SOME ASPECTS OF THE CHEMISTRY OF HALO~~GENO~~BORANES~~COMPLEXES~~

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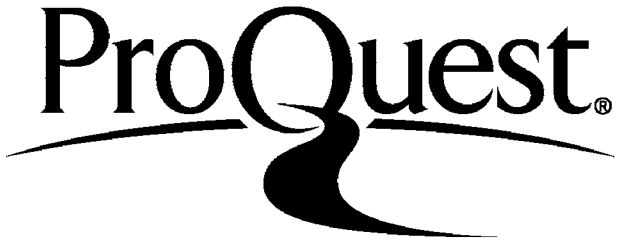


ABSTRACT

The reaction between polyhalomethanes and the borane-dimethyl sulphide complex (BMS) was investigated.

$$CX_4 + BH_3.S(CH_3)_2 \longrightarrow XBH_2.S(CH_3)_2 + HCX_3$$

The reaction between BMS and tetrachloromethane (or tribromochloromethane) followed the kinetic form,

$$-d(BMS) / dt = k(BMS)(XCCl_3) \quad .$$

On the basis of solvent effects and inhibition experiments the following mechanism was proposed ;

(1) $(CH_3)_2S.BH_3$ + Initiator $\longrightarrow (CH_3)_2S.BH_2\cdot$ + product

(2) $(CH_3)_2S.BH_2\cdot + XCY_3 \longrightarrow (CH_3)_2S.BH_2X + \cdot CY_3$

(3) $(CH_3)_2S.BH_3 + \cdot CY_3 \longrightarrow (CH_3)_2S.BH_2\cdot + HCY_3$

The observed relative ease of displacement for the halogen-hydrogen transfer are $I > Br > Cl \gg F$. This parallels the bond strengths of the Carbon-Halogen bond and indicates that step (2) is rate-determining. The halomethanes and halotriphenyl methanes, in their reaction with BMS, have led to convenient methods for producing halogenoboranes for use as hydroborating agents.

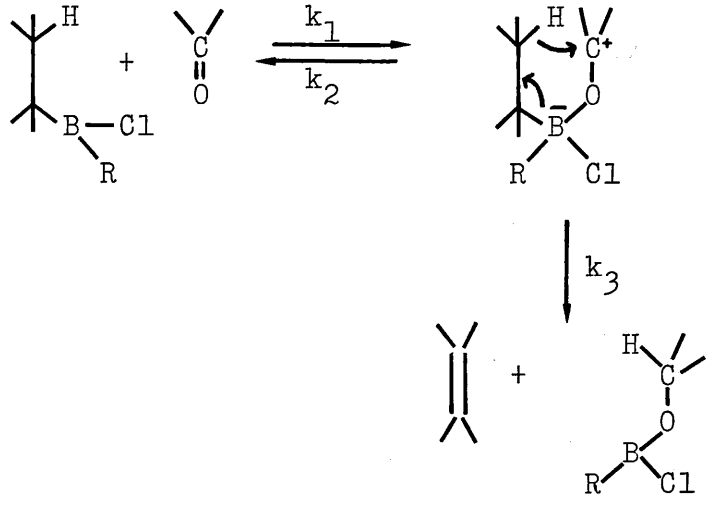
The reaction between BMS and tetrachloromethane was used to generate dialkylchloroboranes. Reaction of these with some substituted benzaldehydes were investigated and found to follow the kinetic form,

$$d(\text{Pent-1-ene})/dt = k(Ar.CHO)((n\text{-}C_5H_{11})_2BCl)$$

for the reaction,

$$Ar.CHO + (n\text{-}C_5H_{11})_2BCl \xrightarrow{9^\circ C} Ar.CH_2O.B(Cl).C_5H_{11} + \text{pent-1-ene.}$$

The rate of the reaction increases with electron withdrawing substituents in the para-position and decreases with electron donating substituents. The rate of the reaction correlates best with σ^+ giving a value of ρ of 2.1. ^{11}B n.m.r studies suggest initial complex formation. The proposed mechanism is,



k_3 (hydride transfer) being the rate-determining step.

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I would also like to thank the staff of the Research Laboratories of Castrol Ltd., Pangbourne, Berks., in particular to Dr.Nigel Webb for his help and encouragement and for his gift of dry transfers which aided me in the typing of this thesis.

I dedicate this thesis to my parents, George and Joyce Jones.

CHAPTER ONE

INTRODUCTION

1.1 GENERAL INTRODUCTION

Before 1956 the only practicable method for producing organoboranes was the reaction of an organometallic compound (often an organomagnesium or zinc derivative) with a boron ester or halide[1] (equations 1 and 2).

$$3ZnR_2 + 2B(OMe)_3 \longrightarrow 2BR_3 + 3Zn(OMe)_2 \qquad (1)$$

$$3RMgX + BF_3 \longrightarrow BR_3 + 3MgXF \qquad (2)$$

(R = alkyl or aryl group)

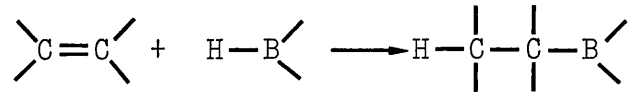
The synthetic use of organoboranes was not explored because of the tedious initial production of the organometallic precursor. However, in 1956 it was found that unsaturated organic compounds are converted into organoboranes by treatment with diborane (or its analogues) in ethereal solvents (equations 3-5). This provided a new route to these useful compounds.[2]

$$3LiBH_4 + BF_3 \text{ (or } BCl_3) + 12RCH{=}CH_2 \xrightarrow[\text{'Diglyme'}]{DG} 4(RCH_2CH_2)_3B + 3LiF \text{ (or LiCl)} \qquad (3)$$

$$3NaBH_4 + AlCl_3 + 9RCH{=}CH_2 \xrightarrow{THF} 3(RCH_2CH_2)_3B + AlH_3 + 3NaCl \qquad (4)$$

$$B_2H_6 + 6RCH{=}CH_2 \xrightarrow{Et_2O} 2(RCH_2CH_2)_3B \qquad (5)$$

The hydroboration reaction is the easy addition of the boron-hydrogen bond to carbon-carbon multiple bonds in unsaturated organic compounds (equations 6 and 7).



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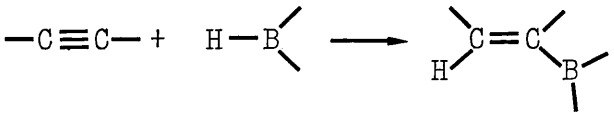
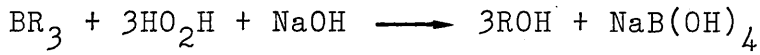


(7)

The hydroboration reaction has made organoboranes easily available for use in organic synthesis.[3,4] One of the useful reactions that organoboranes undergo is the oxidation with hydrogen peroxide in the presence of alkali (equations 8 and 9). The reaction is essentially quantitative and has a high specificity for the boron-carbon bond.[5]



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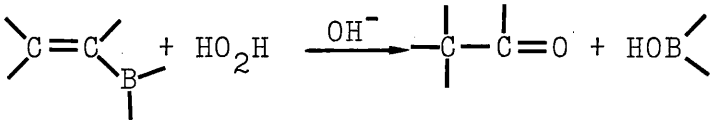


(9)

Thus hydroboration followed by oxidation provides a valuable procedure for the anti-Markovnikov hydration of carbon--carbon multiple bonds.

A good survey of most aspects of the hydroboration reaction and reactions of organoboranes can be found in H.C. Browns' excellent book, 'Organic Synthesis Via Boranes'.[3]

The present chapter summarises the hydroboration reaction and surveys the development and use of haloboranes as hydroborating agents (with the emphasis on monohalogenated boranes).

1.2 HYDROBORATION WITH BORANE

1.2.1 Scope and stoichiometry

In 1948 it was found that when diborane and ethylene were heated in a sealed tube an undetermined amount of triethylborane was formed[6] (equation 10).

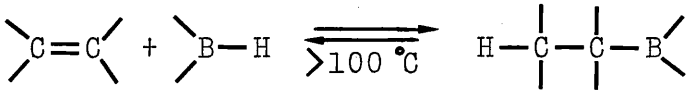
$$C_2H_4 + B_2H_6 \xrightarrow[24\ \text{hours}]{100\,^{\circ}C} (C_2H_5)_3B \qquad (10)$$

Diborane reacts slowly with alkenes in the gas phase but quickly when in the presence of weak Lewis bases such as ethers and sulphides which catalyse the reaction by forming reactive borane complexes[7] (equation 11).

$$B_2H_6 + 2XR_2 \rightleftharpoons 2H_3B.XR_2 \qquad (11)$$

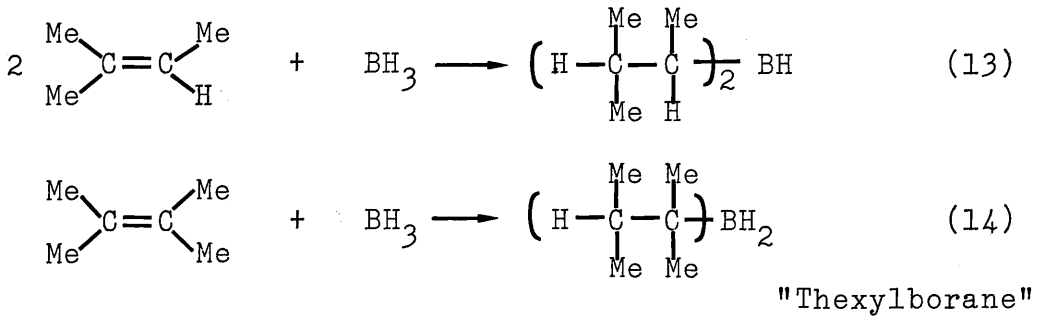
(X = O or S. R = alkyl)

The hydroboration addition is reversible but thermal dissociation usually occurs only above about 100 °C[8,9] (equation 12).



(12)

Hydroboration of most simple alkenes proceeds to the trialkylborane. In the case of more hindered alkenes (such as trimethyl ethylene and tetramethyl ethylene) the reaction proceeds to the dialkyl- or monoalkylborane (equations 13 and 14).



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(14)

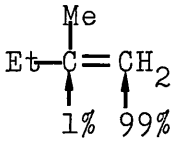
"Thexylborane"

These reactions can be forced to the next stage by changing the conditions (eg. increasing the concentration and reaction time). "Thexylborane" is a useful di-hydroborating agent being well suited for the cyclic hydroboration of dienes.[10,11,12]

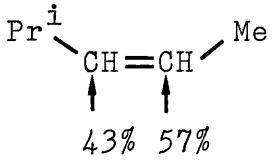
1.2.2 Directive effects

Hydroboration of alkenes places the boron atom predominantly at the least substituted site of the double bond. Simple 1-alkenes react with borane to place 94% of the boron at the terminal position. Branching of the alkyl chain does not influence the distribution.[13]

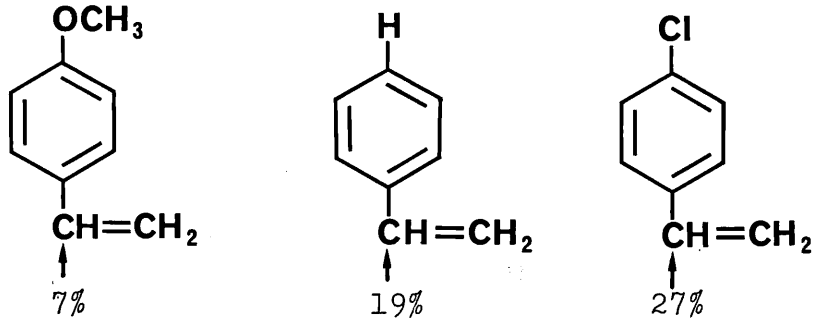
Disubstituted 1-alkenes react to place 99% of the boron at the terminal position.



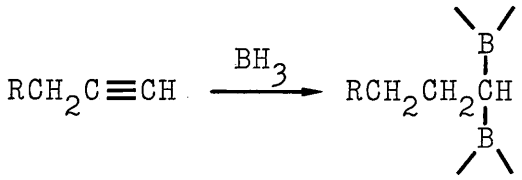
With unsymmetrical disubstituted internal alkenes very low selectivity is obtained.



Aryl groups cause increased non-terminal placement of boron, the amount depending on the substituents in the ring.[14]

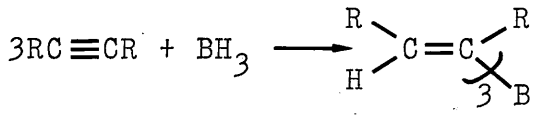


Reaction of alkynes with the appropriate amount of borane gives dihydroboration with formation of gem-dibora products[15] (equation 15).



(15)

By carefully controlling the amount of reagent, dialkyl alkynes ($RC{\equiv}CR'$) can be monohydroborated (equation 16), terminal alkynes still being dihydroborated.[15]

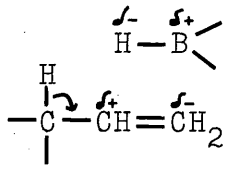


(16)

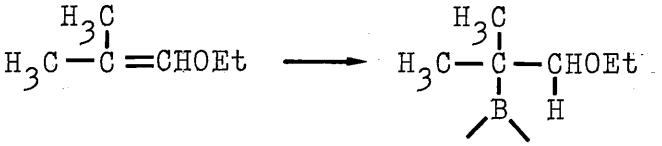
Terminal alkynes can be successfully monohydroborated using disubstituted boranes (eg. 9-BBN).[16]

The direction of addition in the hydroboration reaction appears to be controlled by three factors. These

are the (i) polarisation of the boron-hydrogen bond, $\diagup B^{\delta+}-H^{\delta-}\diagdown$ and the combination of (ii) steric and (iii) electronic effects exerted by the substituents on the alkene or alkyne.

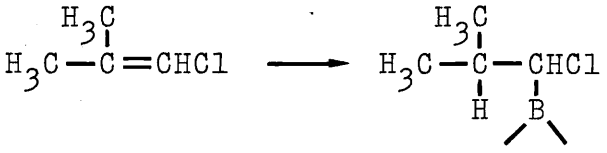


Electronic effects[31] (I and M) play an important role in the hydroboration of alkenes. Vinyl derivatives containing groups with strong +M effect (such as alkoxy groups) direct boron to the β position (equation 17).[17]



(17)

With substituents like boron which have a -M effect, the reverse is true, although the effect is weaker.[18] With chlorine the inductive effect dominates over the mesomeric effect, and directs boron mainly to the α position[19] (equation 18). Bromine exerts a similar, though weaker effect.[20]



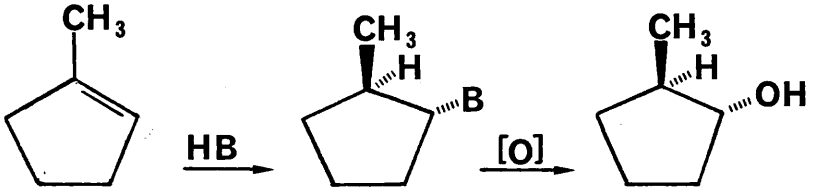
(18)

In the hydroboration of allylic derivatives, addition to the β position with regard to the substituent increases with its increasing electronegativity.[21] Substituted alkynes

behave similarly.[16,22]

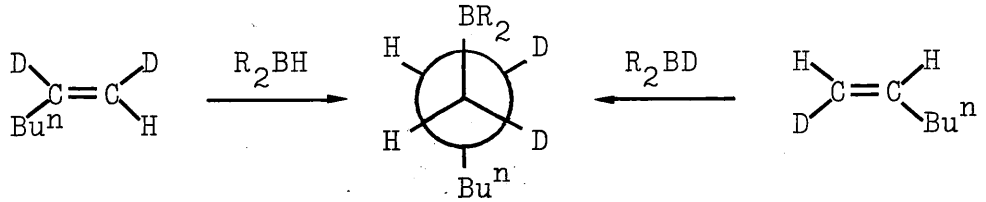
1.2.3 Stereochemistry

The hydroboration reaction involves the cis addition of the boron-hydrogen bond across the double or triple bond.[23] This generalisation was based on early observations of the stereochemical results of hydroboration followed by oxidation. Cyclic alkenes such as 1-methylcyclopentene (equation 19) and 1,2 dimethylcyclohexene are cleanly transformed into trans-2-methylcyclopentanol and cis-1,2-dimethylcyclopentanol respectively.[23]



(19)

On the assumption that the hydrogen peroxide oxidation proceeds with the retention of configuration,[24] the hydroboration reaction must involve a cis addition of the B—H bond across the double bond. Direct evidence for the cis addition of the B—H bond to alkenes and alkynes was found recently from n.m.r studies using deuterated 1-hexene and dialkylboranes (equations 20 and 21).[25]



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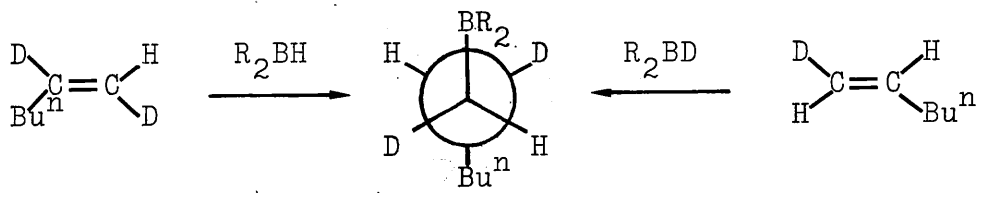
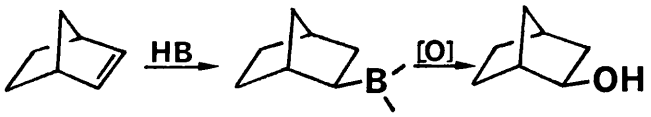


(21)

Hydroboration-oxidation of norbornene gives 99.5% of exo-norborneol (equation 22).[26]

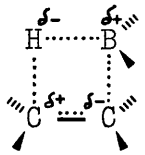


(22)

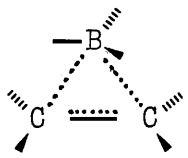
Other compounds such as cholesterol[27] behave similarly, being attacked by borane from the less hindered side. These results have thus led to the generalisation that hydroboration proceeds by anti-Markovnikov cis addition to the less hindered side of the double bond.[24]

1.2.4 Mechanism

The regioselectivity, stereospecific cis addition and lack of rearrangement of the hydroboration reaction have been explained by a concerted four-centre transition state.[13]



This model readily explained the steric and electronic effects exerted by substituents but failed to predict the configuration(R) of (-) 1-deuterio-1-butanol formed from the hydroboration of cis-1-deuteriobutene using optically active diisopinocamphylborane. To explain this an intermediate triangular alkene-borane π complex has been suggested.[28]



On the basis of the triangular model, the transition state

allows the clear prediction of the R configuration of the alcohol.

Investigation of the kinetics of the hydroboration reaction has proved to be very difficult. This is because the hydroboration reaction involves three sequential addition reactions (equations 23-25) as well as monomer-dimer equilibria (equations 26-30), redistribution reactions (equations 31-33) and solvent interactions with the alkylborane intermediates.[29]

$$\text{Alkene} + BH_3 \longrightarrow RBH_2 \qquad (23)$$

$$\text{Alkene} + RBH_2 \longrightarrow R_2BH \qquad (24)$$

$$\text{Alkene} + R_2BH \longrightarrow R_3B \qquad (25)$$

$$BH_3 + RBH_2 \rightleftharpoons H_2BH_2BHR \qquad (26)$$

$$BH_3 + R_2BH \rightleftharpoons H_2BH_2BR_2 \qquad (27)$$

$$2RBH_2 \rightleftharpoons RHBH_2BHR \qquad (28)$$

$$RBH_2 + R_2BH \rightleftharpoons RHBH_2BR_2 \qquad (29)$$

$$2R_2BH \rightleftharpoons R_2BH_2BR_2 \qquad (30)$$

$$BH_3 + R_3B \rightleftharpoons RBH_2 + R_2BH \qquad (31)$$

$$2RBH_2 \rightleftharpoons R_2BH + BH_3 \qquad (32)$$

$$2R_2BH \rightleftharpoons R_3B + RBH_2 \qquad (33)$$

The kinetic studies are made even more difficult by the rapidity of the addition of borane to simple alkenes.[30]

A detailed kinetic study has, however, been carried out of the hydroboration of tetramethyl ethylene (TME).[7] In THF solution the product, 2,3-dimethyl-2-butylborane ("thexylborane"), exists only in the self hydrogen-bridged dimeric form (equation 28). No evidence was found which indicated that the product enters into dimer formation with borane. The reaction is first order in borane and TME,

$$-\frac{dp}{dt} = k\left(BH_3.THF\right)\left(TME\right) \quad .$$

Both hydrogen and boron isotope effects were observed and the overall evidence was consistent with a four-centre transition state.

Theoretical calculations of the hydroboration reaction have predicted a two step process for the gas phase reaction of ethene with BH_3, but the energy profile is uncertain (different molecular orbital calculations giving different activation energies).[32,33]

1.3 DEVELOPMENT AND USE OF MONO- AND DIHALOGENOBORANES

1.3.1 Monochloroborane and its complexes

Monochloroborane is unstable in its gaseous form[34] but exists in ether solutions as a complex of medium stability[35], being more stable in THF than diethyl ether.[36] The etherate complex is, however, more useful since it is more reactive than the THF adduct.[37] It can be prepared by the reaction of diborane with boron trichloride in ether[35] (equation 34).

$$B_2H_6 + Cl_3B.OEt_2 + 2OEt_2 \longrightarrow 3ClBH_2.OEt_2 \qquad (34)$$

The most convenient method for preparing the etherate is the reaction of lithium borohydride with boron trichloride in ether[38](equation 35). Monochloroborane etherate of 90% purity is obtained when ethereal solutions of the reactants are mixed. ^{11}B n.m.r analysis shows minor amounts of borane and dichloroborane to be present.

$$LiBH_4 + BCl_3 \xrightarrow[0\,^{\circ}C]{Et_2O} 2ClBH_2.OEt_2 + LiCl \qquad (35)$$

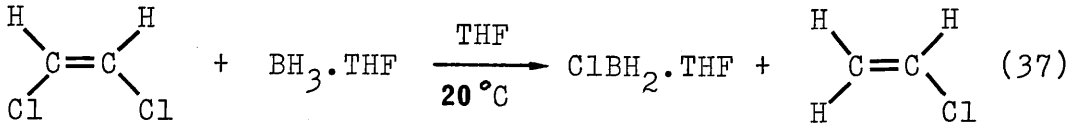
$$\uparrow\downarrow$$

$$BH_3.OEt_2 + Cl_2BH.OEt_2$$

The THF adduct can be prepared by the reaction of hydrogen chloride with borane in THF[37](equation 36) giving 95% pure monochloroborane THF complex.

$$H_3B.THF + HCl \xrightarrow[0\,^{\circ}C]{THF} ClBH_2.THF + H_2 \qquad (36)$$

Recently it was prepared by the reaction of cis-1,2-dichloroethylene with borane in THF to give 94% pure monochloroborane.THF complex[39](equation 37).



(37)

The dimethyl sulphide complex (MCBS) can be prepared by the redistribution of borane-dimethyl sulphide (BMS) with boron trichloride-dimethyl sulphide complex[40](equation 38).

$$2BH_3.SMe_2 + BCl_3.SMe_2 \xrightarrow{25\,^{\circ}C} 3ClBH_2.SMe_2 \qquad (38)$$

The reaction also contains borane and dichloroborane-dimethyl sulphide complexes.[41] The dimethyl sulphide adduct has several advantages over the etherate, being more stable, of higher concentration and allowing hydroboration to be carried out in various solvents.

In 1972 it was reported that monochloroborane-amine complexes could be prepared using the borane-amine complex and an alkyl halide[42](equation 39).

$$BH_3.(amine) + RX \longrightarrow XBH_2.(amine) + RH \qquad (39)$$

(amine = trimethylamine, 4-methylpyridine; RX = CCl_4, CCl_3Br, $C_6H_5CH_2Cl$ or $(C_6H_5)_3CCl$.)

The rate of the reactions depends upon both the amine-borane and the halide used. 4-methylpyridine-borane reacts comp-

letely with 1 equivalent of triphenylmethyl chloride in less than one minute, while heating it in benzyl chloride at 73°C for 20 hours converts only about half of the amine--borane to the amine-chloroborane. 90% of 4-methylpyridine -borane is converted to the chloroborane in one hour in refluxing tetrachloromethane, while trimethylamine-borane requires 24 hours to achieve a similar conversion.

The monohalogenated amine-boranes react further with the haloalkanes, the extent of which depending on the haloalkane used. With triphenylmethyl chloride the reactivity difference between the borane and monochlorinated adduct is large enough so that all the borane complex reacts before any of the monochlorinated complex reacts. This is not the case with tetrachloromethane, where small amounts of the dichloro- complex are formed before all the starting borane is used up.

Two different reaction mechanisms were proposed to explain the differences between the results obtained using triphenylmethyl chloride and the other haloalkanes.[42]

The mechanism proposed for the halogenations using triphenylmethyl chloride is a polar one involving a hydride abstraction from the borane adduct by a carbonium ion paired with chloride ion. This is followed by the formation of the boron-chlorine bond to give the chlorinated borane adduct (equation 40).

$$R_3N.BH_3 + (C_6H_5)_3C^+Cl^- \longrightarrow R_3N.BH_2^+ + (C_6H_5)_3CH + Cl^-$$
$$\longrightarrow R_3N.BH_2Cl + (C_6H_5)_3CH \qquad (40)$$

This mechanism is consistent with the observed solvent effects. In addition there was direct evidence for the existence of the $R_3N.BH_2^+$ ion, being both observed by proton n.m.r and isolated as its PF_6^- salt.

The other mechanism proposed for the haloalkanes is that of a free-radical mechanism (equations 41 and 42).

$$R\cdot + (amine)BH_3 \longrightarrow RH + (amine)BH_2\cdot \qquad (41)$$

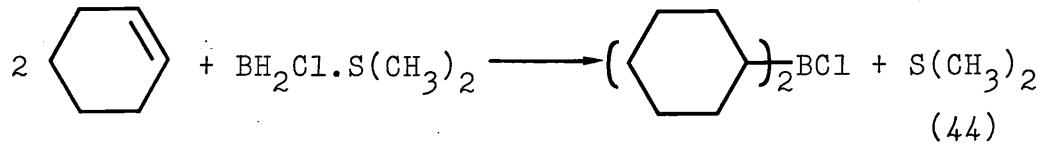
$$(amine)BH_2\cdot + RCl \longrightarrow (amine)BH_2Cl + R\cdot \qquad (42)$$

R· being a radical formed from halogen abstraction of the haloalkane. Evidence of a radical reaction comes from several findings. The reaction using tetrachloromethane is accelerated by the addition of benzoyl peroxide and inhibited by purification of the tetrachloromethane, suggesting that solvent impurities are responsible for initiation of the radical chain. The reaction using bromotrichloromethane proceeds far more quickly than tetrachloromethane, being again accelerated by benzoyl peroxide. The proportions of chlorinated and brominated borane and of the reduction products of bromotrichloromethane remain the same as in the uninitiated reaction when the extent of reaction, temperature or amount of initiator are changed. It is likely that both reactions proceed through the same path. The increased reactivity of bromotrichloromethane compared to tetrachloromethane can be explained by the lowering of bond dissociation energy when a C—Br bond is broken instead of a C—Cl bond.

