-Hexyne-1 (Koch Light) was distilled before use (b.p. 71.0°C/760 mmHg). Tribromo- and trichloro-borane (B.D.H.) were distilled under reduced pressure to remove hydrogen halides. Solvents were dried by standard routes. Halohexenylboranes were prepared by adding the appropriate quantity of n-hexyne-1 to the trihaloborane in solvent and removing volatile products under vacuum [1]. 2-Bromohexene-1 was prepared by a standard route [9]. Acetolysis with acetic acid-d_1 was performed in petroleum spirit (b.p. 40—60°C) or dichloromethane. Aminolysis and preparations of tertiary amine adducts of boranes were performed by standard and reported procedures [10].

Mass spectra

Mass spectra of all bromohexenyl compounds were obtained and characterised by the isotope pattern of the molecular ions, or accurate mass measurement.

The mass spectra of all chlorohexenylboranes showed no peaks assignable to the monomer molecular ions. Significant ions were assigned to $(C_4H_9CH)_nBCl_3$ (n = 3, 4 and 5). The volatile organic products from acetolysis of "chlorohexenylchloroboranes" showed in the mass spectra peaks assignable to ions with structures $(C_4H_9CH)_nHCl$ (n = 3, 4 and 5) and $(C_4H_9CH)_n$ (n = 3, 4 and 5). Chlorohexenylbis(diethylamino)borane and bis(chlorohexenyl)diethylaminoborane showed characteristic monomer parent ions.

NMR spectra were run on a Bruker Spectrospin or Perkin—Elmer R10 spectrometer, and mass spectra were recorded on an A.E.I.M.S. 9.

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