The amine-borane complexes are tightly bound and not generally useful as hydroborating agents, but this limitation was overcome in 1980 when the reaction between tetrachloromethane and BMS was reported[43] (equation 43). The authors claimed an essentially quantitative conversion of BMS into monochloroborane-dimethyl sulphide complex (MCBS) upon refluxing an equimolar mixture of BMS and tetrachloromethane for 20 hours.

$$BH_3.SMe_2 + CCl_4 \longrightarrow ClBH_2.SMe_2 + CHCl_3 \qquad (43)$$

This valuable hydroborating agent was used in a hydroboration reaction using cyclohexene (equation 44) giving a 70% yield of dialkylchloroborane after distillation.



(44)

The MCBS solution was analysed by ^{11}B n.m.r and revealed the presence of BMS and dichloroborane-dimethyl sulphide in small amounts (the authors claimed 5% of the total). When excess tetrachloromethane was used, an increase in the rate of production of MCBS was observed and more dichloroborane complex was formed, though no figures were given. As with the amine-borane complexes, there was evidence of rate enhancement using benzoyl peroxide, but reduction of the peroxide halted the initial catalytic activity.

With triphenylmethyl chloride, BMS reacts quickly but produces large amounts of higher chlorinated derivatives

under the conditions used. No reaction was observed between BMS and chloroform, dichloromethane, 1,2-dichloroethane or benzyl chloride. Successful use of this novel method for producing MCBS could supersede the more established redistribution route.[40] The redistribution method involves the tedious preparation of the boron trichloride complex, and the reported claims for the yield of MCBS are in question.[55] The preparation of MCBS using the readily available BMS and tetrachloromethane using simple air and moisture sensitive techniques could encourage this useful hydroborating agent to be more widely used. The refinement and investigation of this reaction was the initial basis of this thesis.

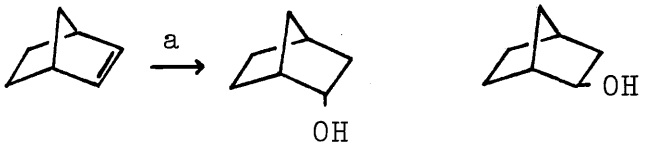
1.3.2 Directive effects of monochloroborane complexes

Monochloroborane-etherate and MCBS hydroborate alkenes at 0 °C and 20 °C respectively, both reagents showing high stereo- and regio-selectivity.[44] The figures shown in Table 1.1 indicate how isomerically pure dialkylchloroboranes and their derivatives can be obtained using MCBS. Monochloroborane as a mono-substituted borane is suited for the cyclic hydroboration of dienes, and many B-chloroboraheterocycles have been prepared using this reagent.[45,46] Any polymeric organoboranes can be easily depolymerised by heating under vacuum. The cyclic hydroboration of cis, cis-1,5-cyclooctadiene with MCBS gives a mixture containing mostly the 1,4 adduct which is thermally isomerised to pure B-Cl-9 borabicyclo(3.3.1)nonane (1,5 adduct)[46] (equation 45).

Internal alkynes are cleanly hydroborated by monochloroborane etherate at 0 °C to produce dialkenylchloroboranes.[38] However, with terminal alkynes, an excess of

Table 1.1 Directive effects of monochloroborane complexes

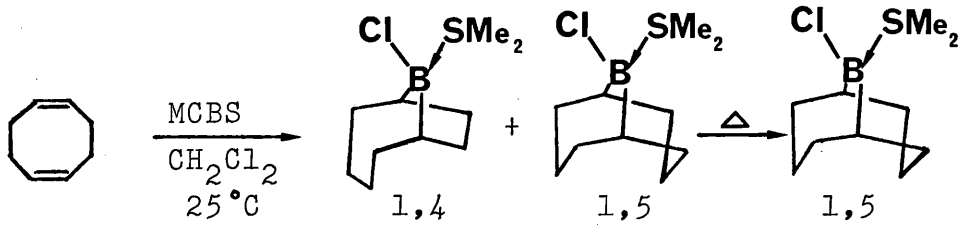
Borane	Alkene / % of boron added to specified position					
	$Bu^nCH=CH_2$		$\begin{matrix} Me \\ \diagdown \\ Et \end{matrix}\!\!>\!C=CH_2$		$\begin{matrix} Me \\ \diagdown \\ Me \end{matrix}\!\!>\!C=C\!<\!\begin{matrix} Me \\ \diagup \\ H \end{matrix}$	
$BH_3.THF$	6	94	1	99	2	98
$ClBH_2.OEt_2$	0.5	99.5	0.1	99.9	0.3	99.7
$ClBH_2.SMe_2$	0.8	99.2	0.1	99.9	0.5	99.5



$BH_3.THF$	1	99
$ClBH_2.OEt_2$	0.2	99.8
$ClBH_2.SMe_2$	0.5	99.5

a - Hydroboration followed by oxidation

alkyne has to be used to reduce dihydroboration.



(45)

Dialkyl- and dialkenylchloroboranes have important applications as precursors for tertiary alcohols;[44] dienes;[47] amines;[48] and ketones.[44]

1.3.3 Monobromo- and monoiodoborane-dimethyl sulphide complexes (MBBS and MIBS)

These complexes can be prepared by the reaction of BMS with boron tribromide-dimethyl sulphide complex or bromine for MBBS and boron triiodide-dimethyl sulphide or iodine for MIBS.[40,49] (equations 46 and 47).

$$2BH_3.SMe_2 + BI_3.SMe_2 \longrightarrow 3IBH_2.SMe_2 \qquad (46)$$

$$2BH_3.SMe_2 + Br_2 \longrightarrow 2BrBH_2.SMe_2 \qquad (47)$$

Hydroboration of alkenes using these complexes are often carried out in dichloromethane[44]; at 25°C for MBBS and at refluxing temperature for MIBS. The directive effects of the reagents[44] are shown in Table 1.2.

1.3.4 Dihalogenoborane-dimethyl sulphide complexes

The most convenient way of handling dihaloboranes is as the dimethyl sulphide complex which can be prepared

in a similar way to MCBS and the other monohalogenated boranes[40,49](equations 48-50).

$$BH_3.SMe_2 + 2BCl_3.SMe_2 \longrightarrow 3Cl_2BH.SMe_2 \quad (48)$$

$$BH_3.SMe_2 + 2BBr_3.SMe_2 \longrightarrow 3Br_2BH.SMe_2 \quad (49)$$

$$BH_3.SMe_2 + I_2 \xrightarrow{CS_2} I_2BH.SMe_2 \quad (50)$$

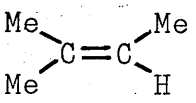
Hydroboration of alkenes using dichloroborane-dimethyl sulphide complex (DCBS) is very slow and is accompanied by disproportionation of the DCBS. This is due to the strength of the complex and is usually overcome by the addition of boron trichloride which removes the dimethyl sulphide from the complex, releasing the dichloroborane.

The dibromo- and diiodoborane-dimethyl sulphide complexes (DBBS and DIBS) add directly to the alkene however.[51] The directive effects are shown on Table 1.2.

A detailed study of the hydroboration of alkynes with DBBS has been carried out.[52] Competition experiments using alkenes and alkynes showed a preference for the addition to triple bonds, particularly internal alkynes. Therefore DBBS is very useful for hydroborating triple bonds in the presence of double bonds. DBBS exhibits high regioselectivity for the hydroboration of alkynes (comparable to 9-BBN), examples being shown in Table 1.2.

The alkenyldibromoboranes formed are isolated as the dimethyl sulphide complex. Alkenyl dibromoboranes are useful precursors to many derivatives. Oxidation gives carbonyl compounds and protonolysis provides 2-alkenes.[52]

Table 1.2 Directive effects of mono- and dihalogenoborane -dimethyl sulphide complexes

Borane	Alkene (or alkyne) / % of boron added to specified position					
	$Bu^nCH=CH_2$				$PhCH=CH_2$	
$BH_3.THF$	6	94	—		19	81
$BrBH_2.SMe_2$	0.4	99.6	—		4	96
$IBH_2.SMe_2$	0.5	99.5	—		4	96
$Cl_2BH.SMe_2$	1	99	3	97	3	97
$Br_2BH.SMe_2$	0.4	99.6	7	93	4	96
$I_2BH.SMe_2$	4	96	25	75	3	97

	$PhC\equiv CMe$		$Pr^nC\equiv CMe$		$Pr^iC\equiv CMe$		$Bu^tC\equiv CMe$	
$Br_2BH.SMe_2$	64	36	25	75	4	96	1	99
9-BBN	65	35	22	78	4	96	1	99

Alkyldichloroboranes are good precursors for the synthesis of many derivatives including secondary amines[53](equation 51) and alkyl hydroperoxides[54](equation 52).

$$RBCl_2 + R'N_3 \xrightarrow{-N_2} RR'NBCl_2 \xrightarrow[H_2O]{NaOH} RR'NH \qquad (51)$$

$$RBCl_2.OEt_2 \xrightarrow{O_2} \xrightarrow{H_2O} RO_2H \qquad (52)$$

CHAPTER TWO

2.1 INVESTIGATION OF REACTIONS BETWEEN BMS AND HALOALKANES

2.1.1 Introduction

The course of the substitution reactions between BMS and haloalkanes were followed by ^{11}B n.m.r. spectroscopy. Full details of the assignments and operating conditions are given in Appendix II. The reactions were usually carried out using 1:1 molar mixtures of the two reagents and the results are expressed as a percentage of the total amount of boron present in the spectra. It is important to note that no boron species other than $BH_{(3-n)}X_n.SMe_2$ were detected.

2.1.2 Results and discussion of products

Table 2.1 shows the relative molar yields of boron species produced from the reaction of the halomethane and BMS.

Refluxing mixtures of BMS and tetrachloromethane reached equilibrium at around 75% conversion to the monochloroborane adduct (MCBS). The position of this equilibrium was unaffected by the initial concentration of the two reactants. After reaching the 70-75% level, further heating leads to the formation of larger amounts of the dichloroborane adduct (DCBS). The observed yield of MCBS contradicts that reported by previous workers[43] and implies that it was the hydroboration of cyclohexene, not the abstraction reaction, that proceeded quantitatively (see section 1.3.1).

In the reactions where a bromine atom was available, this was abstracted preferentially by the BMS. This can be

clearly seen in the reaction using bromotrichloromethane and is even more pronounced in the case of dibromodichloromethane (Table 2.1).

The reactions were also followed using ^{1}H n.m.r. spectroscopy which revealed the presence and relative yields of the halomethanes produced. The results are shown in Table 2.2. It is clear from the presence of species such as dichloromethane that further reaction of the initial abstraction products takes place. This process becomes more important when the relative concentration of the initial halomethane becomes lower. In the case of the reaction between BMS and bromotrichloromethane the halomethanes detected are trichloromethane, dichlorobromomethane and dichloromethane. At equal concentrations of reactants (4.6 mol dm^{-3}) the ratio between trichloromethane and dichlorobromomethane increased in favour of trichloromethane as the reaction proceeded. When an excess of bromotrichloromethane was employed ($CBrCl_3$, 6.3 mol dm^{-3}; BMS, 3.2 mol dm^{-3}), the ratio of these two products was constant until all the BMS had been consumed, when the ratio fell by a small amount.

The steady decrease in the relative amounts of dichlorobromomethane and trichloromethane during the course of the equimolar reaction implies that it is consumed by the monohalogenoborane. This proposal is in agreement with the observed formation of dihalogenoboranes and dichloromethane during the later part of the reaction.

Similar results were obtained with the reaction using dichlorodibromomethane and the same argument applies.

These reactions produce monohalogenated borane

Table 2.1 Relative yields of halogenoborane-dimethyl sulphide complexes

Haloalkane / T°C	Time $x10^{-2}s$	Halogenoborane-dimethyl sulphide complex%					
		BH_2Br	BH_3	BH_2Cl	$BHBrCl$	$BHCl_2$	$BHBr_2$
CCl_4/80	0	—	100	0	—	0	—
	18	—	84	16	—	0	—
	39	—	73	27	—	0	—
	60	—	62	38	—	0.8	—
	87	—	52	47	—	1.4	—
	114	—	45	53	—	2.0	—
	144	—	40	57	—	2.6	—
	174	—	39	59	—	2.7	—
	204	—	37	60	—	3.0	—
	240	—	36	61	—	3.1	—
	720	—	24	70	—	6.0	—
	3480	—	9	74	—	17	—
$CFBr_3$/90	0	0	100	—	—	—	0
	24	3	97	—	—	—	0
	138	56	44	—	—	—	0
	720	84	13	—	—	—	2.9
CCl_2Br_2/90	0	0	100	0	0	0	0
	24	31	63	6.1	0	0	0
	138	72	16	10	1.8	1	1
	720	76	3.0	5.7	6.1	1.2	8.4

Table 2.1 (continued)

Haloalkane / T °C	Time x10^{-2}s	Halogenoborane-dimethyl sulphide complex %					
		BH_2Br	BH_3	BH_2Cl	BHBrCl	$BHCl_2$	$BHBr_2$
$CBrCl_3$/90	0	0	100	0	0	0	0
	51	36	50	14	0	0	0
	93	51	30	19	1	1	0
	120	58	22	20	1	1	0
	762	66	5.0	17	5.4	2.8	4.0
	1683	66	2.5	14	7.2	4.3	5.6
$CBrCl_3$/90[a]	0	0	100	0	0	0	0
	51	48	32	20	0	0	0
	93	60	10	19	3.6	3.7	3.1
	120	63	6.0	19	5.3	3.1	3.9
	762	40	0	6.3	22	5.7	26
	1683	29	0	1	27	7.0	38
CCl_4/80[b]	0	—	100	0	—	0	—
	720	—	10	75	—	16	—
CCl_4/80[c]	0	—	100	0	—	0	—
	1440	—	10	70	—	21	—

a - Ratio of initial concentration of $CBrCl_3$:BMS = 2:1

b - Ratio of initial concentration of CCl_4:BMS = 4:1

c - Solution from standard mixture stripped of tetrachloromethane and trichloromethane and refluxed with CCl_4.

Table 2.1 (continued)

Haloalkane / T °C	Time x10^{-2}s	Halogenoborane-dimethyl sulphide complex%					
		BH_2Br	BH_3	BH_2Cl	$BHBrCl$	$BHCl_2$	$BHBr_2$
CBr_3Cl/90	0	0	100	0	0	0	0
	36	46	49	5.5	0	0	0
	654	72	1.4	2.1	5.7	0.7	17
	852	72	0.6	0.9	5.8	1.2	19
CBr_4/70	0	0	100	—	—	—	0
	108	8.5	92.	—	—	—	0
	711	41	59	—	—	—	0

Table 2.2 Relative yields of halomethanes

Halomethane (initial)	Time $x10^{-2}s$	Ratio of halomethane products $CHCl_3$: $CHCl_2Br$: CH_2Cl_2
$CBrCl_3$	51	3.7 : 1 : 0.03
	93	3.7 : 1 : 0.06
	120	3.8 : 1 : 0.11
	762	4.4 : 1 : 0.24
	1683	4.8 : 1 : 0.24
$CBrCl_3$[a]	51	4.8 : 1 : 0.00
	93	4.7 : 1 : 0.03
	120	4.5 : 1 : 0.03
	762	5.1 : 1 : 0.04
	1683	3.9 : 1 : 0.04
		$CHFBr_2$: CH_2FBr
$CFBr_3$	24	1 : 0.55
	138	1 : 0.55
	720	1 : 0.50
		CCl_2BrH : $CClBr_2H$: CH_2Cl_2 : CH_2ClBr
CCl_2Br_2	24	6.3 : 1 : 0.00 : 0.00
	138	6.8 : 1 : 0.05 : 0.02
	720	8.1 : 1 : 0.30 : 0.10

a - Ratio of initial concentration of $CBrCl_3$:BMS = 2:1

complexes in good yields using simpler techniques than those employed in the redistribution reaction. As synthetic methods, two systems in particular stand out, these being the reactions using tetrachloromethane and fluorotribromomethane. Heating overnight produces the appropriate monohalogenated borane in good yields (70 and 84% respectively); this method has clear advantages over the established routes.[40]

The reaction between BMS and tetrabromomethane in dimethyl sulphide produces 41% of MBBS after 108 minutes. However it also precipitates a large amount of white solid which contains no boron. Elemental analysis corresponds reasonably well with $(CH_3)_2SCBr_4$ which appears to be the sulphonium salt $\left((CH_3)_2SCBr_3\right)^+ Br^-$. The Raman spectrum of the salt was consistent with the proposed formulation.

Reaction between tetraiodomethane and BMS

The reaction was carried out at room temperature and a 10 °C temperature rise was immediately observed accompanied by the formation of a small amount of unidentified solid. The ^{11}B n.m.r. spectrum revealed the major product to be MIBS, and no BMS was detected.

Reaction between iodomethane and BMS

The reaction was carried out at room temperature and a temperature rise of 30 °C was observed. No iodoboranes were detected and as with tetraiodomethane, the formation of $(CH_3)_3S^+ I^-$ accompanied the reaction.

Reaction between silicon tetrachloride and BMS

Prolonged heating of the two reagents resulted in the formation of a small amount of MCBS. Further details are given

in section 2.1.3.

Reaction between haloalkanes and BMS

Prolonged heating of the bromo- and bromochloroalkanes shown in Table 2.5 produced small amounts of MBBS and the relevant alkane. While of no synthetic usefulness, estimated rate constants could be derived and the reactions are examined in more detail in the discussion of the mechanism. In some cases small amounts of precipitates were formed, but in no case was this greater than ca. 0.5g (5% by weight of the original haloalkane).

2.1.3 Investigation of kinetics

The course of the reactions was followed by ^{11}B n.m.r. spectroscopy, care being taken to ensure identical machine operating conditions ie. the same number of scans for each sample, identical recording parameters etc. Detailed information is given in the experimental section and Appendix II. It was not possible to obtain sufficiently accurate measurements of borane concentrations if initial BMS concentrations were below about 1 mol dm^{-3}. Therefore the usual kinetic assumption that no changes in the bulk medium properties occur during the course of the reaction is unlikely to be valid. However, this stricture is more important in heterolytic reactions.

a) Investigation of kinetics of the reaction between tetrachloromethane and BMS at 50°C

The reaction between BMS and tetrachloromethane at 50°C proceeds at a rate which produces no DCBS over the period of observation. The reaction was carried out using neat, equimolar concentrations of reactants, and also using

Table 2.3 Rate constants derived from the kinetic investigation of BMS/tetrachloromethane reactions at 50°C.

Solvent	BMS / mol dm^{-3}	CCl_4 / mol dm^{-3}	$k_2 x10^{+7} dm^3 mol^{-1} s^{-1}$	Mean k_2 $x10^{+7}$
——	4.84	4.84	15.0, 13.5, 13.0	13.8±0.9
——	2.51	7.51	9.0, 9.5, 10.5	9.7±0.6
——	7.05	2.33	23.0, 18.0, 20.0	20.3±2
PhH	1.87	1.87	7.5, 8.0	7.8±0.3
PhH	3.26	1.08	15.0	ca.15
PhH	1.15	3.50	5.0	ca.5
CH_2Cl_2	1.58	1.58	13.0 [a]	ca.13

a - Temperature 48°C

and destruction,

$$-\frac{d(BH_2Cl\cdot)}{dt} = k_2(BH_2Cl)^c(CCl_4)^d$$

of the MCBS are of the same kinetic order. ie. a=c, b=d. Thus at equilibrium,

$$k_1(BMS)^a = k_2(BH_2Cl\cdot)^a \quad .$$

Using this and the evidence that the reaction between BMS and tetrachloromethane has the kinetic form,

$$-\frac{d[BMS]}{dt} = k(BMS)(CCl_4)$$

we can say that a=b=1 so that,

$$\frac{d(BHCl_2)}{dt} = \frac{-d(BH_2Cl)}{dt} = k_2(BH_2Cl)(CCl_4)$$

and values of k_2 can be assigned.

k_1 was found to be $2.2 \pm 0.1 \times 10^{-5}$ $dm^3mol^{-1}s^{-1}$, k_2 as $2.0 \pm 0.2 \times 10^{-6}$ $dm^3mol^{-1}s^{-1}$. Full details are given in Appendix II.

c) Investigation of kinetics of reactions between BMS and polyhalomethanes at 90°C

The results from the reactions between BMS and mixed polyhalomethanes (shown on Table 2.1) were treated in the same way as in b) above, assuming second order kinetics. The second order rate constants obtained are presented on Table 2.4. The results for the reaction using tribromochloromethane are included, but are to be regarded with caution due to the possibility of decomposition of the halomethane to produce bromine when exposed to light. The halomethanes were used as supplied by the manufacturers (with the addition of molecular sieves) because tetrachloro-

Table 2.4 Second order rate constants for reactions between BMS and polyhalomethanes (k_2 / $dm^3 mol^{-1} s^{-1}$) at 90°C

Process	Reagents (mol dm^{-3})				
	$CBrCl_3$(4.6) BMS(4.6)	$CBrCl_3$(6.3) BMS(3.2)	CCl_2Br_2(4.5) BMS(4.5)	CBr_3Cl(4.2) BMS(4.2)	$CFBr_3$(4.6) BMS(4.6)
BMS consumption	$5.4 \pm 0.4 \times 10^{-5}$	$5.3 \pm 0.6 \times 10^{-5}$	5.4×10^{-5}	1.3×10^{-4}	ca. 2×10^{-5}
BMS → BH_2Br	ca. 4×10^{-5}	ca. 3×10^{-5}	4.5×10^{-5}	4×10^{-5}	ca. 2×10^{-5}
BMS → BH_2Cl	1.3×10^{-5}	ca. 1×10^{-5}	ca. 8×10^{-6}	6×10^{-5}	—
BH_2Cl → $BHBrCl$	7.3×10^{-6}	ca. 7×10^{-6}	1-2 $\times 10^{-5}$	2×10^{-5}	—
BH_2Cl → $BHCl_2$	ca. 5×10^{-6}	1.7×10^{-6}	6×10^{-6}	3.1×10^{-6}	—
BH_2Br → $BHBrCl$	2.0×10^{-6}	2×10^{-6}	2.0×10^{-6}	2×10^{-6}	—
BH_2Br → $BHBr_2$	1.6×10^{-6}	1.8×10^{-6}	5×10^{-6}	5×10^{-6}	ca. 3×10^{-6}

methane gave the best results when impure. The rate constant for the reaction using excess bromotrichloromethane (6.3 mol dm^{-3}) was derived using the integrated second order expression for unequal initial reactant concentrations;

$$kt = \frac{1}{(A)_o - (B)_o} \ln \left[\frac{(A)_t (B)_o}{(A)_o (B)_t} \right]$$

The similarity of the rate constants derived from the two bromotrichloromethane reactions is further evidence of a second order reaction involving BMS and the polyhalomethane.

$$\text{ie.} \quad -\frac{d[BMS]}{dt} = k_2 (BMS)(CX_{4-n}Y_n)$$

The second order rate constant for the consumption of BMS by dibromodichloromethane was the same as that found in reactions involving equimolar and excess bromotrichloromethane. Similar values were also found for the reactions involving fluorotribromomethane and tribromochloromethane. The similarity of rate constants could imply a common rate-limiting step, which would involve only the borane. This is discounted because of the observed kinetic form. It is more likely that the similar rate constants indicate a homolytic slow step in the process.

d) Investigation of kinetics of reactions between BMS and tetrabromo(iodo)methane, silicon tetrachloride and haloalkanes

The rate constants for these reactions were derived as for the polyhalomethanes and are shown on Table 2.5. The tetrabromomethane reaction produces significant amounts of salt from the reaction between the halomethane and the

Table 2.5 Second order rate constants for the reactions between BMS and haloalkanes

Reagents/mol dm^{-3}	Process	$k_2(dm^3 mol^{-1} s^{-1})$, T°C
CBr_4 (1.8), BMS (1.8)	BMS $\longrightarrow BH_2Br$[a]	4.8×10^{-6}, 70
	BMS $\longrightarrow BH_2Br$[b]	5.2×10^{-6}, 70
	BMS consumption[a]	5.1×10^{-6}, 70
	BMS consumption[b]	5.3×10^{-6}, 70
CI_4 (1.3), BMS (1.3)	BMS consumption	5×10^{-3}, 40
$CHBr_3$ (5.1), BMS (5.1)	BMS $\longrightarrow BH_2Br$	5×10^{-6}, 90
CH_2Br_2 (5.6), BMS (5.6)	BMS $\longrightarrow BH_2Br$	3×10^{-6}, 90
$(CH_3)_2CBrCl$ (4.7) BMS (4.7)	BMS $\longrightarrow BH_2Br$	4×10^{-7}, 75
CH_2BrCl (5.8), BMS (5.8)	BMS $\longrightarrow BH_2Br$	2×10^{-7}, 75
$(CH_3)_3CBr$ (4.5), BMS (4.5)	BMS $\longrightarrow BH_2Br$	6×10^{-7}, 75
$(CH_3)_2CHBr$ (4.9) BMS (4.9)	BMS $\longrightarrow BH_2Br$	3×10^{-7}, 75
$CH_3(CH_2)_3CH_2Br$ (4.3) BMS (4.3)	BMS $\longrightarrow BH_2Br$	3×10^{-7}, 75
$SiCl_4$ (4.2) BMS (4.2)	BMS $\longrightarrow BH_2Cl$	2×10^{-7}, 70

a - Rate constant calculated after 4 hours reaction time.

b - Rate constant calculated after 20 hours reaction time.

dimethyl sulphide. Therefore the concentration of the tetrabromomethane was not equal to that of the BMS and was not determined. Two values of the rate constants are therefore given, found after 4 hours and 20 hours reaction, the former having more credence because only a small amount of salt formed at that stage.

The tetraiodomethane reaction produces both MIBS and and other unidentified boranes, along with a brown precipitate. Thus only an approximate rate constant for the consumption of BMS is given. The significance of these observations is the ease of displacement of iodine compared to bromine and chlorine.

It is clear from the rate constants that the relative ease of displacement are $I > Br > Cl \gg F$ and $C-Cl > Si-Cl$. This order parallels with the bond strengths (C-I, 213 ; C-Br, 285 ; C-Cl, 327 ; C-F, 485 ; Si-Cl, 391 x 10^3 J mol^{-1})[56] and would indicate that the slow step of the reaction involves cleavage of the carbon-halogen bond.

The rate constants for the single bromine-containing alkanes are fairly similar, but there is an increase in rate as the bulk of the alkyl group adjacent to the halogen increases. Thus the rate of reaction roughly doubles on moving from a straight chain alkyl (n-pentyl) bromide to tertiary butyl bromide. The reaction involving isopropyl bromide, however, has a rate constant similar to that of the straight chain bromoalkane. A similar trend can be seen when 2-bromo-2-chloropropane and bromochloromethane are compared, the more bulky haloalkane reacting with BMS at approximately twice the rate of the dihalomethane. The

enhanced reaction rate that occurs with increased methyl substitution could arise from the stabilisation of the intermediate by the inductive effect of the alkyl groups, or from the steric relief attained during the carbon-bromine cleavage.

2.1.4 Investigation of mechanism

The effect of changing the reaction conditions upon the tetrachloromethane/BMS reaction are shown on Table 2.6. The MCBS yields from some of the reactions are compared to those found for the AnalaR tetrachloromethane reaction to give a clearer indication of the effect of the additives. The results in Table 2.7 are shown in terms of the relative reaction times taking as standard the reaction of AnalaR tetrachloromethane and BMS at reflux temperature (see Appendix II for MCBS growth curve at reflux temperature, 70°C).

The reaction using purified tetrachloromethane was accelerated both by u.v irradiation and by the addition of small amounts (0.1g) of lauroyl peroxide. This implies a free radical mechanism.

AnalaR tetrachloromethane stored over molecular sieves was found to react faster than purified tetrachloromethane. This would imply the presence of an impurity which acts as an initiator. The reaction could be slowed by the addition of hydroquinone (though quinone speeds the reaction slightly) or by traces of water. This behaviour would be difficult to explain in terms of a polar mechanism and suggests that impurities in the tetrachloromethane act as free radical initiators.

Further evidence of a homolytic mechanism comes from the reactions using tetrachloromethane and trichlorobromomethane with BMS carried out using nitrobenzene as a solvent. A solvent with a high dielectric constant would normally accelerate some types of heterolytic processes,

Table 2.6 The effect of additives and changing conditions on the tetrachloromethane/BMS reaction

CCl_4[a]	Conditions	% yields (^{11}B n.m.r) $BHCl_2$	BH_2Cl	BH_3 ($.SMe_2$)
Pu	Refluxed 20 hours (standard conditions)	2	54	44
Pu	CCl_4:BMS ratio = 2:1 20 hours reflux	2	56	42
Pu	Refluxed 17 hours with u.v irradiation	6	71	23
Pu	u.v irradiation for 4 hours at 20°C and irradiated and refluxed for 4.5 hours	4	60	36
Pu	Refluxed 20 hours + lauroyl peroxide (0.1g)	4	62	34
An	Refluxed 20 hours (standard conditions)	6	70	24
An	CCl_4:BMS ratio = 4:1 20 hours reflux	10	75	16
An	Refluxed 20 hours + hydroquinone (0.1g)	3	61	36
An	Refluxed 20 hours + quinone (0.1g)	8	75	17

a - An = BDH AnalaR stored over 3Å molecular sieves,
Pu = Distilled over phosphorus pentoxide.

Table 2.6 (continued)

CCl_4[a]	Conditions	% yields (^{11}B n.m.r) $BHCl_2$	BH_2Cl	BH_3 (.SMe_2)
An	Refluxed for 30 minutes + lauroyl peroxide(1.0g)	0	25	75
An	Refluxed 4 days	9	74	17
An	Refluxed 20 hours, CCl_4 not stored over sieves.	2	49	49
An	Refluxed 20 hours in dark	9	74	17
An	u.v irradiated for 4 hours at 22°C	0	11	89
An	u.v irradiated using a filter, for 4 hours at 22°C	0	15	85
An	Reagents 1.6 mol dm^{-3} in PhH, 22 hours at 52°C	0	10	90
An	Reagents 1.6 mol dm^{-3} in CH_2Cl_2, 22 hours at 48°C	0	14	86
An[b]	Reagents 1.9 mol dm^{-3} in $PhNO_2$, 3 days at 50°C	0	0	100[c]

b - bromotrichloromethane was similarly inhibited when nitrobenzene was used as a solvent at 90°C.

c - BMS concentration confirmed by hydrolysis using a gas burette.

Table 2.7 The effect of additives on the tetrachloromethane / BMS reaction relative to the standard reaction using AnalaR tetrachloromethane

CCl_4[a]	Conditions	yield of MCBS/%	Approximate time for standard reaction to attain the same level of MCBS[b]/hr.
Pu	Refluxed 20 hours	54	3.5
Pu	Refluxed 17 hours + u.v irradiation	71	20
Pu	Refluxed 20 hours + lauroyl peroxide	62	7
Pu	Refluxed 4.5 hours, irradiated 8.5 hours	60	5.5
An	Refluxed 20 hours, undried CCl_4	49	2.5
An	Refluxed 20 hours + hydroquinone	61	6.5

a - An = BDH AnalaR stored over 3A molecular sieves
Pu = Distilled over phosphorus pentoxide.

b - Based on the growth curve for the reaction between BMS and AnalaR tetrachloromethane at 70 °C.

but both the above reactions were completely stopped. This is probably due to the trapping of haloalkyl radicals.

Large changes in the nature of the solvent have little effect on the observed rates. This also suggests a radical rather than a polar mechanism. Hexachloroethane, the product of dimerisation of trichloromethyl radicals, was not detected in reactions using standard AnalaR tetrachloromethane reaction conditions. ($<0.01\%$ with respect to the tetrachloromethane).

The u.v irradiation of the AnalaR tetrachloromethane / BMS mixture at room temperature produced slightly less MCBS than when a soda glass filter was used to absorb the u.v light. This could arise because the tetrachloromethane already contains sufficient initiators for the reaction. If the reaction is taking place as rapidly as possible, then higher concentrations of radicals may inhibit the reaction by trapping radical intermediates and blocking the reaction sequence.

A possible mechanism consistent with these observations is shown below (equations 53-55).

$$Me_2S.BH_3 + \text{Initiator} \longrightarrow Me_2S.BH_2^{\cdot} + \text{product} \qquad (53)$$

$$Me_2S.BH_2^{\cdot} + XCY_3 \longrightarrow Me_2S.BH_2X + {}^{\cdot}CY_3 \qquad (54)$$

$$Me_2S.BH_3 + {}^{\cdot}CY_3 \longrightarrow Me_2S.BH_2^{\cdot} + HCY_3 \qquad (55)$$

This would fit the kinetic form if the concentration of borane radical were proportional to the BMS concentration. The observed relative ease of displacement for the halogen -hydrogen transfer are $I > Br > Cl \gg F$. This order parallels

the bond strengths of the carbon-halogen bond and indicates the slow step to be equation 54. This is also consistent with the increased rate obtained when methyl groups are inserted into a bromoalkane (the methyl groups stabilising the radical by their inductive effect, or promoting the loss of bromine due to their steric effect).

The rates of the abstraction reactions of the boranes (BH_2X) fall in the order X = H, Cl, Br both for the removal of bromine from bromotrichloromethane, dibromodichloromethane, tribromochloromethane and fluorotribromomethane and for the slower abstraction of chlorine from tetrachloromethane, bromotrichloromethane, dibromodichloromethane and tribromochloromethane. This sequence appears to reflect the increasing steric requirements of the borane.

The halogen substituent appears to activate the halomethane towards halogen loss. Thus the rate of abstraction for bromine falls in the order, $CBr_4 > CHBr_3 > CH_2Br_2 >$ n-pentyl bromide (this order is only approximate because n-pentyl bromide was studied at a lower temperature). The order still follows after statistical correction for the number and nature of the halogens (eg. tetrabromomethane has 4 times as many available bromine atoms as n-pentyl bromide). This also could be due to steric factors since methyl substitution of bromoalkanes causes a slightly enhanced rate. However, electronic requirements may also be important. Trichloromethane, the reaction product of the tetrachloromethane reaction, undergoes no further reaction. However if steric requirements were the only important factor, then t-butyl chloride (which is similar

in size to tribromochloromethane) would react with BMS, which is not the case. The different contributing factors result in a delicate balance which is shown by the inertness of the following compounds ; Hexachloroethane, 1,1,2,2-tetrachloroethane (either with or without lauroyl peroxide), 1-bromo-1-chloro-2,2,2-trifluoroethane, 1,2-dibromotetrachloroethane, trichlorofluoromethane, dichloromethane and t-butyl chloride. Aromatic halogen is stable; even 2,3,4,5,6 pentabromotoluene does not lose bromine to BMS.

The dimethyl sulphide part of the borane complex appears not to be involved in the free radical reaction. Boron hydride bonds are weaker than carbon-hydrogen bonds[57] and this explains why hydrogen is extracted from the boron and not the carbon.

In these reactions there is a considerable parallel with the amine-borane processes[42], mentioned in Chapter one, and a similar mechanism is proposed.

2.2 INVESTIGATION OF REACTIONS BETWEEN BMS AND HALOTRIPHENYLMETHANES

The reactions between chloro- and bromotriphenylmethane with BMS were carried out in benzene or dichloromethane at approximately 10°C over two hours. The yields of boranes (from ^{11}B n.m.r spectroscopy) are shown on Table 2.8. In the case of some of the reactions carried out in dichloromethane it was difficult to keep the temperature below 10°C because of the exothermic nature of the reaction. In these reactions the BMS had to be added over a period of 30 minutes (lower concentrations could be used, but make the ^{11}B n.m.r spectra difficult to obtain without prior removal of solvent). If the BMS was added too rapidly (and the temperature allowed to rise) then the chlorotriphenylmethane would react fully with only part of the BMS (equation 56). This was shown by the lack of a temperature rise

$$2\ (C_6H_5)_3CCl + BH_3.SMe_2 \longrightarrow 2\ (C_6H_5)_3CH + Cl_2BH.SMe_2 \quad (56)$$

when the remaining BMS was added. This gave a mixture containing 54% BMS, 40% DCBS and only 7% MCBS. When this mixture was refluxed for 20 hours, the BMS further reacted with the DCBS resulting in an equilibrium mixture similar to that obtained during the tetrachloromethane / BMS reaction

$(C_6H_5)_3CCl$ / BMS ; 72% MCBS , 11% DCBS , 17% BMS

CCl_4 / BMS ; 70% MCBS , 6% DCBS , 24% BMS.

The reactions were noticeably slower in benzene, it

Table 2.8 Yields of halogenoborane-dimethyl sulphide complexes from BMS / halotriphenylmethane reactions

Halide (RX)	RX:BMS ratio	Solvent	% yields of complexes (SMe_2)					
			BH_3	BH_2Cl	BH_2Br	$BHCl_2$	$BHBr_2$	BCl_3
$(C_6H_5)_3CCl$	1:1	C_6H_6	41	17	—	41	—	1
$(C_6H_5)_3CCl$	2:1	C_6H_6	7	5	—	73	—	15
$(C_6H_5)_3CCl$	1:1	CH_2Cl_2	54	7	—	40	—	0 [a]
$(C_6H_5)_3CCl$	1:1	CH_2Cl_2	39	20	—	42	—	0 [b]
$(C_6H_5)_3CCl$	2:1	CH_2Cl_2	15	0	—	53	—	32 [a]
$(C_6H_5)_3CBr$	1:1	CH_2Cl_2	0	—	100[c]	—	0	—
$(C_6H_5)_3CBr$	2:1	CH_2Cl_2	0	—	54	—	46	—

a - First half of BMS addition very exothermic, temperature rise of ca. 30°C.

b - Repeat of equimolar reaction, keeping temperature below 10°C.

c - After several weeks at 4°C, the mixture disproportionates to 84% MBBS, 6% DBBS and 10% BMS.

being possible to add the BMS much more rapidly than with dichloromethane without a large temperature rise. This implies a large solvent effect consistent with previous studies[42] using amine-boranes, where a polar mechanism is proposed (equation 57).

$$Me_2S.BH_3 + (C_6H_5)_3C^+ X^- \longrightarrow Me_2S.BH_2^+ + (C_6H_5)_3CH + X^- \longrightarrow Me_2S.BH_2X + (C_6H_5)_3CH \quad (57)$$

The reaction between BMS and two mole equivalents of chlorotriphenylmethane in benzene provides a good yield of DCBS with very little BMS. The reaction between equimolar amounts of bromotriphenylmethane and BMS provides an essentially quantitative yield of MBBS. These are attractive, simple methods for producing MBBS and DCBS.

2.3 PREPARATION OF DIALKYLCHLOROBORANES USING MCBS PRODUCED VIA THE BMS/TETRACHLOROMETHANE REACTION

2.3.1 Introduction

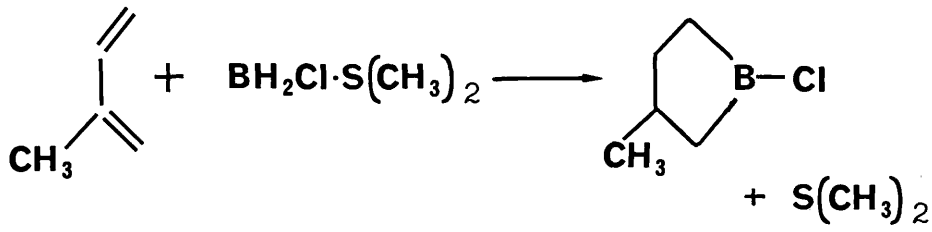
The MCBS solution obtained from the reaction between BMS and tetrachloromethane contained amounts of BMS and DCBS. The suitability of this impure MCBS mixture was tested using a variety of alkenes and di-alkenes. The dialkylchloroboranes obtained were of use in later work involving their reaction with aldehydes (see Chapter three).

2.3.2 Hydroboration of 1-alkenes and isoprene using MCBS

The terminal alkenes were hydroborated by standard techniques (described in Chapter four), the general reaction (equation 58) being shown below.

$$ClBH_2.SMe_2 + 2\ R'CH{=}CH_2 \longrightarrow R_2BCl + SMe_2 \qquad (58)$$

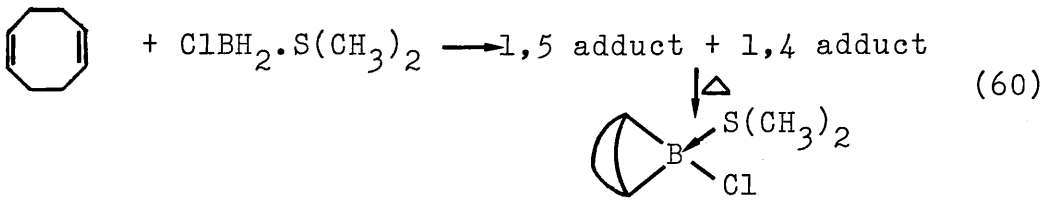
The crude products were vacuum distilled and analysed by ^{11}B n.m.r spectroscopy. The dialkylchloroboranes were analysed for chlorine and in the case of pent-1-ene and oct-1-ene, by GLC of the oxidation products. Isoprene was hydroborated in a similar manner the expected cyclic reaction being shown by equation 59.



The results are shown in Table 2.9. In all cases the ^{11}B n.m.r spectra gave results typical of dialkylchloroboranes[58] (+78 ppm) and chlorine analysis results were satisfactory. The reaction products from the pentene and octene reactions were oxidised using alkaline hydrogen peroxide and the extracted alcohols were analysed by GLC. In both cases only trace amounts (<1%) of pentan-2-ol and octan-2-ol, respectively, were found. This agrees with previous work indicating that the boron in MCBS add almost exclusively to the terminal carbon of the alkene.[13]

2.3.3 Hydroboration of 1,5 cyclooctadiene by MCBS

Hydroboration of 1,5 cyclooctadiene led to a mixture of unidentified isomers, thermal isomerisation giving pure B-Cl-9BBN.SMe_2 (76% yield, equation 60).



(60)

The melting point of the white crystalline solid (102-104°C) agrees with the literature value[46] (104-105°C). Hydrolysable chlorine analysis gave a value (%Cl = 18.6) close to the expected value of 19.0%. ^{11}B n.m.r spectroscopy gives a sharp singlet at 13.0 ppm (10% in deuterated chloroform) and differs to the literature value of 18.5 ppm and may reflect a difference in solvents used (no solvent quoted for the literature shift).

Table 2.9 Hydroboration products from the reaction between MCBS and various alkenes

Alkene	Product[a]	B.Pt/°C (mm Hg)	Yield[b] /%	Hydrolysable chlorine/%[c]
Pent-1-ene	$(n\text{-}C_5H_{11})_2BCl$[d]	78(6)	91	17.8(18.8)
2-methyl-pent-1-ene	$(CH_3CH_2CH_2\text{-}CH(CH_3)CH_2)_2BCl$	92(5)	92	16.1(16.4)
4,4-dimethyl-pent-1-ene	$((CH_3)_3CCH_2\text{-}CH_2CH_2)_2BCl$	58(0.02)	88	13.9(14.5)
Oct-1-ene	$(n\text{-}C_8H_{17})_2BCl$	102(0.03)	90	12.8(13.0)
2-methyl-1,3-butadiene (isoprene)	1-chloro-3-methylbora-cyclopentane[d]	72(30)	80	29.1(30.5)

a - All the products were liquids at room temperature.

b - Based on the moles of MCBS used.

c - Figures in brackets are the predicted chlorine contents.

d - Spontaneously flammable in air.

2.3.4 Discussion

The hydroboration of simple alkenes using the MCBS reaction mixture from the tetrachloromethane / BMS reaction gives similar results to those obtained using the redistribution method.[40] The presence of 20% BMS in the hydroboration solution did not lead to serious polymerisation problems with the reactions using dienes.

Thus the MCBS produced using the abstraction method is evidently suitable for use as a hydroborating agent for alkenes and dienes.

CHAPTER THREE

INVESTIGATION OF REACTIONS BETWEEN DIALKYLCHLOROBORANES AND ALDEHYDES / KETONES

3.1 INTRODUCTION

While no previous studies involving the interaction between dialkylchloroboranes and aldehydes/ketones have been published, there has been work carried out using the related compounds, trialkylboranes and boron trichloride. This introduction summarises studies relevant to this work.

3.1.1 Reaction between boron trichloride and aldehydes

There has only been one study concerned with the interaction of boron halides with aldehydes. In this Frazer et al[59] examined the reaction of boron trichloride with eleven aldehydes, each showing different steric or electronic features. With the exception of tribromoethanal (which failed to react at 20°C) all the aldehydes reacted, even at -80°C.

Ethanal, butanal and iso-butanal each produced the corresponding bis(1-chloroalkyl) ether (equation 61).

$$6RCHO + 2BCl_3 \longrightarrow 3(RCHCl)_2O + B_2O_3 \qquad (61)$$

2-Butenal reacted to form a solid alkyldichloroborinate of uncertain structure (either $CH_3CHClCH{=}CHOBCl_2$ or $CH_3CH{=}CHCHClOBCl_2$). The borinate decomposed on heating to form 1,3 dichlorobut-1-ene.

Monochloroethanal reacted to produce bis(1,2-dichloroethyl) ether and tris(1,2-dichloroethyl) borate. Heating

this borate gave the ether (equation 62). By comparing

$$3ClCH_2CHO + BCl_3 \longrightarrow (ClCH_2CHCl)_2O + (ClCH_2CHClO)_3B$$

$$(ClCH_2CHCl)_2O \longleftarrow \qquad (62)$$

this with the first three aldehydes a clear reduction in the reactivity of the central carbon atom can be seen, caused by the electronegative chlorine atom (this could also be explained by the improved stability of the ester towards pyrolysis). Consistent with this, di- and tri--chloroethanal both produced stable borates, $(Cl_2CHCHClO)_3B$ and $(Cl_3CCHClO)_3B$ respectively.

Benzaldehyde reacted to produce a mixture of dichloroborinate and chloroboronate esters which yielded dichlorophenylmethane upon heating (equation 63).

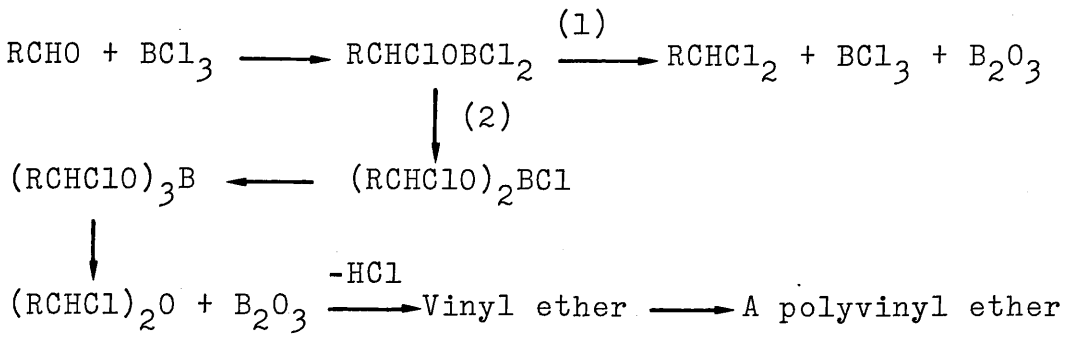
$$3PhCHO + 2BCl_3 \longrightarrow PhCHClOBCl_2 + (PhCHClO)_2BCl$$

$$\longrightarrow PhCHCl_2 + B_2O_3 \qquad (63)$$

Phenylethanal gave a resin, presumably a polyvinyl ether, formed by elimination of hydrogen chloride from the bis(1-chlorophenylethyl) ether initially produced. This suggestion is based on the known tendency of α-chloroethers to lose hydrogen chloride, forming vinylic ethers which are known to polymerise easily.

β-Phenylpropanal produced tris(1-chloro-3-phenylpropyl) borate which gave unidentified products on attempted distillation.

The probable reaction sequences are shown in Scheme 1, the reactivity of the central carbon atom being the likely determining factor.



Scheme 1

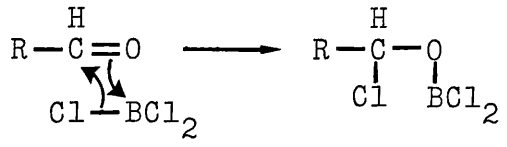
Alkyldichloroborinates decompose to form either an alkyl chloride (route 1, equation 64) or by disproportionation (route 2, equation 65).

$$3ROBCl_2 \longrightarrow 3RCl + B_2O_3 + BCl_3 \qquad (64)$$

$$2ROBCl_2 \longrightarrow (RO)_2BCl + BCl_3 \qquad (65)$$

The first reaction is favoured by the presence of an electron-releasing group attached to the α-carbon, thus benzaldehyde and 2-butenal formed dichlorborinates that gave the corresponding chlorides. The other aldehydes favoured the other route, progressing to various stages.

The speculated mechanism for the initial attack is a four-centre broadside type, affording a 1-chloroalkyl dichloroborinate ;



The possibility of initial electrophilic attack to give a co-ordination compound, $RCHO.BCl_3$ was ruled out because tribromoethanal was not observed to react with boron trichloride. Steric hindrance (F-strain) would prevent nucleophilic or 4-centre broadside attack, but not electrophilic attack of the carbonyl bond to form a complex.

3.1.2 Reactions between trialkylboranes and aldehydes/ketones

In 1936 it was found that triethylborane reacts with aldehydes at elevated temperatures forming borinates (equation 66).[60]

$$(C_2H_5)_3B + RCHO \xrightarrow{150^\circ C} (C_2H_5)_2BOCH_2R + C_2H_4 \qquad (66)$$

(R= CCl_3CHO, PhCHO or p-Cl-C_6H_4CHO)

The reaction was extended to the higher trialkylboranes in 1965 [61] (equation 67).

$$(RR'CHCH_2)_3B + PhCHO \xrightarrow{80\text{-}160^\circ C} RR'C{=}CH_2 \qquad (67)$$

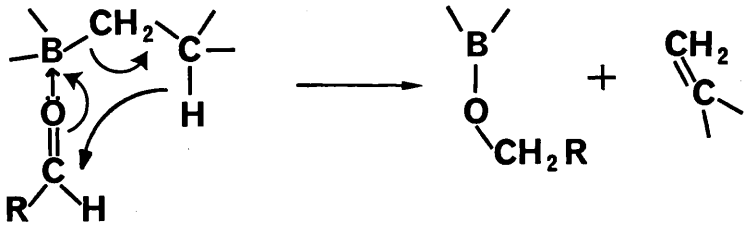
$$+ (RR'CHCH_2)_2BOCH_2Ph \xrightarrow[150\text{-}200^\circ C]{PhCHO} RR'CHCH_2B(OCH_2Ph)_2 + RR'C{=}CH_2$$

(R= H, CH_3, C_2H_5, $(CH_3)_2CH$, n-C_4H_9, R'= H, CH_3)

Competition experiments carried out by Mikhailov et al[62]

in 1965 using different alkyl groups attached to the boron atom defined a series of diminishing reducing power of the trialkylborane R_3B in which R = $CH_3CH(CH_3)CH_2- > CH_3CH_2CH_2- \gg CH_3CH_2CH_2CH_2- > CH_3CH_2- > CH_3CH(CH_3)-$. The rate of elimination of the alkene from the trialkylborane increases with an increase in the number of methyl groups on the β-carbon atom, indicating a reaction involving hydride elimination.

Mikhailov proposed that the reaction between trialkylboranes and benzaldehyde proceeded via the initial formation of a complex [62], $R_3B \leftarrow :O=CHPh$. This was indicated by the yellowish-green colour of the reaction mixtures. No shift in the infra-red carbonyl absorption band was observed, which would suggest a weak complex. The breakdown of the complex was thought to proceed via a cyclic process in which the elimination of the hydride ion from the β carbon atom proceeds simultaneously with the formation of the alkene double bond,



More recently the reduction of aldehydes and ketones using B-alkyl-9-borabicyclo[3.3.1] nonanes (B-alkyl-9BBN) has been studied by M.Midland et al.[63,64,65] In 1978 the ready dealkylation of these organoboranes when treated with benzaldehyde was reported.[64] The rate of dealkylation is dependent upon both the number and nature of β-

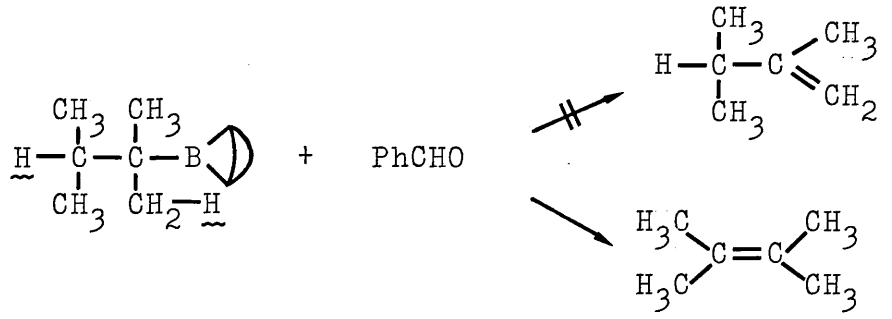
substituents and the number of α-substituents on the B--alkyl group. The reaction rate increases enormously with increased substitution at the position β to the boron. B-ethyl-9-BBN is a very poor reducing agent ($t_{\frac{1}{2}}$, 4 days in THF at 65°C). Those B-alkyl-9-BBN's which have a secondary β hydrogen react far faster ($t_{\frac{1}{2}}$, 2 hours), and there is little difference in effect between β-phenyl and β-alkyl substituents. Those B-alkyl-9-BBN's with a tertiary β hydrogen react rapidly enough to be effective reducing agents; thus, B-isobutyl-9-BBN has a $t_{\frac{1}{2}}$ of 20 minutes at 65°C.

A methyl substituent in the α position causes a slight increase in the reduction rate, but a second such substituent causes a large retardation eg. 2,3-dimethyl--2-butyl-9-BBN has a $t_{\frac{1}{2}}$ of 5 days.

Cyclic alkyl 9-BBN's such as the cyclopentyl and exo-norbornyl derivatives react quickly compared to acyclic secondary alkyl 9-BBN's, usually having a $t_{\frac{1}{2}}$ of about 20 minutes. This reactivity is increased further in cyclic alkyl 9-BBN's containing a tertiary β hydrogen. An exception to this general observation is the cyclohexyl compound which has a $t_{\frac{1}{2}}$ of 7 hours.

The greater reactivity of the tertiary β hydrogen in the alkyl group, compared to primary or secondary β hydrogens, also shows itself in the regiochemistry of the eliminated alkene. The elimination always occurs towards the more highly substituted hydrogen. For example, in the case of 2,3-dimethyl-2-butyl-9-BBN the elimination could involve either the primary or tertiary hydrogen substituent.

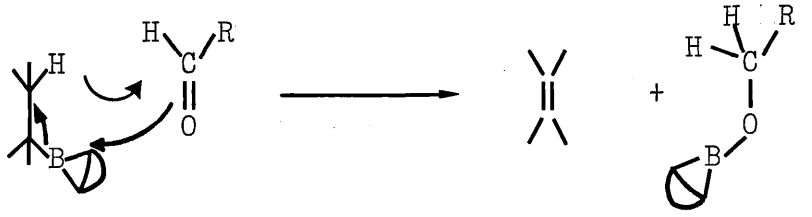
However, only 2,3-dimethyl-2-butene is found (scheme 2).



Scheme 2

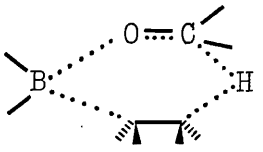
Preliminary kinetic investigations indicated a second order process (k_2, 4.1 x 10^{-5} l $m^{-1}s^{-1}$ at 25°C) for the reaction of B-octyl-9BBN and benzaldehyde in dichloromethane. The rate of reduction is affected by para-substituents in the benzaldehyde, electron donating groups slowing the reaction, while electron withdrawing groups speed the reaction. Ketones are reduced very slowly in comparison to aldehydes eg. 3-methyl-2-butyl-9-BBN has a $t_{\frac{1}{2}}$ of 11 minutes with benzaldehyde, and a $t_{\frac{1}{2}}$ of 22 hours when using acetophenone.

They concluded that the reaction proceeds via a bimolecular cyclic mechanism - as proposed by Mikhailov[62] (scheme 3), similar to the Meerwein-Ponndorf-Verley (MPV) reaction[64], the rate of which is affected by the structure of the organoborane and carbonyl compounds.



Scheme 3

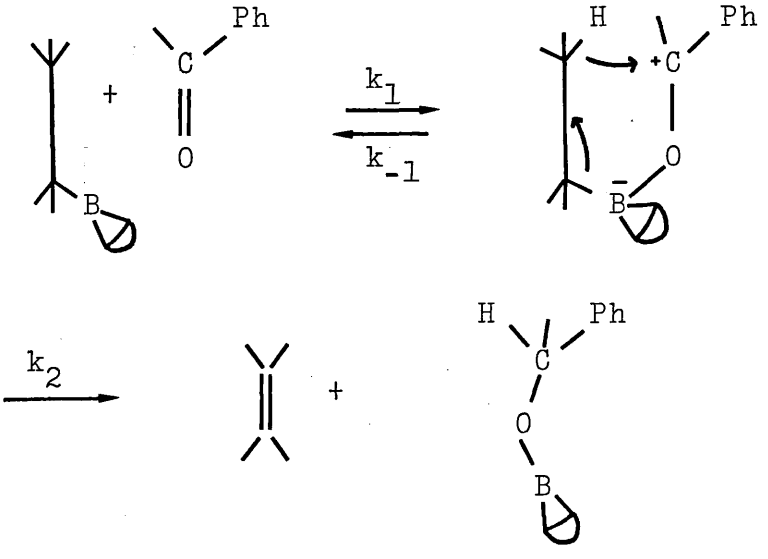
The difference in reactivity between cyclohexyl- and cyclopentyl-9-BBN s' is explained by the need for the B—C—C—H group in the alkyl-9-BBN s' to form a syn coplanar arrangement in the transition state,



This can be easily achieved with the B-cyclopentyl group, and hence a fast reaction is observed. However, the B--cyclohexyl group must assume the less favourable boat cyclohexane conformation in order to achieve the coplanar B—C—C—H arrangement, hence explaining the unusually slow reaction. The planar structure allows maximum overlap of orbitals in the developing π-system of the eliminated alkene.

Both Midlands' and Mikhailovs' research groups have previously reported on the formation of a yellow colour upon adding aldehydes to organoboranes.[62,63] In 1979 it was found that this was due to an aldehyde-organoborane complex.[66] This was proved by using B-methyl-9-BBN and p-(dimethylamino) benzaldehyde, where a bright red colouration was seen and a shift in the aldehyde proton using ^{1}H n.m.r was observed (from 9.70 to 9.45 ppm). Benzaldehyde also forms a complex, but to a lesser degree. The increased complexation using an electron donating species in the ring is consistent with a stabilisation of the positive charge on the carbonyl carbon in the complex.

In 1982 Midland et al reported on a kinetic study of the reduction of substituted benzaldehydes with B-alkyl--9-BBN compounds.[67] Second order rate constants were found for a series of para-substituted benzaldehydes (NO_2, Cl, CN, H, CH_3, CH_3O, and $(CH_3)_2N$) using B-n-octyl-9-BBN. The rate of reduction correlated with σ^+ giving a ρ of +1.03. The correlation with σ^+ is indicative of a resonance interaction of the para substituent with the carbonyl. The positive ρ value agrees with a hydride transfer to the carbonyl. The formation of the previously discovered complex is likely to be part of the overall reaction. In the complex only a rotation is needed to bring the hydride into the proper orientation for transfer. Internal rotation of the complex should occur at a much faster rate than a purely concerted six-centred process. The full reaction sequence is shown in Scheme 4.



Scheme 4

The hydride transfer, k_2, is the rate determining step since if the formation of the complex were not rate determining then electron donating substituents would increase the rate of reaction by stabilising the intermediate. Using the above mechanism the observed rate constant is equal to $(k_1/k_{-1})k_2$. Therefore the observed Hammett ρ for the reaction is a linear combination of ρ for the equilibrium constant k_1/k_{-1} and ρ for the hydride transfer. The positive value of ρ obs might indicate that the hydride transfer is dominant.

The high regioselectivity of the dealkylation and the selectivity of the initial hydroboration reaction indicates a possible use of this method as an alkene group protector.

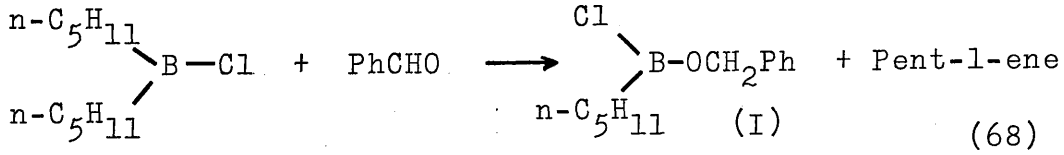
3.2 INVESTIGATION OF THE REACTION BETWEEN DIPENTYL CHLOROBORANE AND BENZALDEHYDE

3.2.1 Results and discussion of reaction products using equimolar reactants

The addition of benzaldehyde to a solution of dipentylchloroborane in dichloromethane at 0°C in an equimolar ration leads to the instantaneous formation of a lemon yellow colouration. This colour fades to pale yellow when the solution is brought to room temperature and left (to fully react) for 2 hours.

^{1}H n.m.r spectroscopy reveals the formation of pent--1-ene (70% yield by n.m.r, 82% by analysis of removed alkene). Infra-red spectroscopy shows the presence of monosubstituted benzene (700(s) and 740(s) cm^{-1}). The strongest band in the spectrum appears at 1350 cm^{-1} and is typical of the B—O stretching frequency.[68] No carbonyl absorption band is seen, but C—O stretching is seen as a strong band at 1100 cm^{-1}. A band at 915 cm^{-1}(w) can be assigned to B—Cl [68] and is absent when the sample is hydrolysed (by brief exposure to the atmosphere).

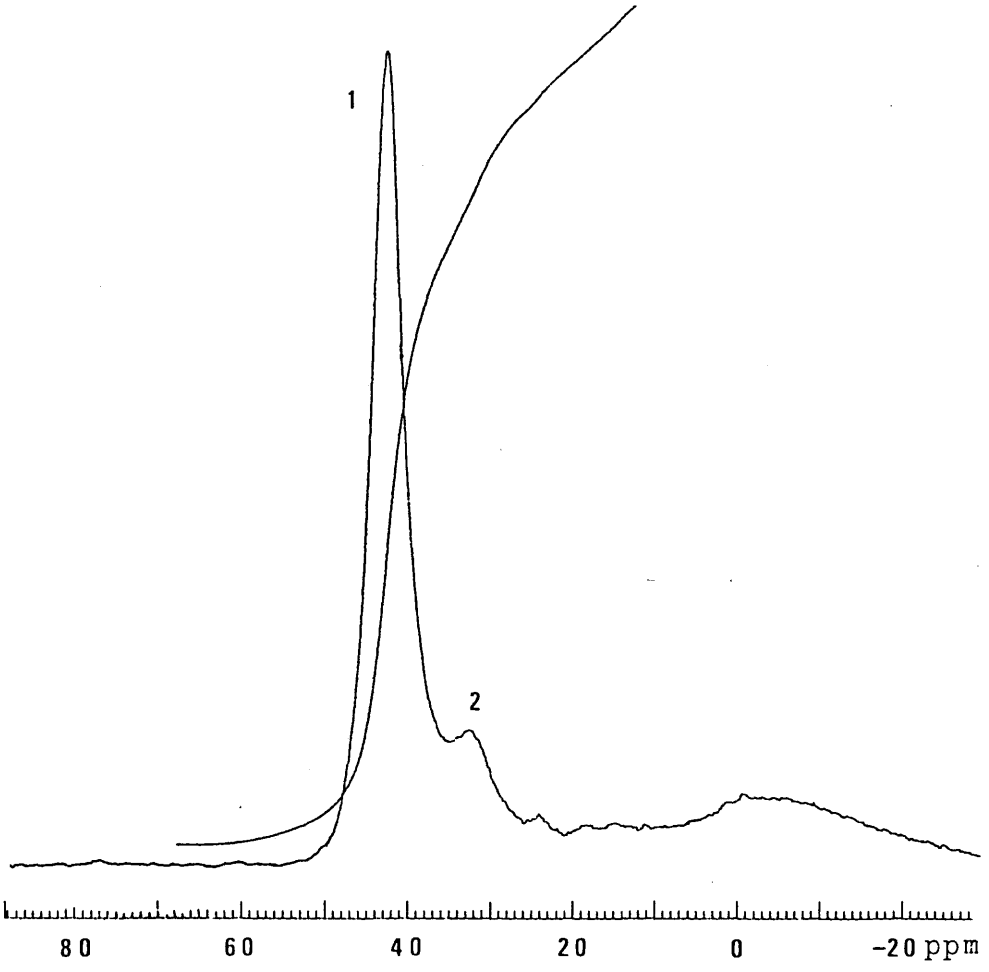
The most likely reaction is shown by equation 68.



(68)

The ^{11}B n.m.r spectrum (Figure 3.1) of the reaction products shows a major peak at +43 ppm (1) which is typical of

Figure 3.1 80 MHz ^{11}B n.m.r spectrum of I



chloroborinates (eg. $CH_3OBClC_2H_5$, +42 ppm[58]). The smaller peak (ca.10% of the larger) occurs at +33 ppm (2) and is typical of a boronate (eg. $C_2H_5B(OCH_3)_2$, +32 ppm[58]). The broad peak between +10 and -20 ppm is due to boron in the glass sample tube and is only seen when a large number of scans is used. No dipentylchloroborane (+78 ppm) is present.

Hydrolysable chlorine content of the product(s) is 11.6%, total chlorine being 14.7%. The theoretical chlorine content based on a 80% pentene loss is 14.9%. Approximately one fifth of the total chlorine is not easily hydrolysable and is clearly not present as B—Cl .

The ^1H n.m.r spectrum (Figure 3.2) consists of three groups of peaks;

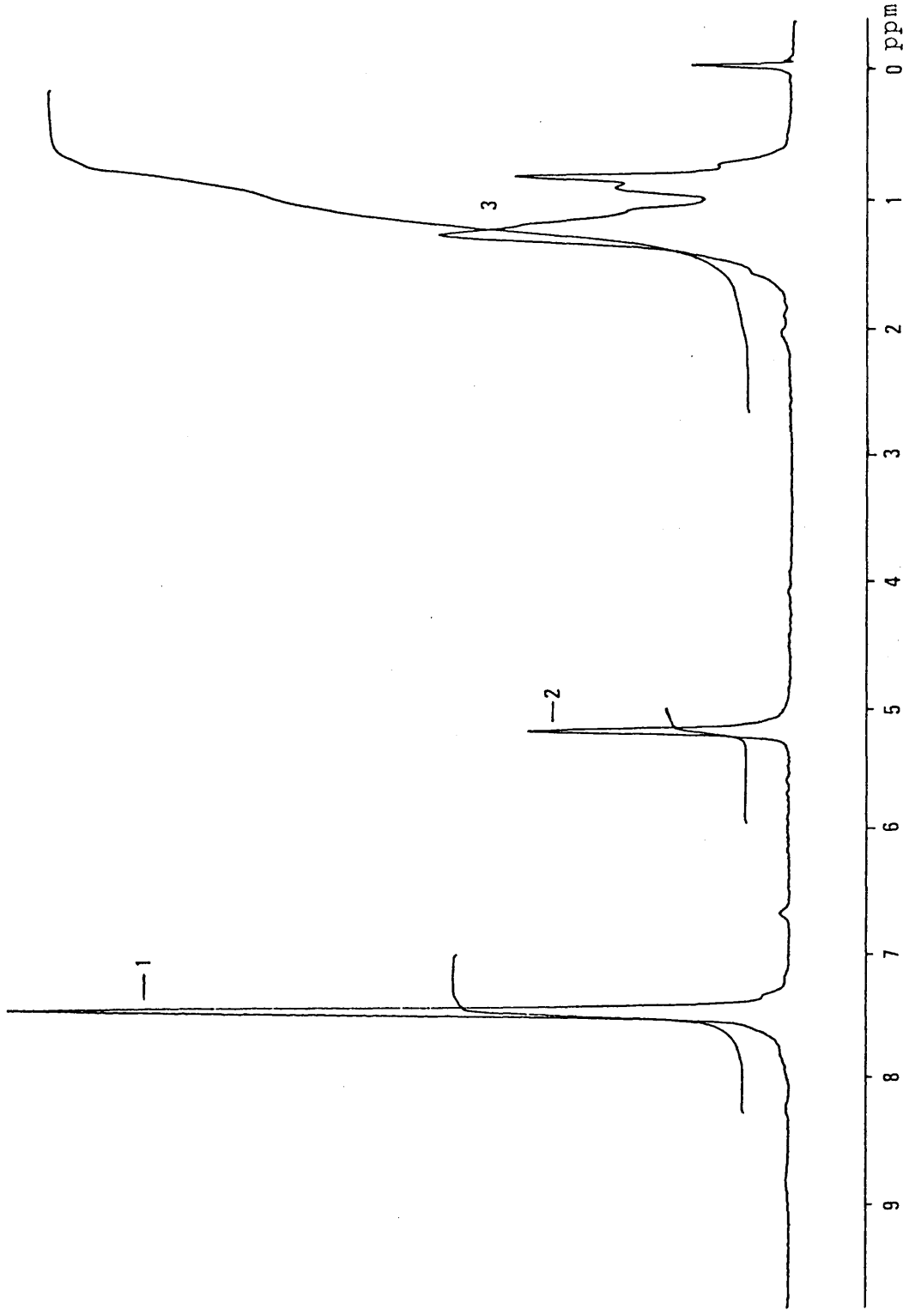
(1) 7.3 ppm, Phenyl protons (5H)

(2) 5.1 ppm, $PhCH_2O$ methylene (1.4H)

(3) 0.5-2.0 ppm, C_5H_{11} alkyl (12.1H)

The ratio of the integral values is not consistent with the proposed product(I) and is explained by the incomplete loss of pentene (an 85% loss of pentene gives an expected integral ratio of 5 : 1.7 : 12.7). Unidentified peaks occur at 6.75 and 2.1 ppm. The former peak can be more clearly seen in Figure 3.3 (1) which was carried out at a higher frequency (but contains the pentene product). The ratio between the peak at 6.75 ppm and the $PhCH_2O$ methylene (2) is 1 : 7 . The peak is assigned to the methine proton in PhCH(Cl)OB . Shoolerys rules give a value for the chemical shift of ca. 6.9 ppm.

Figure 3.2 60 MHz ^{1}H n.m.r spectrum of I



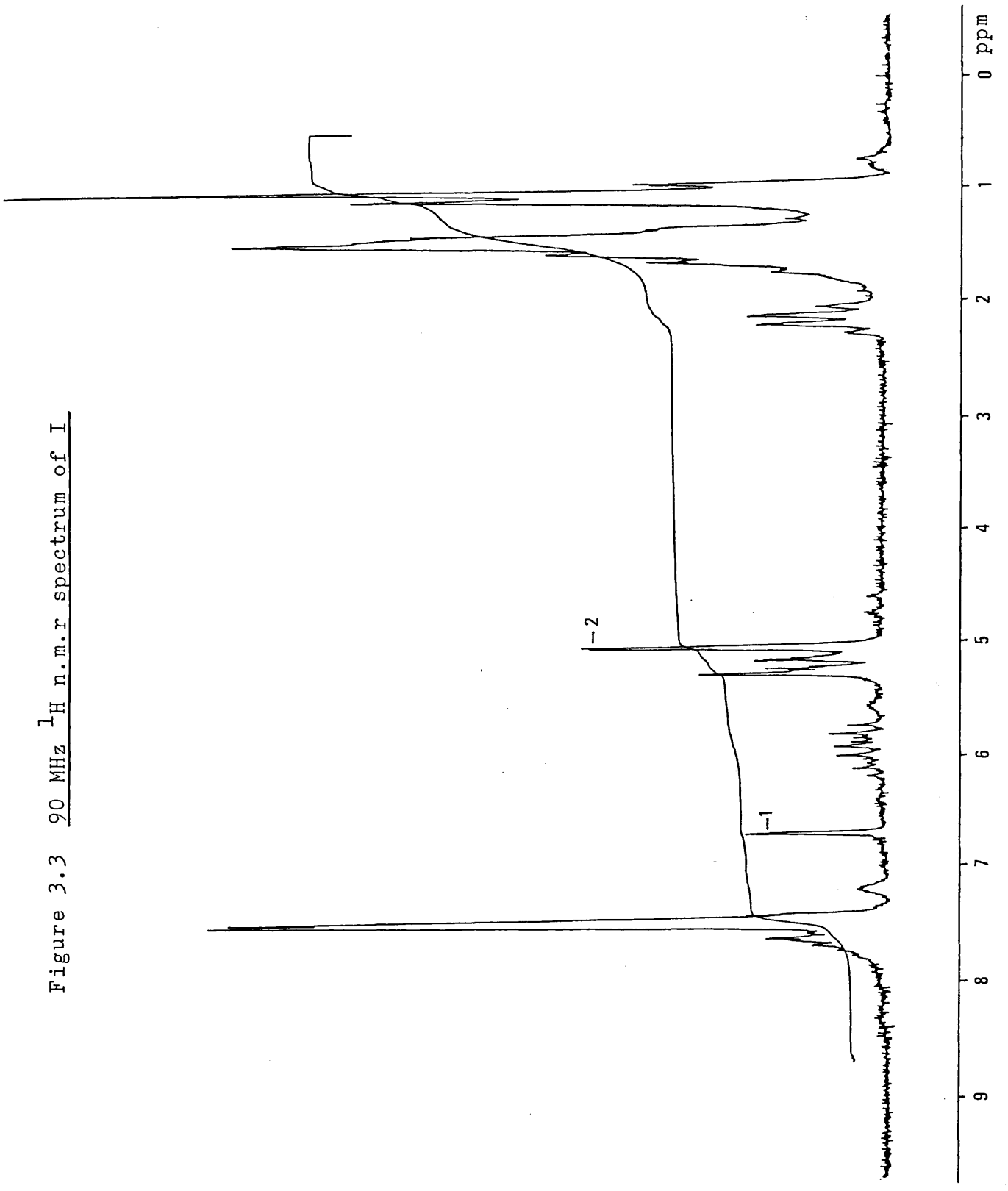


Figure 3.3 90 MHz ^{1}H n.m.r spectrum of I

The decoupled ^{13}C n.m.r spectrum (Figure 3.4) consists of three main regions;

(1) 128, 138 ppm, Phenyl group.

(2) 69 ppm, $PhCH_2O$ methylene carbon.

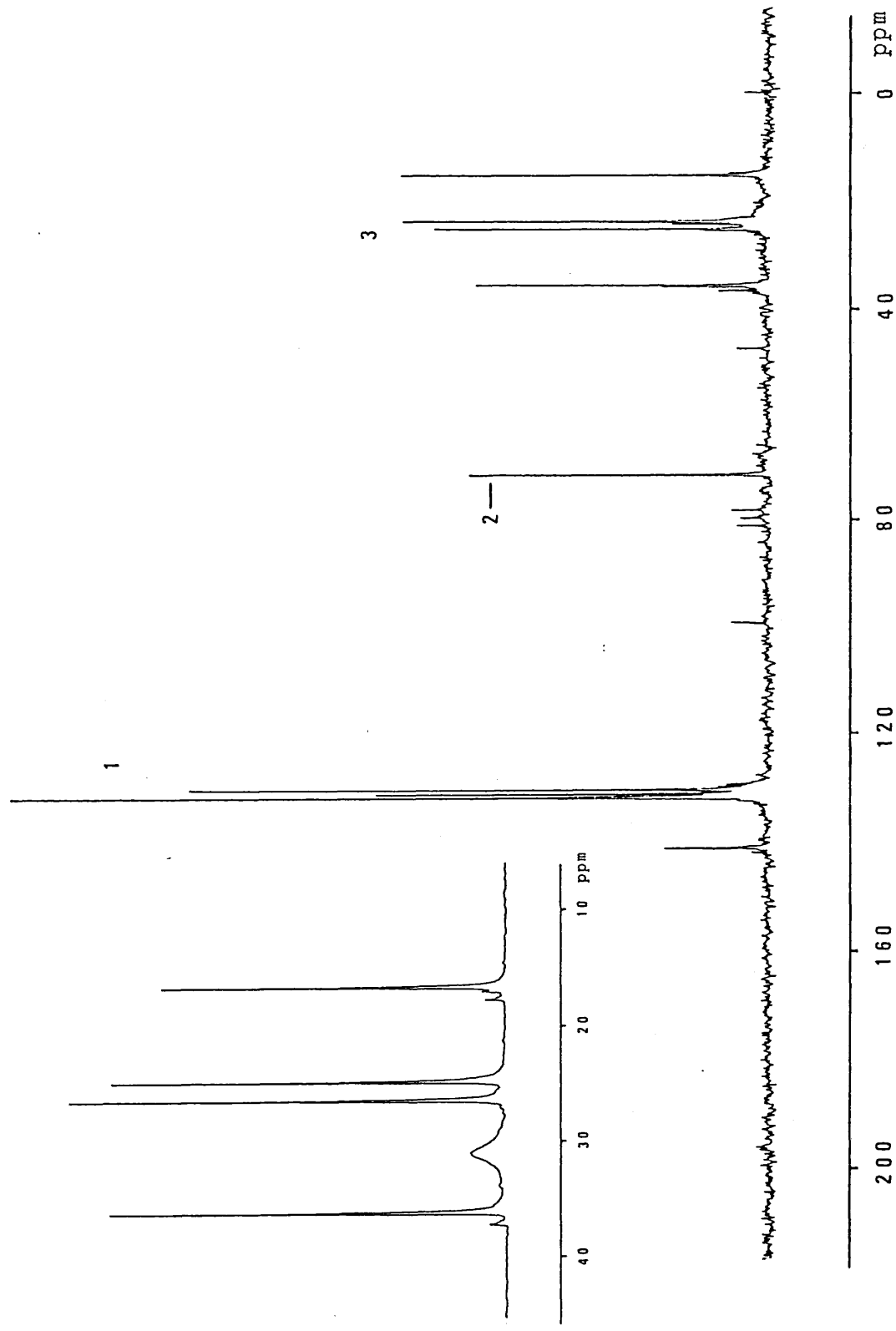
(3) 34, 24, 33, 14 ppm, n-pentyl group (compared with $(n\text{-}C_5H_{11})_2BCl$ inset). The C-1 carbon is absent from the spectrum, the boron atom broadening the signal.

The peak at 96 ppm is assigned to the methine carbon in PhCH(Cl)OB .

The fully coupled ^{13}C n.m.r spectrum is shown in Figure 3.5 (this is actually the spectrum for the reaction using excess aldehyde which gives a similar spectrum, but being a more concentrated sample produces a spectrum more suitable for display). The peak at 69 ppm (2) is split into a triplet ($J\ ^{13}C\text{-}^{1}H$ = 145 Hz) confirming its assignment as a methylene group. The peak at 96 ppm (1) is split into a doublet ($J\ ^{13}C\text{-}^{1}H$ = 176 Hz) and confirms the assignment of a methine group.

Attempted purification of the products by low pressure (0.05 mm Hg) distillation resulted in an almost continuous distillation between 70-130°C with no clear fractions. The distillation products appeared to contain a mixture of boronates (^{11}B) and hydrolysable chlorine containing volatiles were found in the cold trap leading to the vacuum pump. No evidence of the proposed major product was found, the mixture obviously undergoing pyrolysis/disproportionation.

Figure 3.4 22.5 MHz ^{13}C n.m.r spectrum of I (dipentylchloroborane inset)



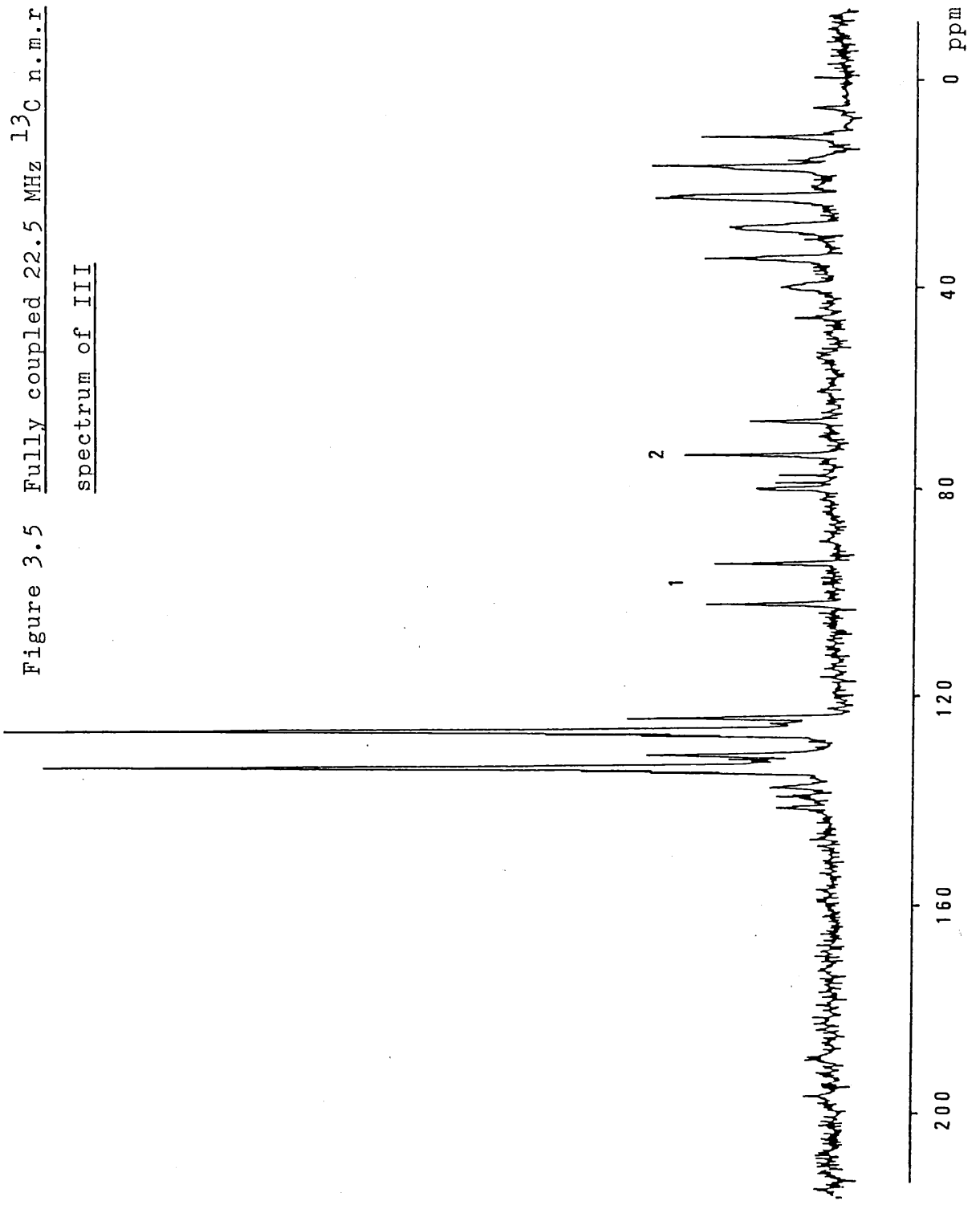
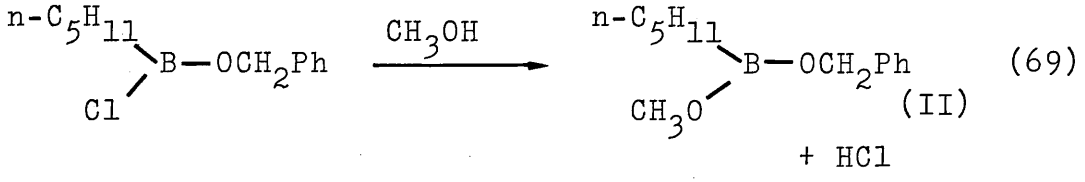


Figure 3.5 Fully coupled 22.5 MHz ^{13}C n.m.r spectrum of III

Since purification of the products appeared futile, a stable derivative was prepared by reacting the products with methanol (equation 69), boronates being more thermally stable than chloroborinates.[69]



(69)

The crude mixture was distilled (B.Pt 98-100°C, 0.03mm Hg) giving a 64% yield of boronate (based on the original dipentylchloroborane). The ^{1}H n.m.r spectrum (Figure 3.6) consists of four groups;

(1) 7.3 ppm, Phenyl protons (5H)

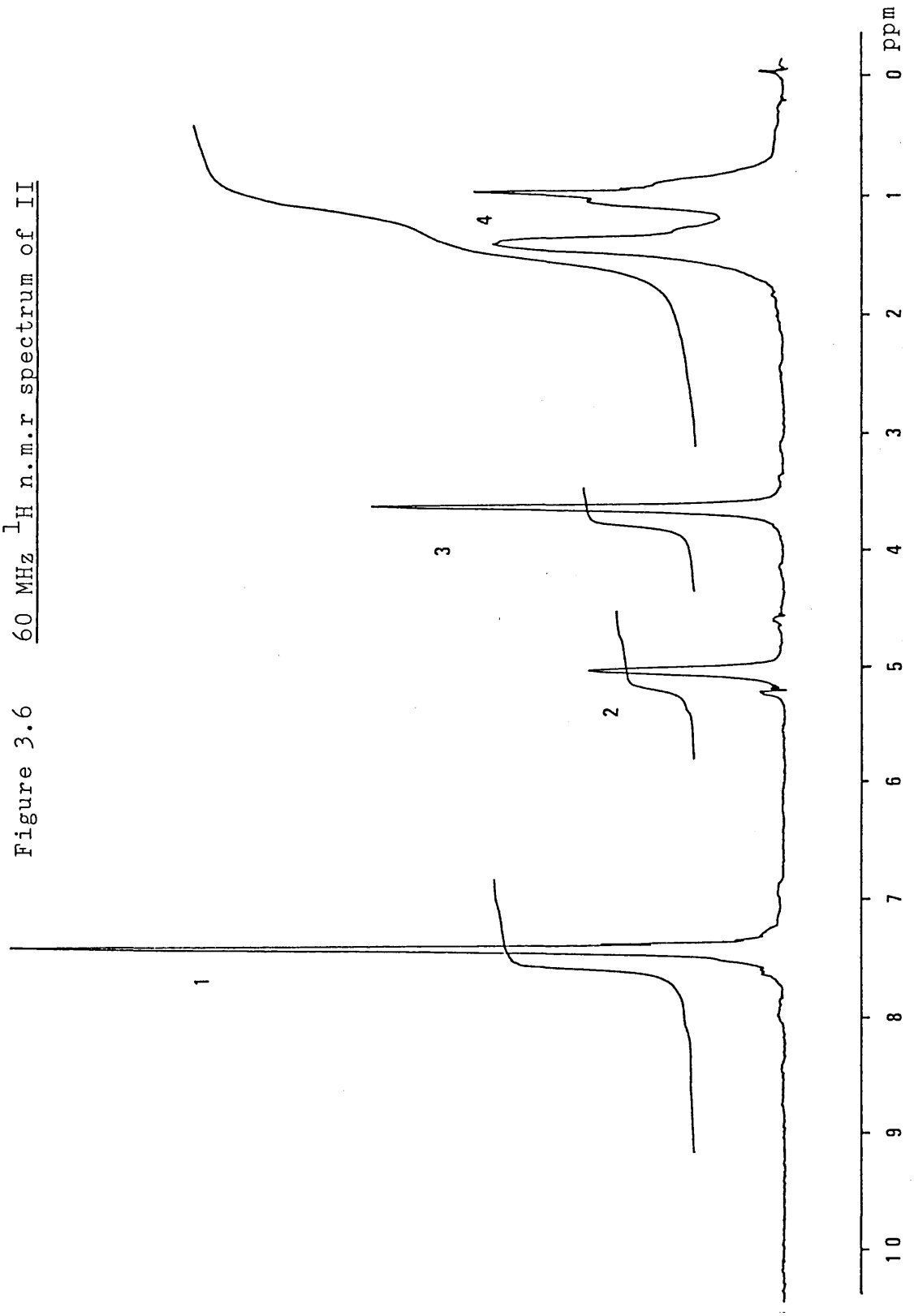
(2) 5.0 ppm, $PhCH_2O$ methylene protons (2H)

(3) 3.6 ppm, CH_3O methyl protons (3H)

(4) 0.5-2.0 ppm, n-C_5H_{11} alkyl protons (11)

the results being consistent with the proposed boronate. The ^{11}B n.m.r spectrum consists of mainly one peak at +32 ppm which corresponds to that expected for a boronate.[58] A minor peak (ca. 5%) at +54 ppm has a shift indicative of a borinate.[58] Elemental analysis and total chlorine analysis confirms the identity of the boronate, C 70.9%(calc.71.0), H 9.8%(calc.9.6), B 4.8%(calc.4.9), Cl ca.0.1%. The results confirm the identity of the boronate and imply that the initial product (I) is as speculated.

Figure 3.6 60 MHz ^{1}H n.m.r spectrum of II



3.2.2 Results and discussion of reaction products using dipentylchloroborane and excess benzaldehyde

The reaction between dipentylchloroborane and benzaldehyde was carried out using a 1:2 molar ratio respectively, under the same conditions as the equimolar reaction. The reaction produces a similar yield of pent-1-ene (83% by analysis of removed alkene, based on the original borane). The infra-red spectrum is similar to that for the equimolar reaction, but the ^{11}B n.m.r spectrum (Figure 3.7) consists of a peak at +33 ppm (1) which was the minor peak in the equimolar reaction.

Chlorine analysis of the reaction mixture gives a value close to that expected for an 80% loss of pentene (Cl total = 10.4%, predicted for 80% pentene loss = 10.3%). Readily hydrolysable chlorine makes up the majority of this chlorine (9.7%) and could come from B—Cl or readily hydrolysable C—Cl .

The ^{1}H n.m.r spectrum (Figure 3.8) consists of four main regions;

(1) 7.3 ppm, Phenyl protons (10H)

(2) 6.7 ppm, ClCHOB methine proton (1H)

(3) 5.0 ppm, $PhCH_2O$ methylene proton (2H)

(4) 0.5-2.0 ppm, n-pentyl protons (11H)

The spectrum also contains unknown peaks at 5.2, 5.3, and 4.6 ppm which amount to ca. 15% of the methylene peak.

The decoupled ^{13}C n.m.r spectrum (Figure 3.9) is very similar to the equimolar reaction but the methine peak (1) at 96 ppm is much stronger being similar in height to

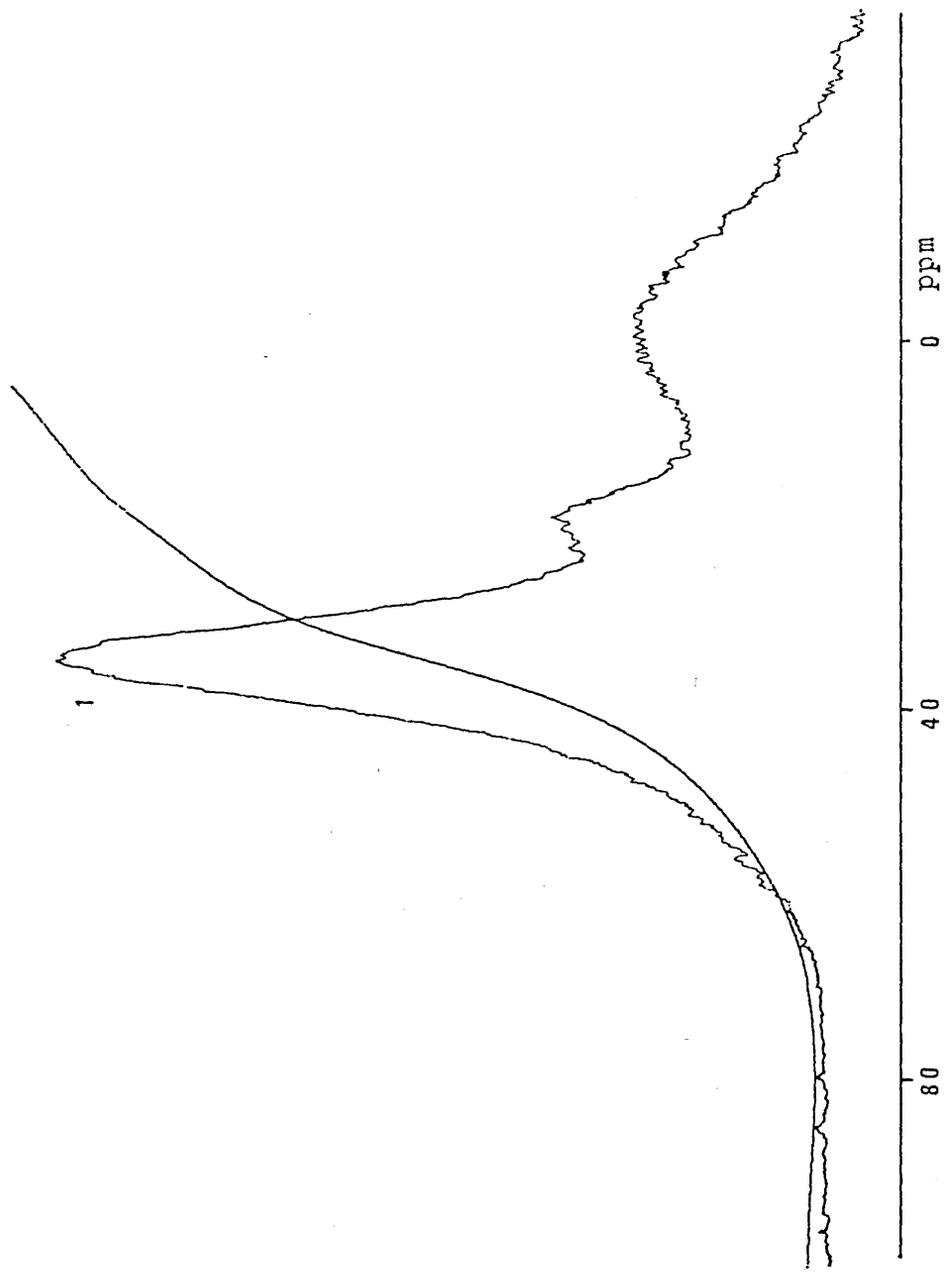


Figure 3.7 80 MHz ^{11}B n.m.r spectrum of III

Figure 3.8 60 MHz ^{1}H n.m.r spectrum of III

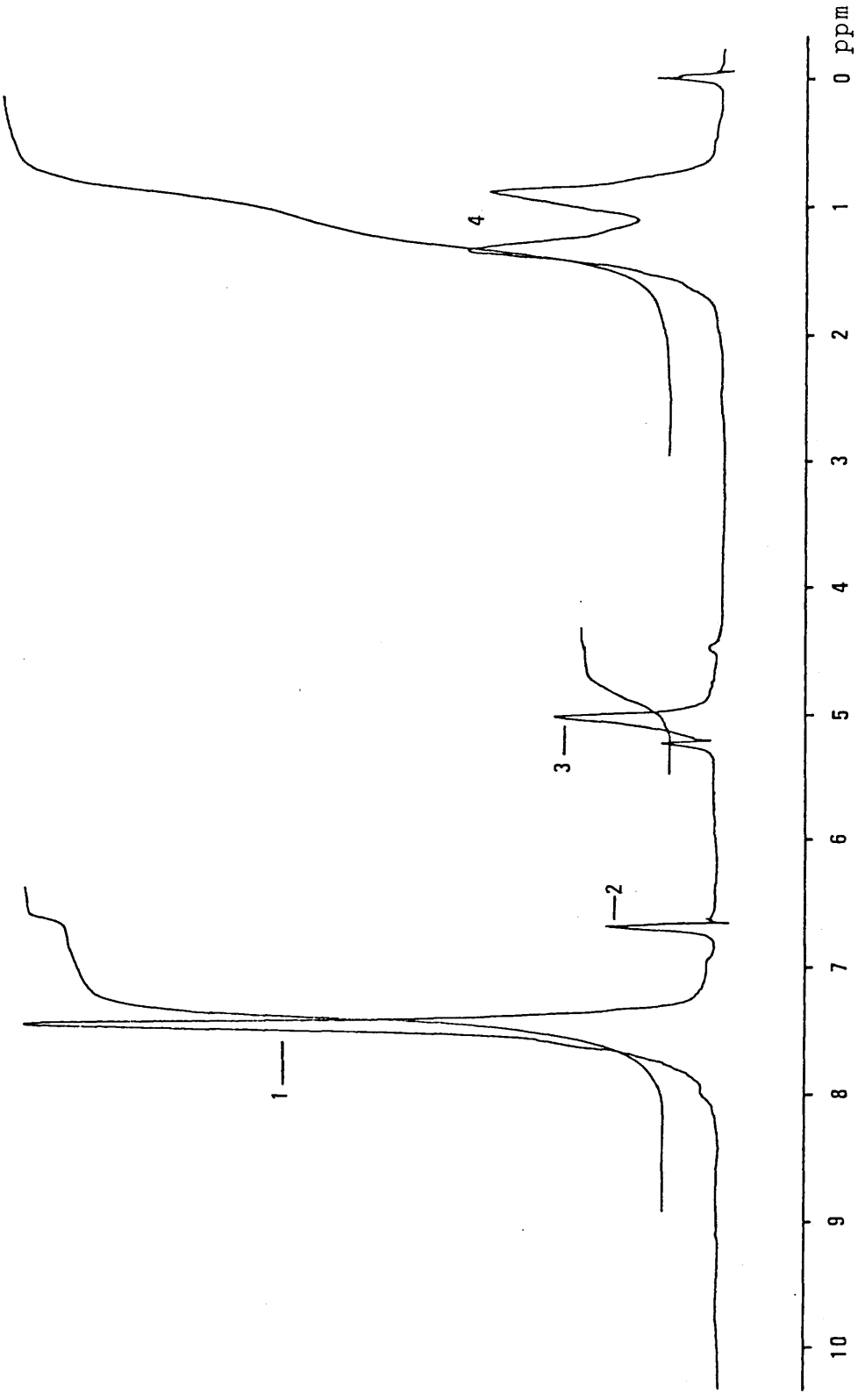
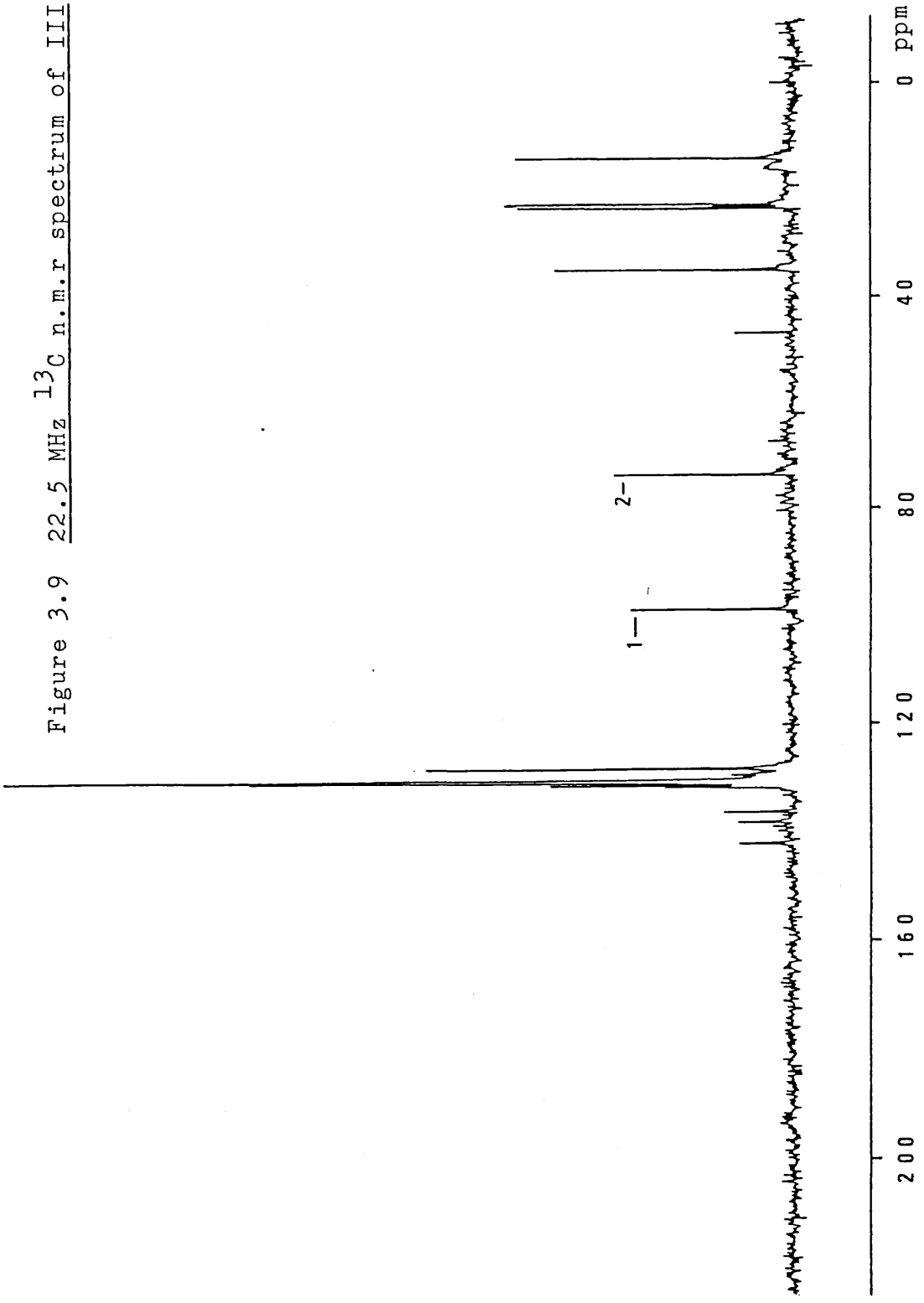
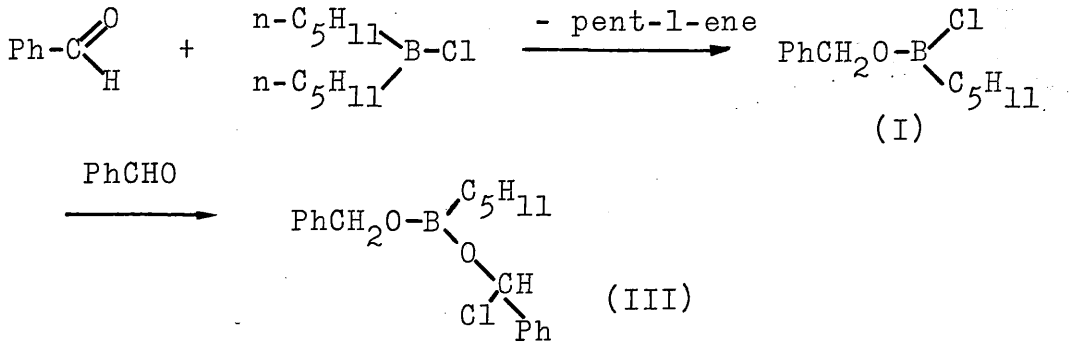


Figure 3.9 22.5 MHz ^{13}C n.m.r spectrum of III



the $PhCH_2O$ methylene signal (2). The above information suggests the overall reaction shown in Scheme 5, both



Scheme 5

reactions being accompanied by unidentified products. The structure of product (I) is consistent with all the spectroscopic evidence and the stable methoxy derivative of this was prepared and analysed by spectroscopic and classical techniques. Neither (I) or (III) could be isolated pure, both giving pyrolysis products on attempted distillation.

Product (III) is a boronate and should have a ^{11}B n.m.r chemical shift of about +33 ppm in agreement with that found. ^{1}H n.m.r gives good integral values for the proposed compound and ^{13}C n.m.r confirms the presence of (III) in the initial, equimolar reaction. The chlorine present in (III) is likely to be readily hydrolysable (eg. in 1-chloroalkylborates[59]) and would explain the chlorine analysis results. Further evidence of the PhCH(Cl)OB methine group present in (III) comes from the reaction between boron trichloride and benzaldehyde. This reaction has been found to give a mixture of dichloroborinate and chloroboronate (equation 70)[59].

$$3PhCHO + 2BCl_3 \longrightarrow PhCHClOBCl_2 + (PhCHClO)_2BCl \quad (70)$$

Both these products contain the same methine group proposed for (III). This reaction was repeated and the products analysed by ^{1}H n.m.r (Figure 3.10) and ^{13}C n.m.r (Figure 3.11). The methine group (1) has the same chemical shift as that found in (III) for both spectra, indicating that the structure of (III) is as proposed.

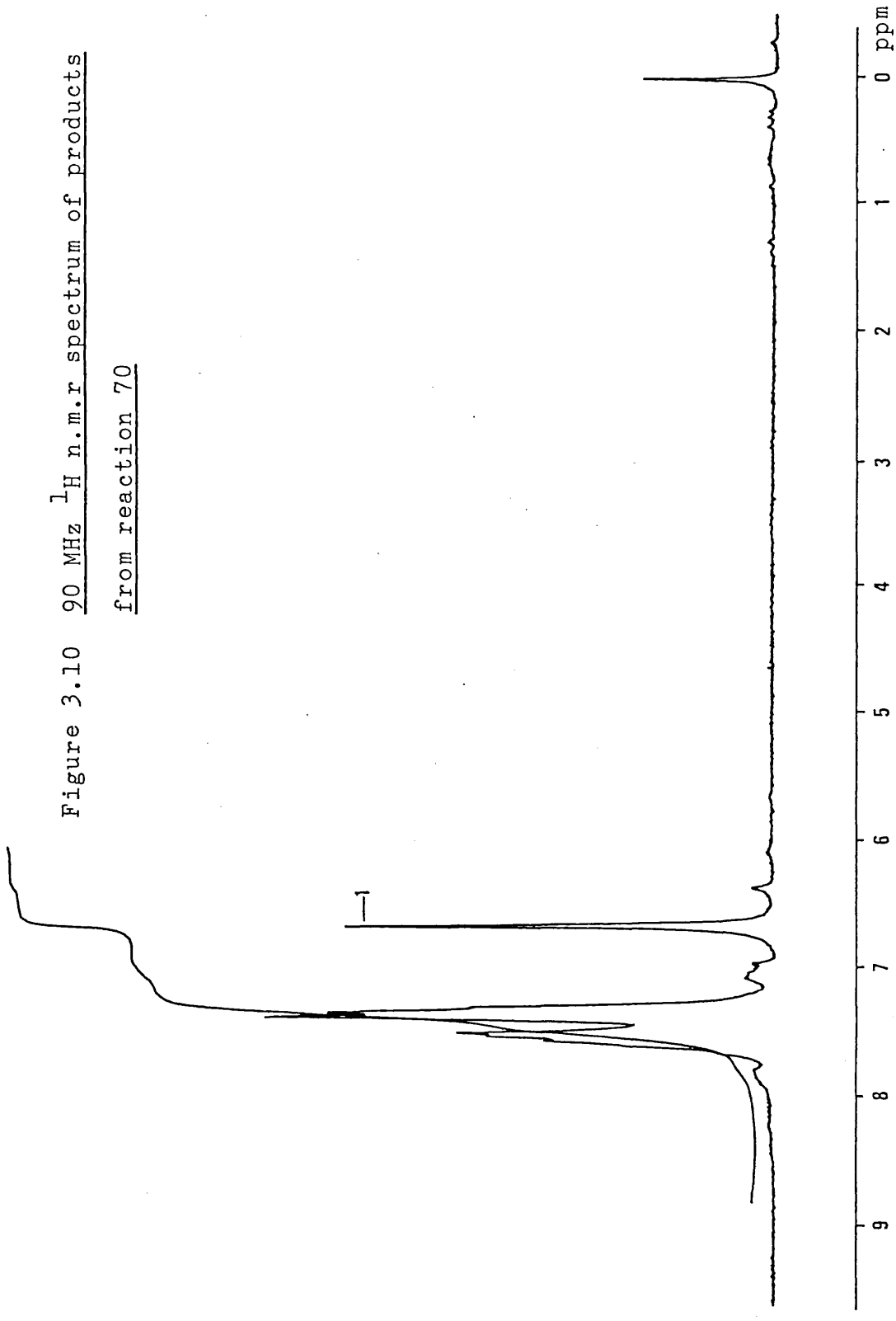
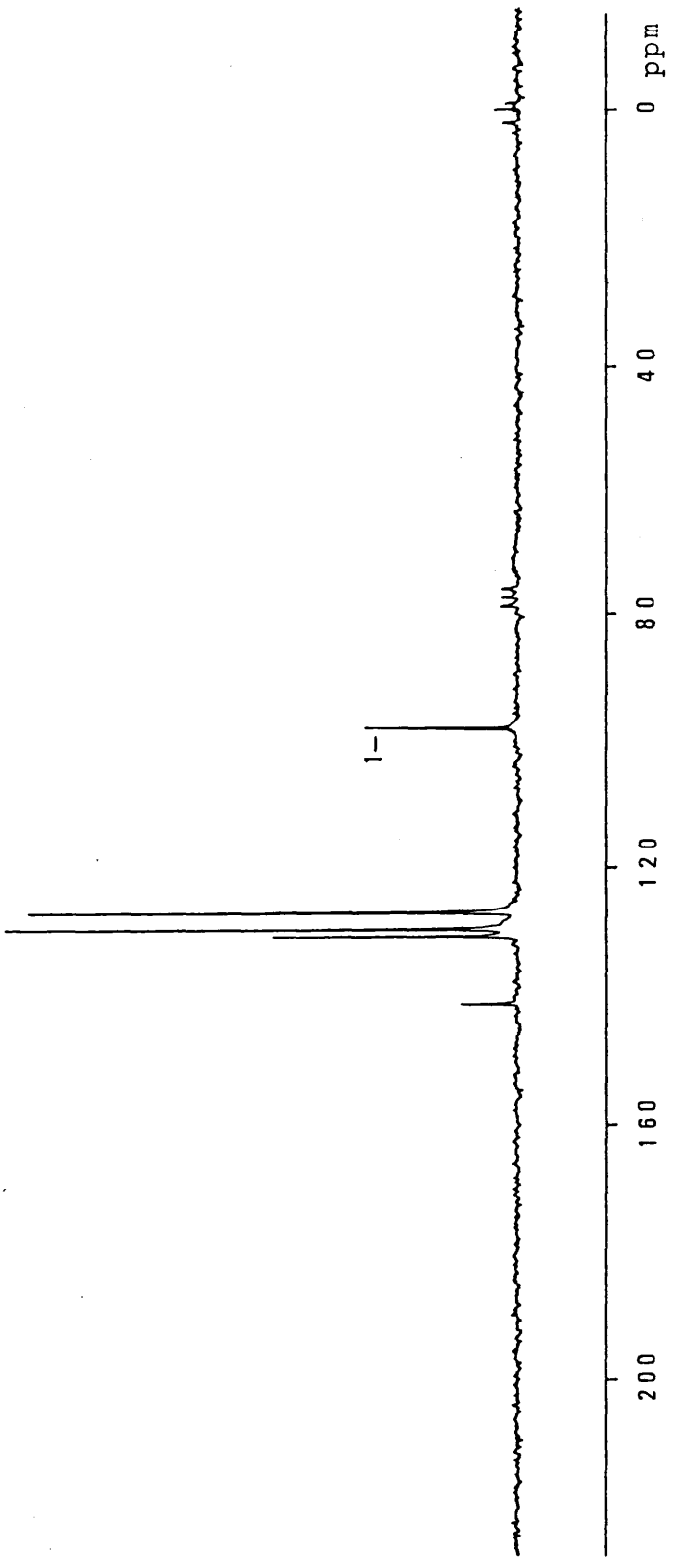


Figure 3.10 90 MHz ^{1}H n.m.r spectrum of products from reaction 70

Figure 3.11 22.5 MHz ^{13}C n.m.r spectrum of products from reaction 70



3.3 INVESTIGATION OF KINETICS OF THE REACTION BETWEEN DIALKYLCHLOROBORANES AND SUBSTITUTED BENZALDEHYDES

The reactions between dialkylchloroboranes and substituted benzaldehydes were followed by observing the growth of alkene during the course of the reaction by ^1H n.m.r spectroscopy. The reaction involving dipentylchloroborane was followed using equimolar concentrations of reactants and excess dipentylchloroborane. Excess benzaldehyde was not used, as this would result in the increased formation of the secondary product, leading to a false rate constant. Full details of the data treatment are given in Appendix III. The second order rate constants for these reactions are shown in Table 3.1 along with those for the substituted benzaldehydes and other dialkylchloroboranes. The good plots obtained from all the experiments and the similarity of rate constants derived from different reactant concentrations implies that the dialkylchloroboranes and substituted benzaldehydes react together to form alkene by second order kinetics (first order in each reactant),

$$d\,(\text{Alkene}) / dt = k_2\,(\text{ArCHO})(R_2BCl)$$

The half lives obtained for the consumption of benzaldehyde are also consistent with the reaction being first order with respect to benzaldehyde (full details in Appendix III).

Electron withdrawing groups on the benzaldehyde increase the rate of reaction, the rate constant increasing

Table 3.1 Second order rate constants for the formation of alkenes

Aldehyde	Aldehyde /mol dm^{-3}	R_2BCl R=	R_2BCl /mol dm^{-3}	T/°C	k_2 x10^4 /$dm^3 mol^{-1} s^{-1}$
PhCHO	1.93	n-C_5H_{11}	1.93	9	3.3
PhCHO	1.95	n-C_5H_{11}	1.95	9	3.2
PhCHO	0.99	n-C_5H_{11}	1.85	9	3.1
PhCHO	0.76	n-C_5H_{11}	2.19	9	3.1
PhCHO	0.64	n-C_5H_{11}	1.93	9	3.3
PhCHO	1.96	n-C_5H_{11}	1.96	9	5.0[a]
PhCHO	1.95	n-C_5H_{11}	1.95	7	0.87
PhCHO	1.35	n-C_5H_{11}	1.35	16	6.2
PhCHO	1.74	$CH_3CH_2CH_2$- $CH(CH_3)CH_2$-	1.74	9	300
PhCHO	1.67	n-C_8H_{17}	1.67	9	6.6
p-NO_2-PhCHO	0.78	n-C_5H_{11}	0.78	9	120
p-Cl-PhCHO	1.45	n-C_5H_{11}	1.45	9	15
p-MeO-PhCHO	1.85	n-C_5H_{11}	1.85	9	0.1

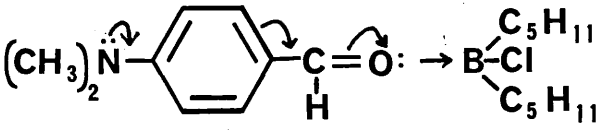
a - Solvent deuterated dichloromethane, others deuterated chloroform.

as the p-substituent in benzaldehyde changes in the order OCH_3, H, Cl, NO_2.

3.4 INVESTIGATION OF THE MECHANISM FOR THE REACTION BETWEEN DIALKYLCHLOROBORANES AND SUBSTITUTED BENZALDEHYDES

The addition of substituted benzaldehydes to solutions of dialkylchloroboranes at or below 0°C leads to the instantaneous formation of bright colours. With p-$N(CH_3)_2$ the colour is green, p-CH_3O green, p-H yellow, p-Cl yellow and p-NO_2 orange.

The aldehyde proton for benzaldehyde shifts upfield in the ^1H n.m.r spectrum from 9.9 to 9.0 ppm which implies a partial loss of carbonyl character. Similarly p-$N(CH_3)_2$ benzaldehyde has an aldehyde proton shift of 0.5 ppm upfield. Similar evidence of complex formation has been reported by previous workers [66] (see section 3.1). B-Methyl-9-BBN forms a yellow/orange solution with benzaldehyde accompanied by an aldehyde proton shift of 0.07 ppm upfield. The greater shifts observed with dialkylchloroboranes are presumeably due to their greater Lewis acidity. The p-$N(CH_3)_2$ group stabilises the complex enough for it to be isolated as the bright green solid (IV) .



(IV)

The possibility of IV being the amine-borane adduct is discounted due to the absence of the carbonyl band in the infra-red. Elemental analysis confirms the identity of the complex; C 67.4%(calc. 67.6), H 10.0%(calc.9.8), N 4.0% (calc.4.2), B 3.4%(calc 3.2). Chlorine analysis gives a

total of 10.4%, hydrolysable chlorine making up 10.3%. The ^{11}B n.m.r spectrum shows a very broad peak ($\Delta_{\frac{1}{2}}$ ca. 70 ppm) centred on +16 ppm which would indicate a greater electron density on the boron atom compared with dipentylchloroborane.

The ^{1}H n.m.r spectrum (Figure 3.12) consists of four main groups;

(1) 9.2 ppm, aldehyde proton (1H).

(2) 6.8, 7.8 ppm, phenyl protons (4H)

(3) 3.3 ppm, $(CH_3)_2N$ methyl protons (6H)

(4) 0.9, 1.3 ppm, pentyl protons (22H)

The spectrum is in accordance with the proposed complex, and no product peaks deriving from elimination or addition reactions can be seen. The complex is stable for some months at 4°C, but pent-1-ene production is observed when a solution of the complex is heated at 60°C for several minutes. When the solid is heated it starts to decompose when the temperature reaches 70°C, the solid having no clear melting point. Further evidence of complex formation is found when the product is hydrolysed, whereupon the original aldehyde is formed.

Evidence of complex formation between benzaldehyde and dipentylchloroborane was obtained from a variable temperature study using ^{1}H and ^{11}B n.m.r spectroscopy. When equimolar amounts of reagents were mixed and held below 0°C, an immediate and stable yellow colour was produced. After 15 minutes at 0°C, no free dipentylchloroborane (^{11}B n.m.r, +78 ppm) could be seen, but a very broad band ($\Delta_{\frac{1}{2}}$ ca. 70 ppm, compared with 4 ppm for dipentylchloroborane at 24°C)

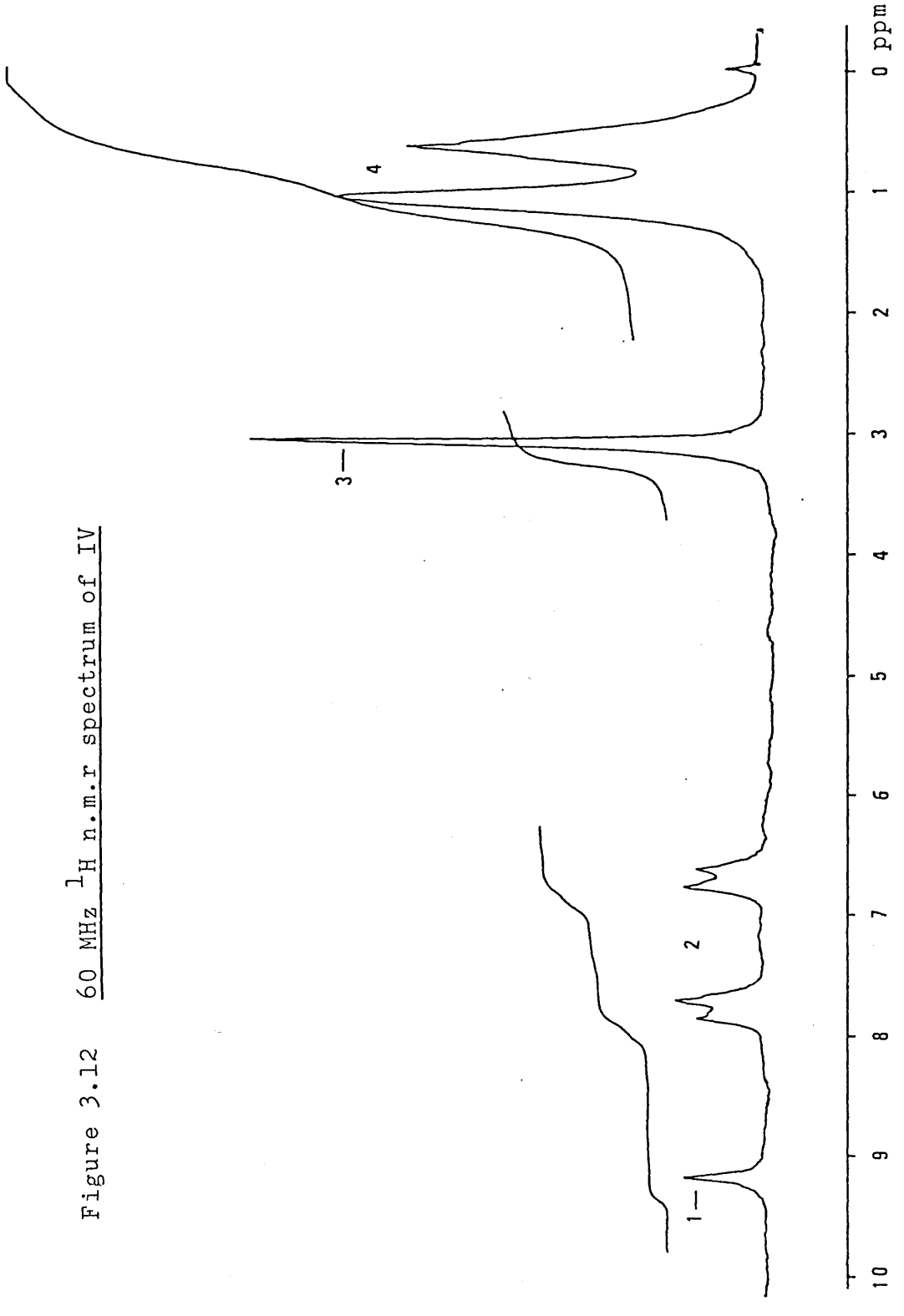


Figure 3.12 60 MHz ^{1}H n.m.r spectrum of IV

appeared, centred at 43 ppm. At this temperature no pentene or any other product peaks were seen in the ^{1}H n.m.r spectrum, but the aldehyde proton was shifted 0.9 ppm upfield. As the temperature was increased (10°C), the broad ^{11}B n.m.r band at 42 ppm sharpened and at higher temperatures (17-30°C) a second peak arose, moved progressively to +76 ppm and diminished as a new peak at +33 ppm formed. Pentene production was observed when the temperature of the solution rose above 0°C. A similar experiment using an excess of benzaldehyde was carried out causing the sharp product peak at +42 ppm to be replaced by one at +33 ppm which was the minor peak in the equimolar reaction. The peaks (+42 and +33 ppm) correspond to the products discussed earlier (I and III). The peak which shifted in position from the proposed complex peak (+43 ppm) to that for dipentylchloroborane (+78 ppm) could be evidence of the break up of the complex.

Methanolysis of an equimolar reaction solution kept at 0°C for 40 minutes resulted in the formation of free aldehyde (70% by ^{1}H n.m.r of the aldehyde proton) and two boron species. The ^{11}B n.m.r spectrum contained peaks at 54 ppm (80%) and 33 ppm (20%). The former shift is typical for a borinate and distillation of the products gave two different fractions. The smaller fraction (10% based on dipentylchloroborane) was analysed and is identical to the sample obtained for the methanolysis of the fully reacted dipentylchloroborane/benzaldehyde reaction (II). The larger fraction (B.Pt 48°C, 0.10 mm Hg, 60% yield) had a ^{11}B n.m.r shift of 54 ppm and a ^{1}H n.m.r spectrum (Figure 3.13) containing just methoxy (1) and alkyl (2)

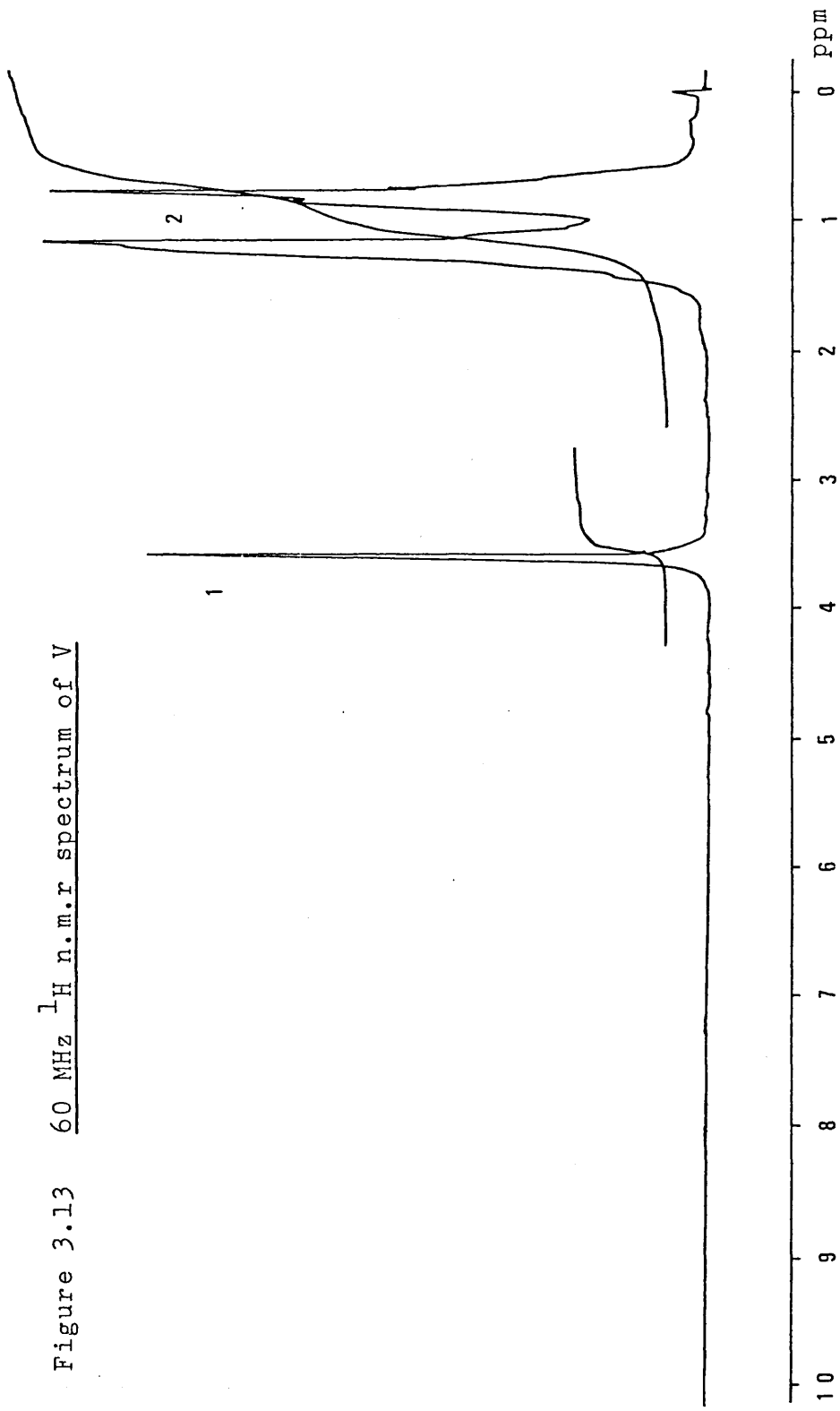
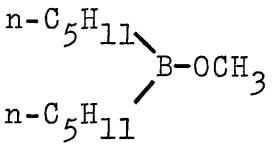


Figure 3.13 60 MHz ^{1}H n.m.r spectrum of V

protons (in the ratio 3:22). The product was assigned as the simple methanolysis product of dipentylchloroborane (V).



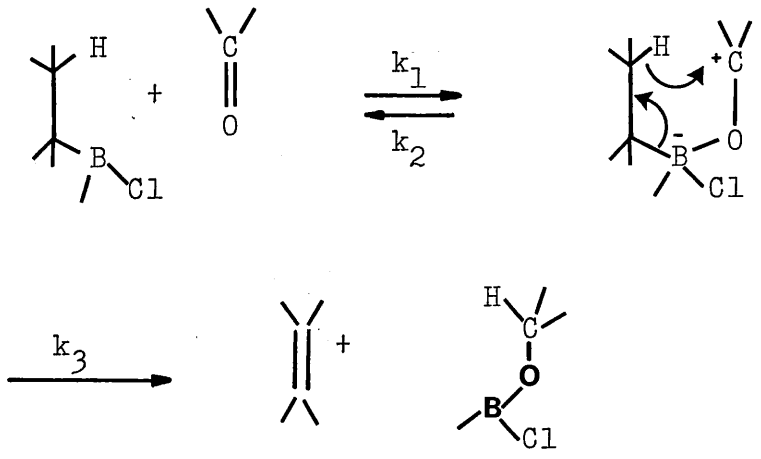
(V)

Elemental analysis gave C 71.6%(calc. 71.8) and H 13.2% (calc. 13.6) which confirms the proposed borinate. Therefore, the peak which occurs at 0°C (yellow product) giving a ^{11}B n.m.r shift of 43 ppm is either the complex formed between the aldehyde and borane, or the average signal arising from a fast interchange between free and complexed dipentylchloroborane. The latter possibility was explored further by observing the ^{11}B n.m.r spectrum below 0°C. At -32°C, where the yellow colour is clearly seen, two broad peaks at 75 and 10 ppm are seen when the reactants are equimolar. The poor quality of the spectra at this temperature makes integration difficult but the peak at 75 ppm, which is likely to be free dipentylchloroborane, is about three times the size of the peak at 10 ppm which could be due to the complex. When excess benzaldehyde is used the peak at 10 ppm increased at the expense of the free dipentylchloroborane to the extent that the proposed complex peak is approximately twice the size of the free dipentylchloroborane. When both systems are warmed to -8°C, the peaks converge giving a broad flat-topped peak centred at 42 ppm. Further warming to 0°C shows only a single broad peak centred at 42 ppm. The proposed complex peak at 10 ppm is similar to that for the dimethylamino product (IV) (16 ppm)

and the amount of complex appears to be dependant on the benzaldehyde concentration. Thus the signal seen at 0°C is likely to be the average signal between rapidly exchanging free and complexed dipentylchloroborane.

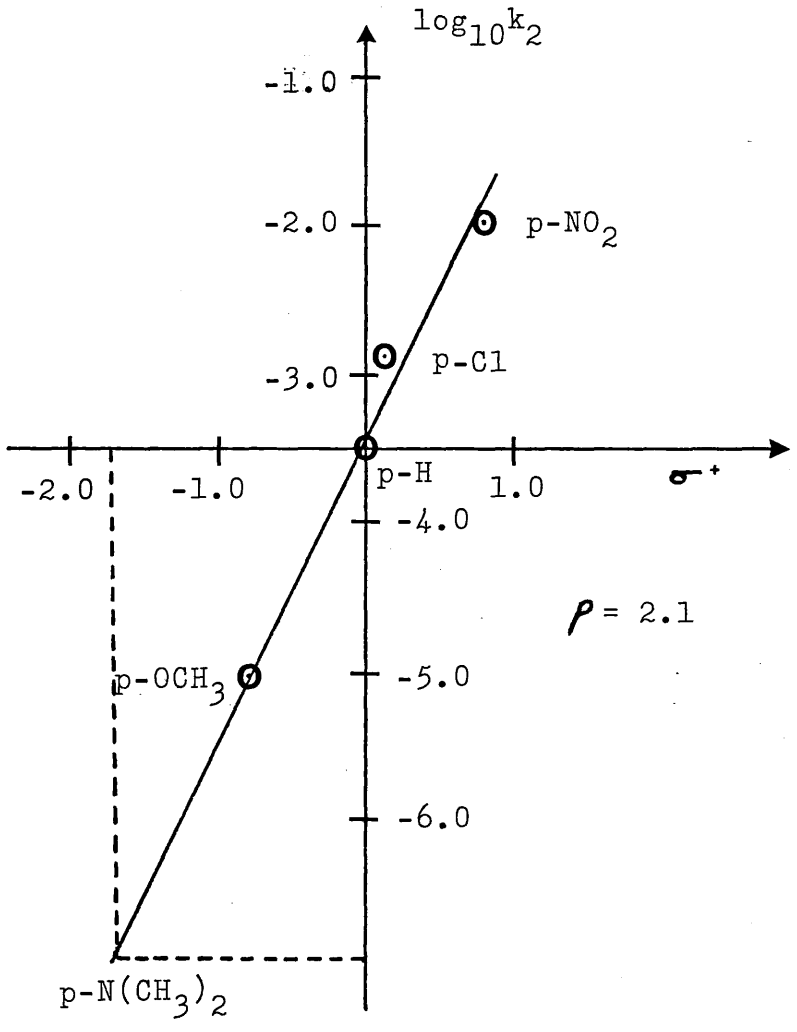
The rate of reduction of the para substituted benzaldehydes correlates with σ^+ (Figure 3.14). This is indicative of a resonance interaction of the para substituent with the carbonyl. The positive slope (ρ = +2.1) is consistent with a hydride transfer to the carbonyl (as in the reaction between benzaldehydes and trialkylboranes, discussed in section 3.1). Resonance interactions are destroyed upon going to the transition state. The Hammett plot predicts a rate constant of about 1 x $10^{-7}dm^3mol^{-1}s^{-1}$ using para-dimethylamino benzaldehyde which is 3 x 10^3 times slower than using benzaldehyde, explaining its apparent stability.

The most obvious reaction mechanism is similar to that proposed between B-Alkyl-9-BBN's and benzaldehyde,[63] where an analogy with the Meerwein-Ponndorf-Verley reaction was drawn (Scheme 6).



Scheme 6

Figure 3.14 Hammett plot for the reduction of substituted benzaldehydes with dipentylchloroborane at 9°C



The variable temperature experiments suggest that the complex is present in significant amounts and is in equilibrium with free dipentylchloroborane. The amount of complex also appears to depend on the concentration of aldehyde, supporting the proposed equilibrium. The complex is presumeably part of the overall reaction mechanism because only a rotation is needed to bring the hydride into the required orientation for transfer. If the reaction operated by a purely concerted six-centred process then it would have to be argued that the bimolecular reaction occurred at a faster rate than the internal rotation of the complex. The hydride transfer, k_3, is presumably the rate determining step because if the slow step were complex formation then electron donating groups would stabilise the complex therefore increasing the reaction rate. The hydride transfer is rapidly promoted when a methyl group is substituted in the β position. This could be due to the electronic effect associated with a hydride transfer from a tertiary carbon or the relief of additional steric strain in the complex. The n--octyl system increases the rate by a factor of two ; further evidence of steric factors is discussed in the next section (3.5.2).

The apparent second-order rate constant according to the proposed mechanism is $(k_1/k_2)k_3$ or $K_{complex}.k_3$. Therefore the observed ρ for the reaction is a combination of ρ for the equilibrium constant and ρ for the hydride transfer. The former should have a negative value (ρ for the protonation of substituted benzaldehydes is -1.85[70]), while the hydride transfer ρ should be positive (ρ for the sodium

borohydride reductions of substituted acetophenones is +3.06[71]). The observed positive value suggests that the hydride transfer is dominant. The ρ for the Meerwein-Ponndorf-Verley reduction of substituted acetophenones is 1.45 to 1.75[72] and the larger ρ value for the dipentylchloroborane / benzaldehyde reaction may indicate more hydride character in the transferring hydrogen.

3.5 INVESTIGATION OF REACTIONS BETWEEN DIALKYLCHLORO-BORANES AND ALIPHATIC ALDEHYDES / KETONES

3.5.1 Introduction

Trialkyl and dialkylchloroboranes have been used in the past as catalysts for the polymerisation of aliphatic ketones and aldehydes.[73,74,75] This makes a quantitative study of the reactions between aldehydes (especially the lower members) and dialkylchloroboranes difficult. The reactions described were carried out in a semi-quantitative manner (relying mainly on spectroscopic evidence) in order to investigate steric effects in the aldehyde/dialkylchloro-borane elimination reaction.

3.5.2 Results and discussion of products

Various aldehydes having different steric and electronic features were reacted with dipentylchloroborane at 0 °C, leaving the solutions at room temperature for 2 hours. Table 3.2 summarises the results, describing the yield of pentene (which for most reactions was estimated by the addition of a known quantity of chloroform into the ^{1}H n.m.r sample) and the relative ratios of boron species present in the samples. The boron species had chemical shifts common to all the reactions. Evidence of initial complex formation was seen by the formation of an instantaneous yellow colour with all the reactions.

Aldehyde polymerisation was pronounced in the reaction using ethanal (acetaldehyde), the infra red spectrum showing the trimer, paraldehyde (VI) to be present (640(w), 840(w), 860(w), 950(m), 1180(s), 3000(w) cm^{-1}). The spectrum

Table 3.2 Yields of pentene and borane species from the reaction between dipentylchloroborane and aldehydes/ketones

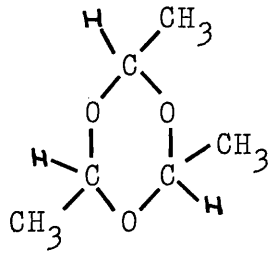
Aldehyde/ketone	Pentene yield%	% yield of borane species 78	54	42	33	/ppm
CCl_3CHO	76	16	0	57	27	
$(CH_3)_3CCHO$	65	16	15	37	32	
CBr_3CHO	62	36	0	36	29	
$CH_3CH{=}CHCHO$	30	40	32	0	28	
cy-$C_6H_{11}CHO$	60[a]	27	10	34	30	
$CH_3CH(CH_3)CHO$	61	22	19	32	27	
$CH_3CH_2CH_2CHO$	29	42	27	0	32	
$CH_3CH_2CH(CH_3)CHO$	62	28	9	47	16	
$CH_3(CH_2)_6CHO$	30	16	58	0	25	
$CH_3(CH_2)_6CHO$[b]	71[a]	10	18	55	18	
CH_3CHO	20	52	30	0	18	
$(CH_3)_2CO$	5[a]	5	88	0	7	
Ph_2CO	0	70[c]	0	0	0	

a - Alkene yield determined by bromine analysis of alkene.

b - Borane used, $(CH_3CH_2CH_2CH(CH_3)CH_2)_2BCl$.

c - ^{11}B spectrum contained a peak at 10ppm, 30% of the total.

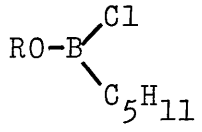
was confirmed by the standard infra red spectrum in the



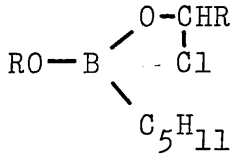
(VI)

Sadtler catalogue (Number 5181). The formation of the trimer was also confirmed by its formation using only small amounts (1% by weight) of dipentylchloroborane or tripentylborane, in which the methyl doublet (2.0 ppm) and methine quartet (5.5 ppm) could be seen in the ^{1}H n.m.r spectrum.

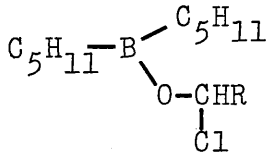
The ^{11}B n.m.r peaks at 42 ppm are assigned to the initial pentene elimination product,



The peaks at 33 ppm are typical for boronates and are assigned to the further reaction of the elimination product with another mole of aldehyde,



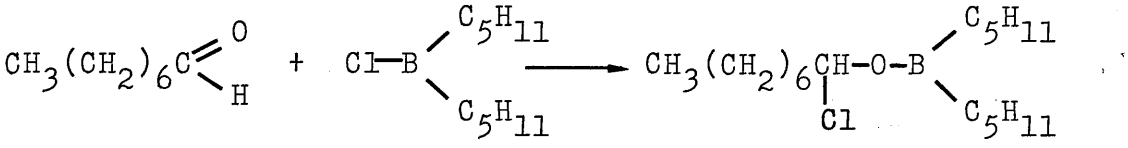
The peaks at 54 ppm are typical of borinates and arise presumably from the addition of B—Cl across the carbonyl group in a similar manner to boron trichloride[59],



The total yields of the initial elimination product (45ppm)

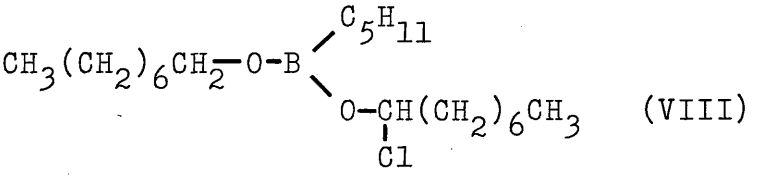
and the product at 3.3 ppm are similar to the yield of pentene, as would be expected if their assignments are correct.

The difference between the activities of the aldehydes can be most clearly seen in the case of octanal which being a long chain aldehyde appears to undergo less polymerisation. This aldehyde reacts with dipentylchloroborane to give mainly the proposed addition product (VII) (equation 71)



(VII) (71)

The other product is likely to arise from the further reaction of initially-formed elimination product to give VIII.



(VIII)

Both VII and VIII have identical methine groups and these and the CH_2O methylene protons can be seen as triplets at 5.6 (2) and 3.8 (1) ppm respectively in the ^1H n.m.r spectrum (Figure 3.15) which also contains the eliminated alkene. Octanal reacts with the 2-methyl substituted dipentylchloroborane to give far more elimination products. This is seen by the larger amount of CH_2O methylene protons (1) compared to methine protons (2) (Figure 3.16).

Butanal gives a ^1H n.m.r spectrum similar to that of

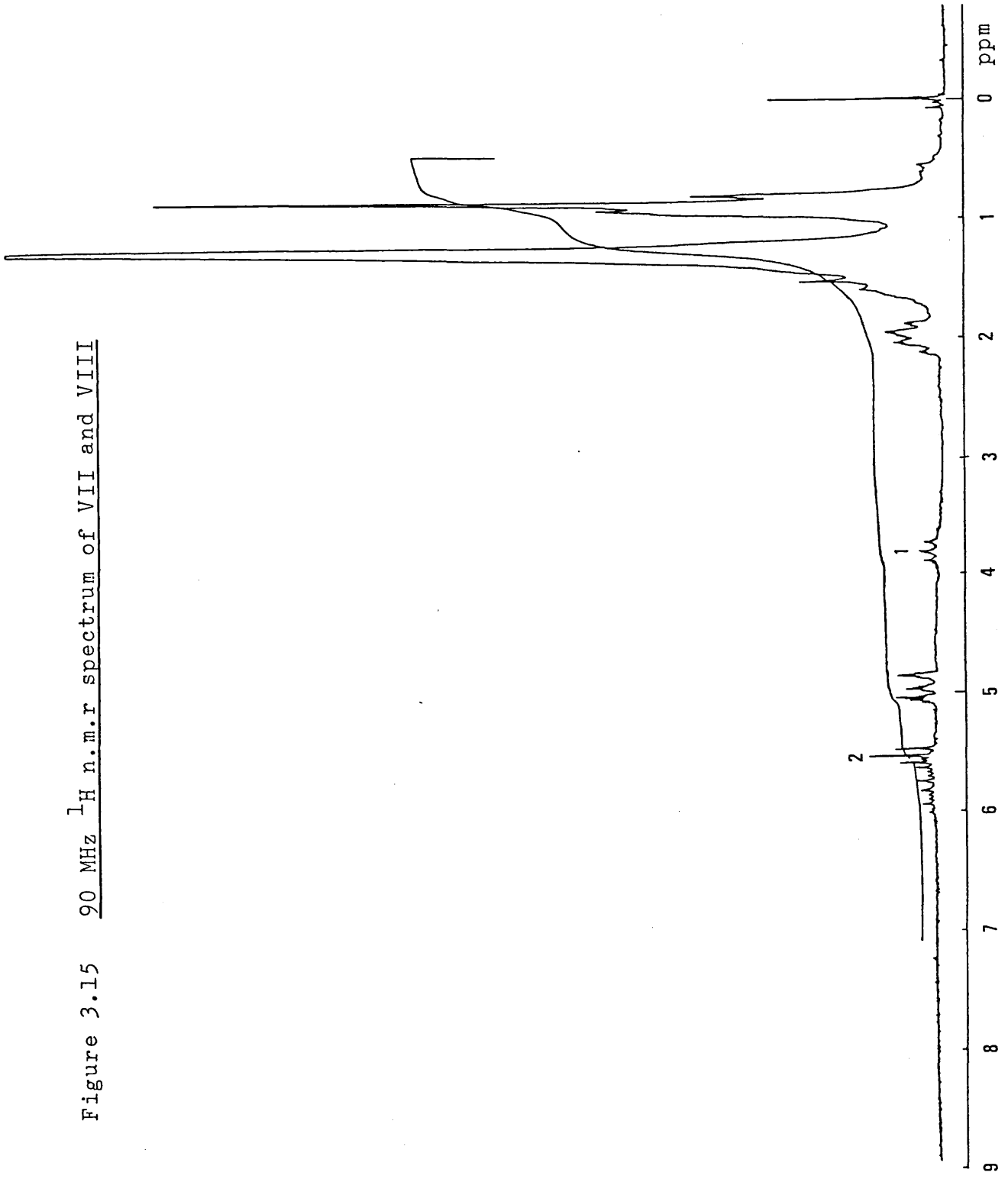


Figure 3.15 90 MHz ^{1}H n.m.r spectrum of VII and VIII

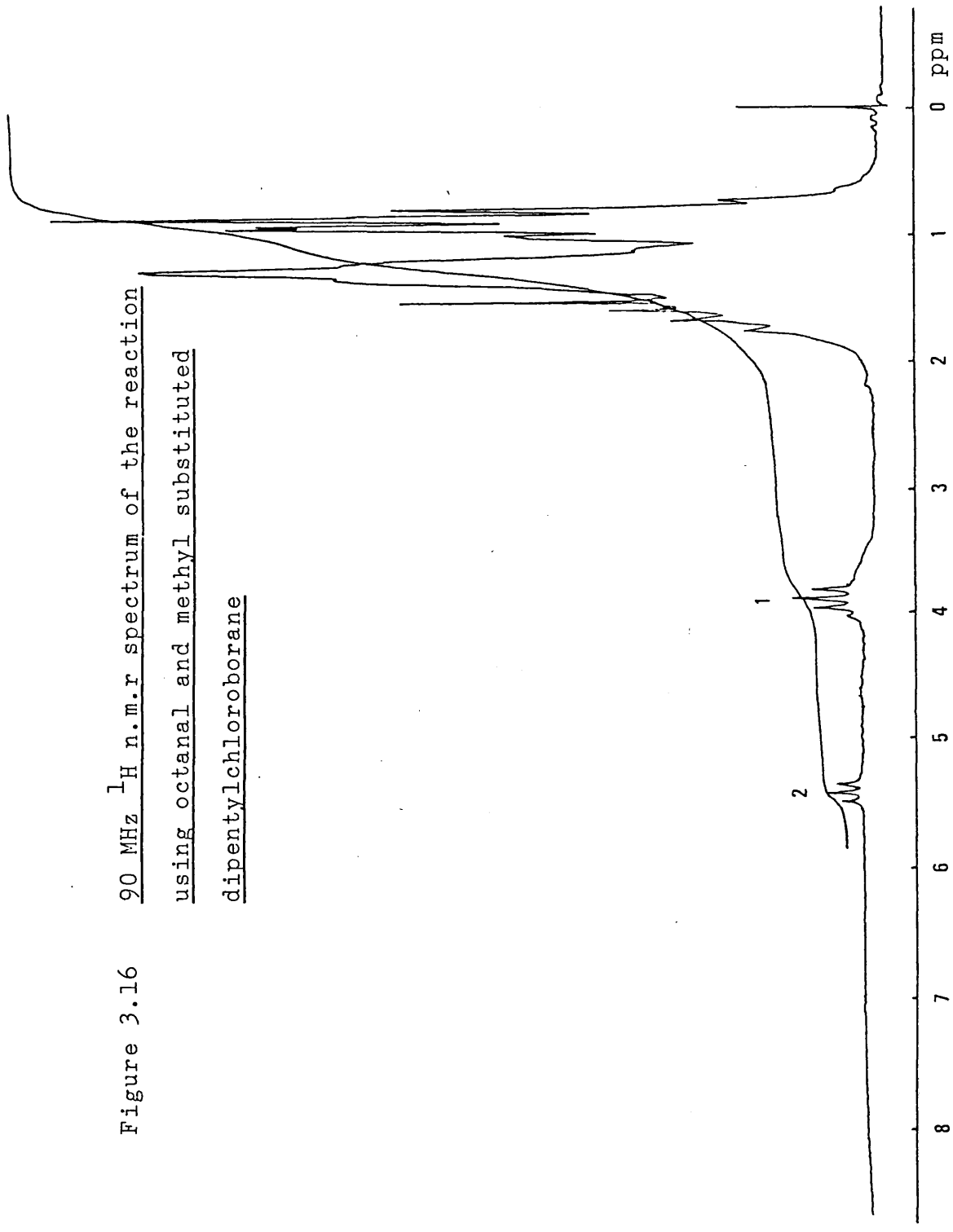
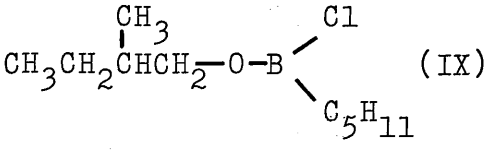


Figure 3.16 90 MHz ^{1}H n.m.r spectrum of the reaction using octanal and methyl substituted dipentylchloroborane

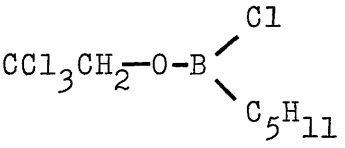
octanal, showing triplets due to CH_2O methylene and CHClOB methine protons at 3.8 and 5.4 ppm respectively, the peak areas being similar (in accordance with the ratio of products). Substitution of a methyl group in the 2-position of the aldehyde causes larger amounts of elimination product (IX) to be formed, confirming the ^{11}B n.m.r results. This is shown by the doublet at 3.9 ppm (1) in the ^{1}H n.m.r spectrum (Figure 3.17).



(IX)

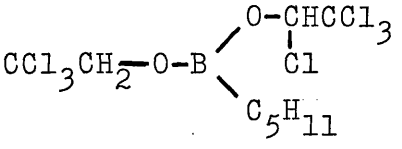
The methine group arising from the further reaction of the elimination product and from the addition product is just visible as a doublet at 5.5 ppm (2) adjacent to the olefinic protons.

The major product for the trichloroethanal reaction is the initial elimination product (X). The reaction is



(X)

accompanied by a smaller amount of secondary addition product (XI). The CH_2O methylene and CHClOB methine protons



(XI)

are seen in the ^{1}H n.m.r spectrum (Figure 3.18) at 4.4 and 6.1 ppm respectively, the former being the major peak (as

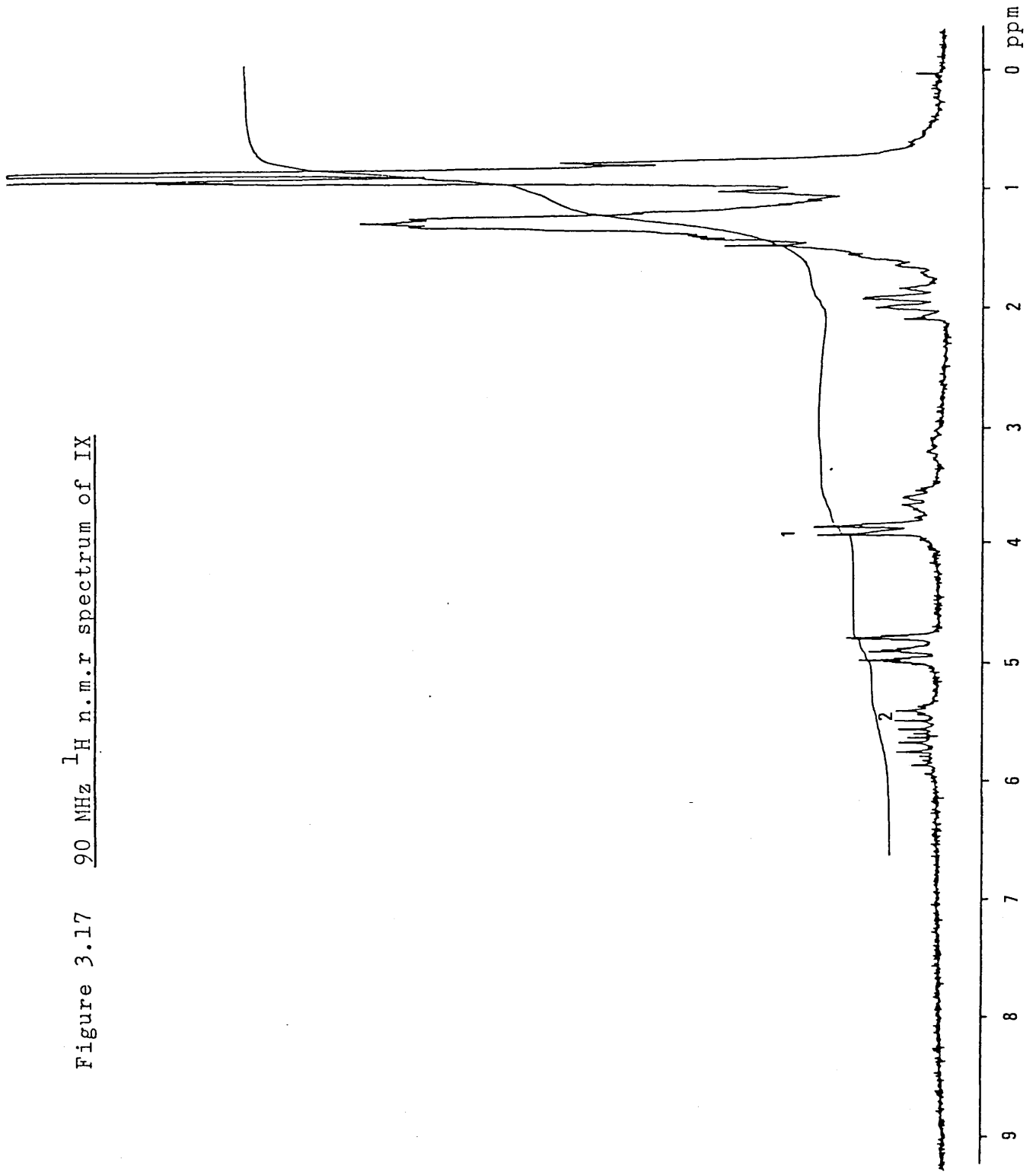


Figure 3.17 90 MHz ^{1}H n.m.r spectrum of IX

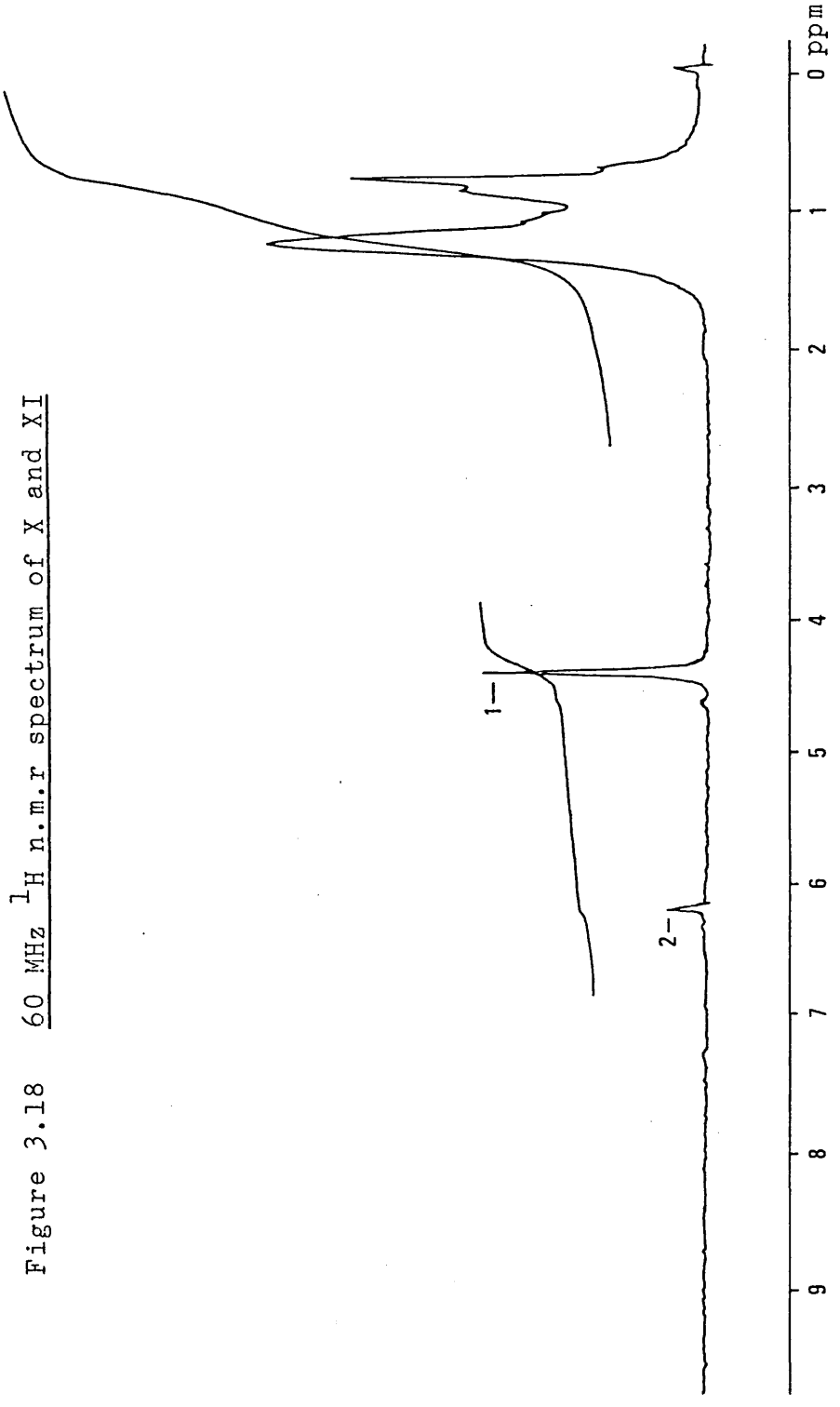


Figure 3.18 60 MHz ^{1}H n.m.r spectrum of X and XI

suggested by the ^{11}B n.m.r results). The downfield shift of both groups by about 0.6 ppm (compared to octanal and butanal) is in accordance with the presence of the CCl_3 group.

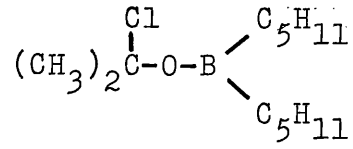
The reaction using tribromoethanal gives a similar ^{1}H n.m.r spectrum to trichloroethanal, as does trimethylethanal. In the latter reaction, however, the methylene and methine protons appear as singlets with shifts of 3.4 and 5.1 ppm respectively. The upfield shift is due to the effect of the methyl groups.

The reaction products using trichloroethanal and trimethylethanal were esterified using methanol and in both cases only two products were observed in the ^{11}B n.m.r spectra. These peaks occurred at 54 and 33 ppm. The former is typical of borinates and the latter for boronates. In the case of trichloroethanal the relative yields were 19 and 81% respectively. This is approximately equal to the ratio between the unreacted dipentylchloroborane and the sum of the products X and XI, therefore confirming their identity. Trimethylethanal produces similar results giving 39% borinate (ca. equal to the initial amount of dipentylchloroborane and borinate) and 61% boronate (ca. equal to the elimination product and secondary addition product) again confirming the ^{11}B n.m.r assignments.

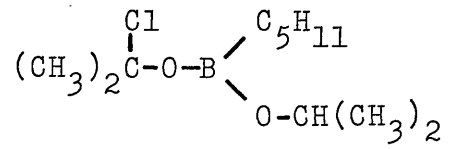
No reaction products are observed with the reaction using benzophenone and the carbonyl band in the infra red appears unchanged. However the ^{11}B n.m.r spectrum shows two peaks. These are the reactant peak at 78 ppm and a broad peak centred on 10 ppm. The broad peak may be due

to complex formation.

The reaction using acetone gives large amounts of the addition product (XII) along with 7% of the further reacted elimination product (secondary addition product, XIII).



(XII)



(XIII)

The ^{1}H n.m.r spectrum (Figure 3.19) reveals the methyl protons in XII as a singlet at 1.8 ppm (1). The probable doublet centred on 1.6 ppm (2) can be assigned to the methyls in XIII (adjacent to the C-OB group). The badly defined multiplet at 4.3 ppm (3) could be the methine proton in XIII, leaving the peaks at 3.0 and 3.5 ppm as unidentified.

Substitution of large groups at the C-2 position of the aldehyde increases the amount of elimination product in relation to addition product. This occurs regardless of the electronic nature of the substituent (eg. Cl or CH_3) and implies a steric factor in the transition state, supporting earlier evidence (section 3.4). The amount of elimination product is enhanced even when α-protons are present, such as with hexahydrobenzaldehyde, although these aldehydes may be more susceptible to polymerisation. Substitution of the alkyl chain of the chloroborane at the C-2 position also increases the amount of elimination product. Thus it appears that after initial complex formation the reaction can proceed by two paths (Scheme 7).

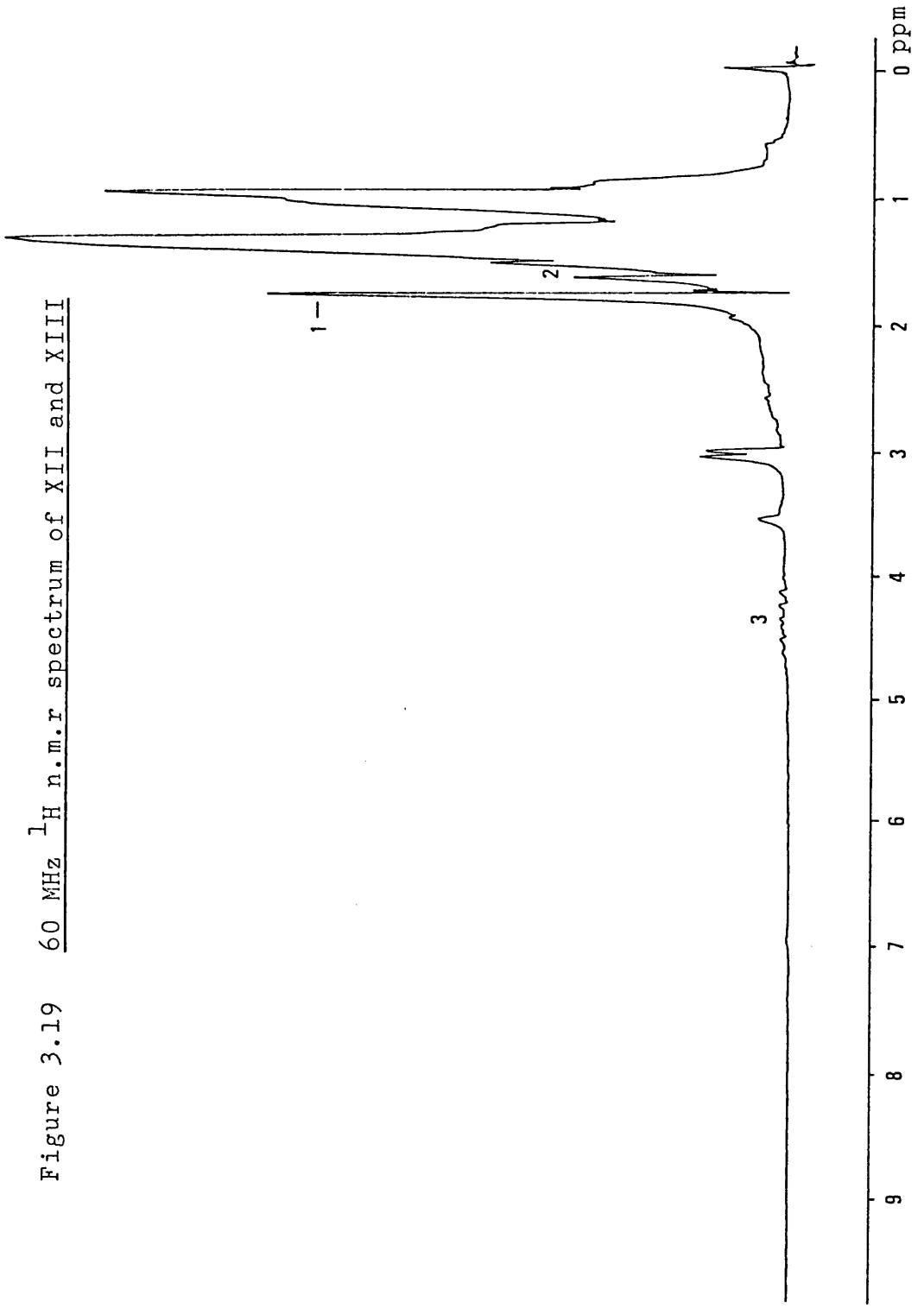
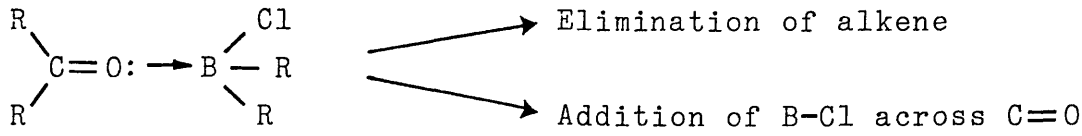


Figure 3.19 60 MHz ^{1}H n.m.r spectrum of XII and XIII



Scheme 7

Space filling models of the various possible addition products show large steric hindrance to rotation of the groups when the aldehyde bulk is increased. This explains the preferential loss of alkene with the very large groups. In the case of benzophenone the steric hindrance is so pronounced that even B—Cl addition across the carbonyl is restricted and only slight complex formation is observed.

CHAPTER FOUR

EXPERIMENTAL DETAILS

4.1 GENERAL PREPARATIVE TECHNIQUES

4.1.1 Introduction

The sensitivity of boranes and organoboranes towards air has led to the development of many specialised techniques for their handling. The techniques used in the course of the present work are described in this section.

4.1.2 General apparatus

Most of the reactions reported in this thesis were carried out in standard Quickfit apparatus. The only other equipment used was a source of inert gas, a rubber septum-capped inlet, an oil bubbler and hypodermic syringes and needles. A typical apparatus used for a hydroboration reaction is shown in Fig.4.1. The glassware was assembled hot, using silicone grease on the ground joints, and allowed to cool under a stream of nitrogen (introduced through septum A). The nitrogen source was constructed from PVC tubing connected at one end to a nitrogen manifold (or pressure regulator of a nitrogen cylinder) and on the other end to a standard 6 inch, 20 gauge hypodermic needle. A septum-capped T-piece was spliced into the tubing to allow the flushing of syringes with nitrogen (Fig.4.2). After cooling, the nitrogen source connected to the bubbler was allowed to maintain a static pressure of nitrogen. This protected the solution from leaks and prevented bubbler oil being sucked back if a pressure reversal occurred during the reaction.

Figure 4.1 Basic reaction setup using common glassware

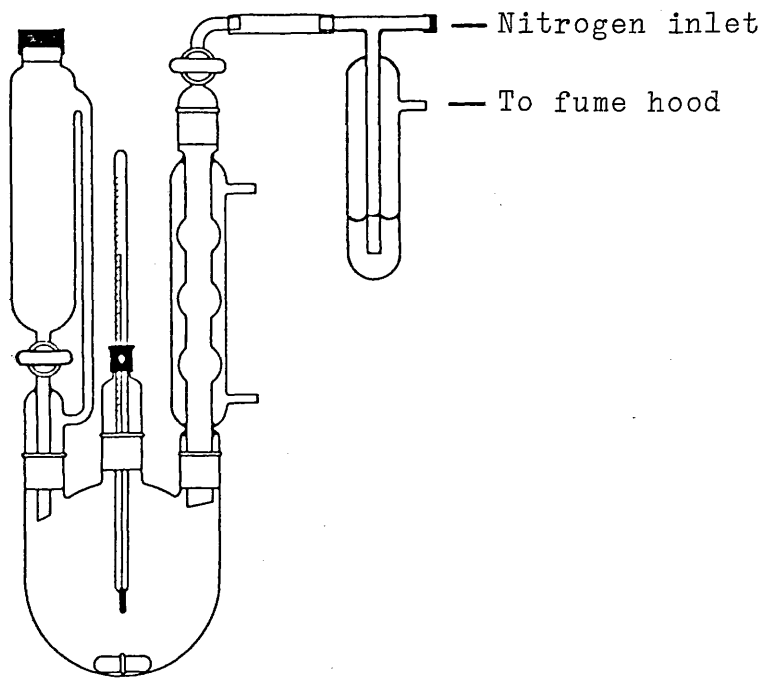
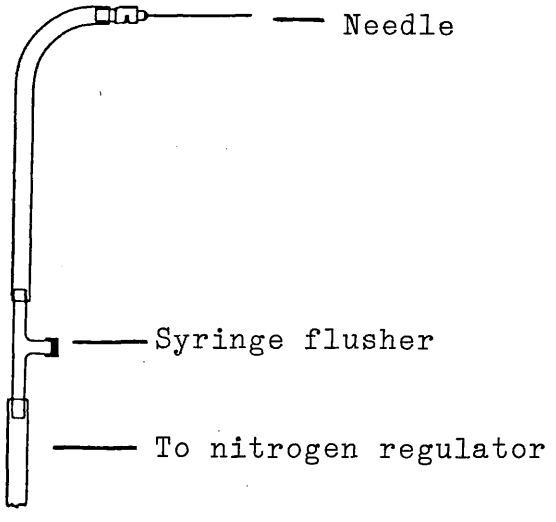


Figure 4.2 Nitrogen flusher



Many of the reactions mentioned in this thesis were carried out in standard ground-glass apparatus using the septum-inlet adaptor shown in Fig.4.3. This has the advantage over the large septum shown in Fig.4.1 in being more conveniently located for the introduction of liquids as well as keeping solvent vapours away from the septum thereby reducing deterioration and swelling.

4.1.3 Special glassware

The kinetic work involving the BMS reactions required careful monitoring of the temperature. For this, round-bottomed flasks were blown which allowed the tips of Quickfit thermometers to be immersed in the reaction solutions. A typical set-up is shown in Fig.4.4.

Oil bubblers were used to provide a seal between the reaction vessel and the atmosphere. Occasionally pressure reversals occurred in the reaction vessel, causing the liquid in the bubbler to be sucked back. To prevent this liquid being sucked into the reaction vessel, bubblers were made with an enlarged head space (Fig.4.5).

4.1.4 Liquid transfer using syringes

The syringes used during this work were standard glass Luer hypodermic syringes ranging in size from 0.5cm^3 to 20cm^3. Before use the syringe barrel, plunger and needle were disassembled and dried in an oven (4 hours at 140 °C or overnight at 120 °C). While still hot a small amount of silicone grease was placed on the Luer tip to act as a sealant, and the needle was attached. The syringe was then flushed with nitrogen several times using the syringe flusher shown in Fig.4.2. During the flushing procedure

Figure 4.3 Septum-inlet adaptor

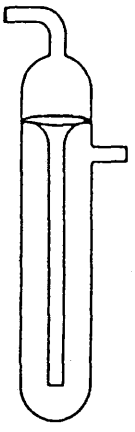


Figure 4.5 Oil bubbler

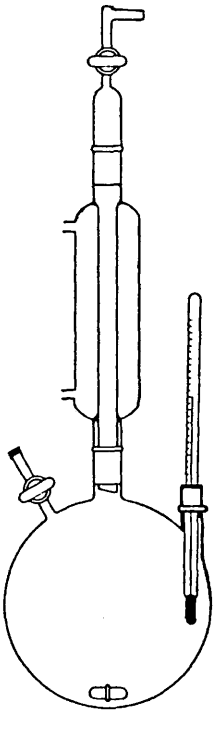


Fig 4.4 Glassware used for kinetic work

the syringe was leak tested by inserting the tip of the needle into a rubber stopper. The plunger was depressed about halfway and released. If no leaks were present, the plunger returned to its original position. After flushing, the plunger was depressed fully and the needle tip was inserted into a rubber stopper. The syringe was left to cool and was then ready for use.

Two methods were used to dispense precise amounts of liquids from the syringe. The simplest method was to rely on the graduations on the syringe barrel. A more accurate method, more commonly used, was to weigh the syringe before and after the liquid was dispensed. The contents of the syringe were protected from the atmosphere during the weighing procedure by inserting the needle tip into a small rubber stopper. In order to transfer liquids by syringe, the storage and receiver vessels were capped by suitable sized rubber septa. The storage vessel was pressurised with nitrogen and the receiver was flushed with nitrogen using a 1 inch needle to release the nitrogen (unless the receiver was fitted with an oil bubbler). The syringe was flushed and leak tested as described above and then inserted through the septum of the storage vessel. The needle was placed below the surface of the liquid and the pressure above the liquid was allowed to fill the syringe to approximately 20% above the desired level. The needle was then raised above the liquid level. After bending the needle gently, the syringe was inverted so that any bubbles of gas rose to the top. The bubbles were dispelled by depressing the plunger until the correct

volume remained in the syringe. The plunger was withdrawn slightly, drawing in a blanket of gas and clearing the needle. Keeping the syringe inverted, the needle was withdrawn from the storage vessel and inserted through the septum of the receiver (or into a rubber stopper if the weighing method was used). After the needle was inserted into the receiver the contents of the syringe were discharged. Care was taken to dispel the gas before the liquid since failure to do so would have resulted in adding an incorrect amount of liquid. This is because the needle must remain filled with liquid when the syringe is emptied. A small amount of nitrogen was sucked into the syringe, followed by removal of the needle. The needle tip was pushed into a rubber stopper if the syringe was to be used again soon. Syringes and needles were cleaned using the device shown in Fig.4.6. Suction (water pump) was used to pull solvents from wash bottles through the syringes and needles.

4.1.5 Liquid transfer using double-ended needles

When amounts of liquid over 20cm^3 needed to be transferred, then the method known as the double-ended needle technique was employed (Fig.4.7). A length of stainless steel needle tubing (from 500 to 700 cm) with a standard bevel on each end was commonly used. One end was inserted through the septum of the pressurised storage flask leaving the tip above the level of the liquid. The needle was purged by blowing nitrogen through the storage flask. The other end of the needle was inserted through the septum of the measuring vessel which was vented by a 1 inch vent

Figure 4.6 Syringe flusher

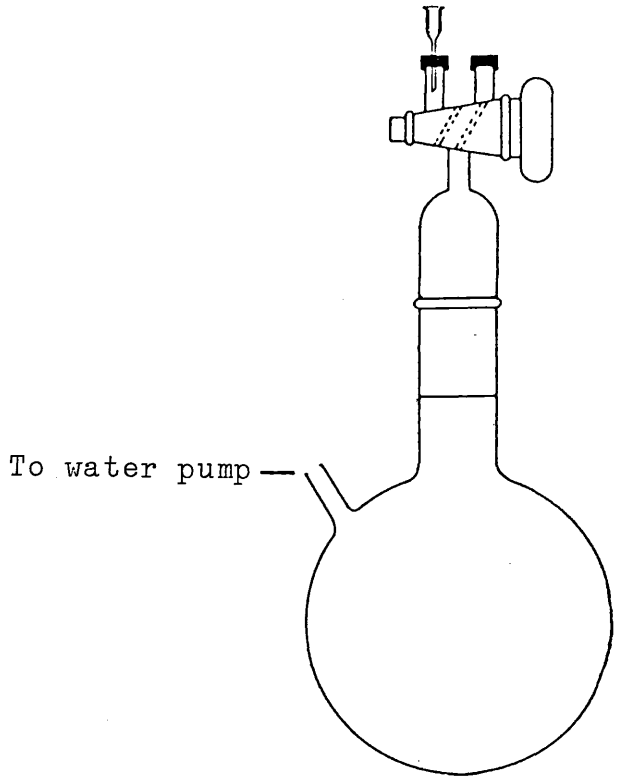
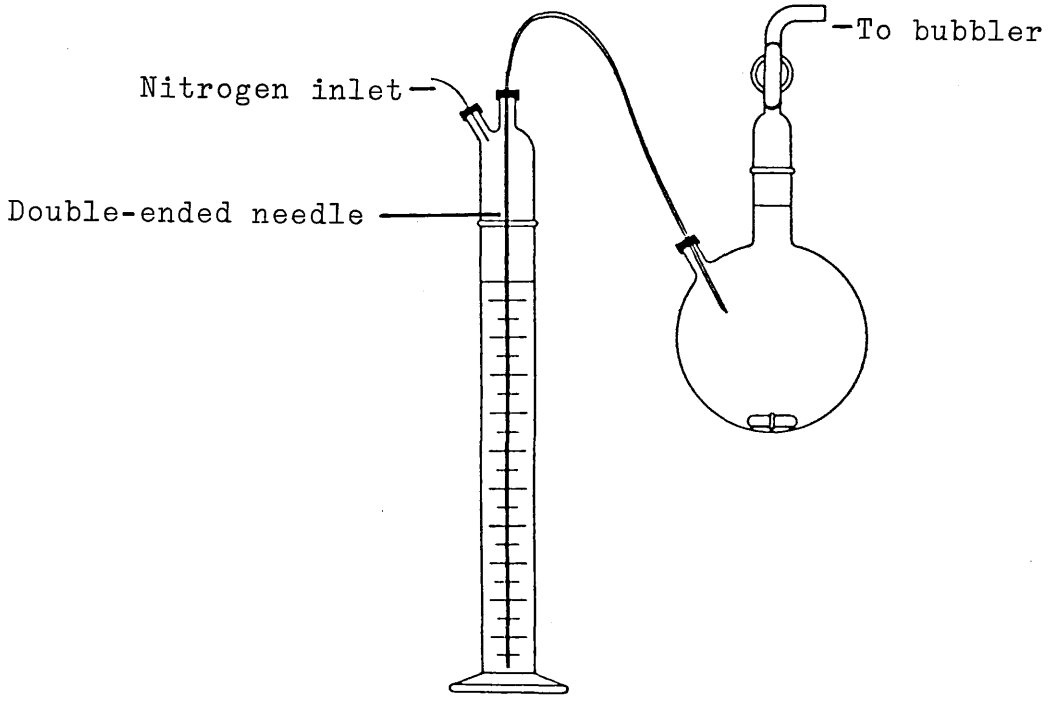


Figure 4.7 Transferring liquid using a double-ended needle



needle. After lowering the needle below the surface of the liquid the nitrogen pressure was allowed to force the liquid through the needle. When the required amount of liquid had been transferred the needle was lifted above the surface of the liquid. The nitrogen needle was transferred to the measuring vessel and the double-ended needle was withdrawn from the storage flask and inserted into the receiver vessel. The vent needle was then removed from the measuring vessel and inserted into the receiver flask (unless fitted with an oil bubbler). Liquid from the measuring vessel was then transferred to the receiver flask by lowering the double-ended needle below the surface of the liquid. The needle was cleaned using the device described earlier (Fig.4.6).

4.2 BORANE AND ORGANOBORANE ANALYSIS

4.2.1 Sample preparation for n.m.r. spectroscopy

Air-sensitive samples were prepared for n.m.r. analysis using dry 5mm n.m.r. tubes fitted with rubber septa (no.13, Suba Seal). The tubes were flushed with nitrogen from a needle, using a vent needle to release the pressure. Samples were then transferred into the tubes using the syringe techniques mentioned earlier. Samples containing small amounts of particulate matter were filtered using the device shown in Fig.4.8. The sample was introduced into the assembly using a syringe and then forced through the sintered-glass (coarse, 5mm thick) into the n.m.r. tube using nitrogen pressure. The septa were replaced with plastic caps, this operation being carried out in a nitrogen filled dry bag. The tops of the tubes were then sealed using Parafilm. 5 and 10mm tubes which required sealing under vacuum were handled using the assembly shown in Fig.4.9. The sample was introduced through the septum using a syringe and was degassed using the freeze-thaw method. Care was taken to use a fresh septum when placing the system under a vacuum. The following n.m.r. spectrometers were used; Varian EM 360 (60MHz, ^{1}H), Jeol FX 90Q and Bruker SM 250.

4.2.2 Infrared spectra

Infrared spectra of air sensitive liquids were obtained using a standard infrared cell (0.025mm). The cell was fitted with two rubber septa (no.13) and flushed with nitrogen using a vent needle to release the pressure. The

Figure 4.8 Transferring a liquid through a filter

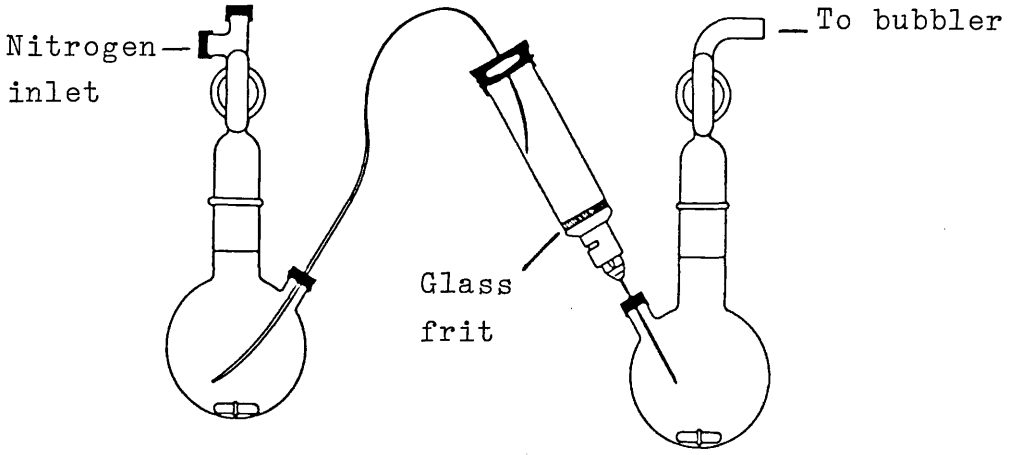
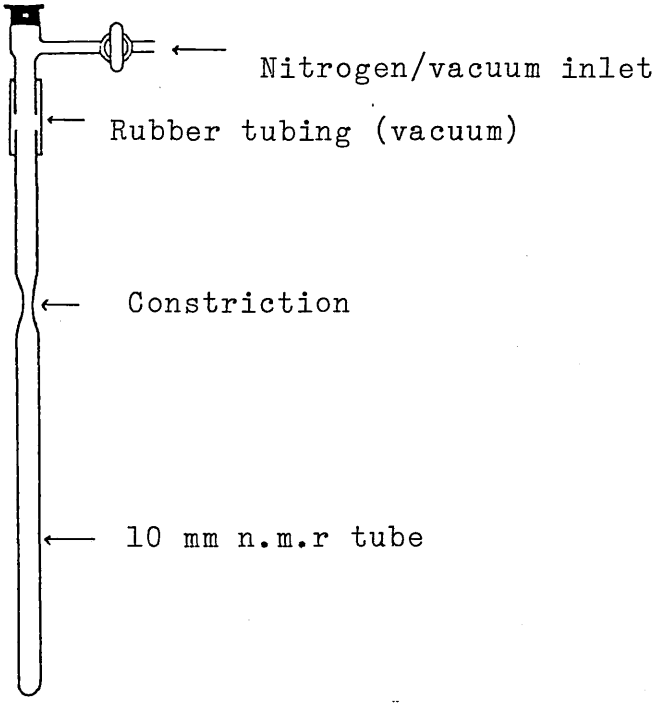


Figure 4.9 Apparatus for sealing n.m.r samples



sample was introduced through the septum using a syringe and the septa were replaced with teflon stoppers. If the sample was very air-sensitive, the operation was carried out in a dry bag. Infrared spectra of solids were usually run in solution. Where this was difficult or undesirable, the solid was mulled with nujol in a dry bag and applied to alkali halide plates in the usual way. The spectra were recorded on a Perkin Elmer 337 or Pye Unicam SP1000 spectrometer.

4.2.3 Hydrolysable chlorine analysis

The ampoule shown in Fig.4.10 was removed from an oven (140°C), fitted with a septum (no.13) and flushed with nitrogen using a vent needle to release the pressure. After weighing, a small amount of sample (ca. 0.3g) was introduced using a syringe, and the ampoule was reweighed. The ampoule was then placed in a 250cm^3 conical flask containing water (50cm^3, deionised and degassed) and ethanol (50cm^3 BDH) and stoppered with a large septum. The ampoule was broken by shaking the flask and the contents were left for 30 minutes to ensure complete reaction of the hydrolysable chlorine. The solution (containing hydrogen chloride) was then titrated with sodium hydroxide solution (0.05M) using phenolphthalein indicator. The solution was warmed near the end-point to remove any dissolved carbon dioxide. This process was repeated until three consistent values were obtained (usually three or four operations were sufficient).

4.2.4 Total chlorine analysis

The sample (ca. 0.3g) was weighed using the procedure described above and placed in a 50cm^3 round bottomed flask

Figure 4.10 Ampoule for chlorine analysis

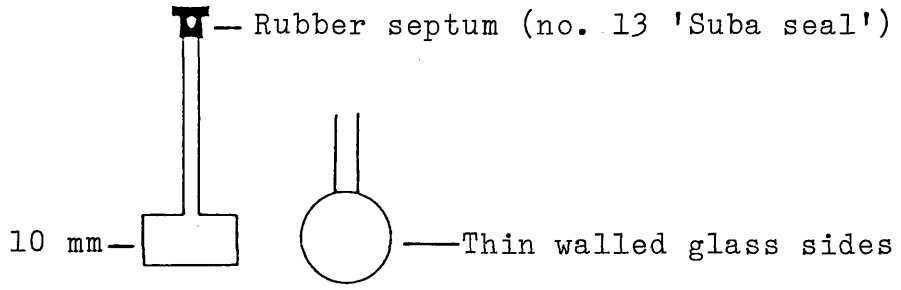
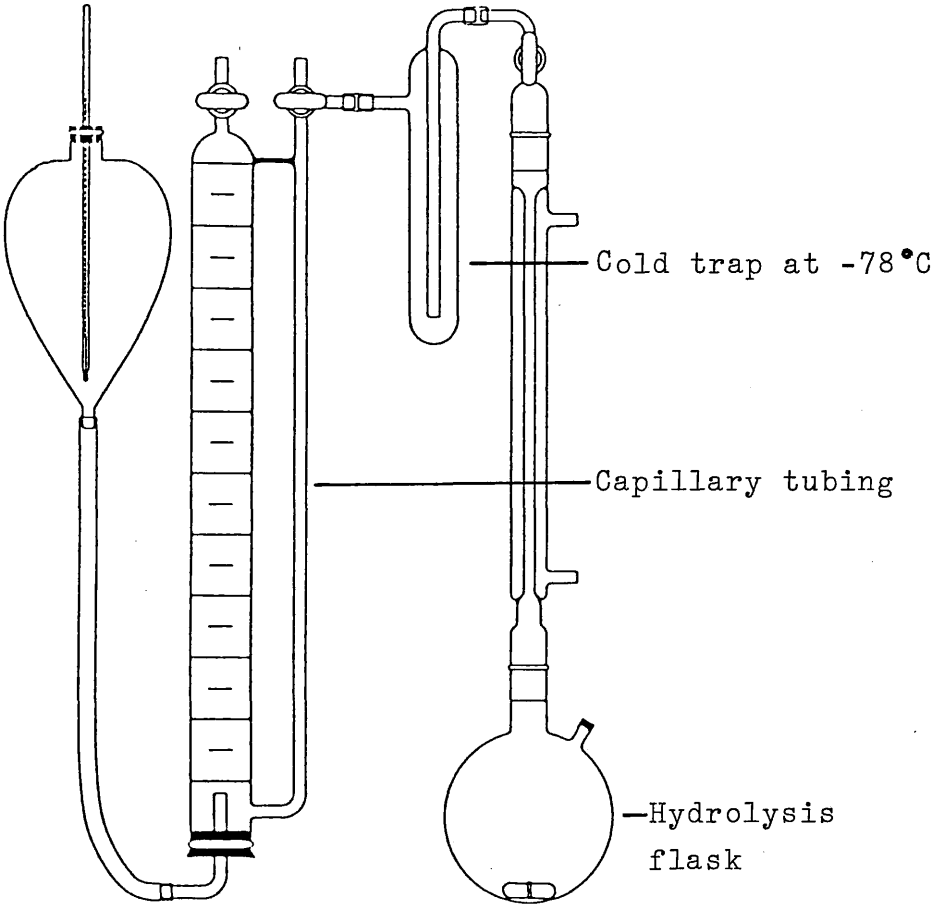


Figure 4.11 Gas burette for analysing borane solutions



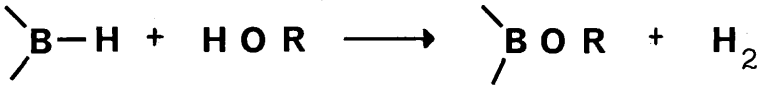
containing ethanol ($10cm^3$, BDH) and potassium hydroxide solution ($15cm^3$, $5mol\ dm^{-3}$). The flask was stoppered and the ampoule broken. After 30 minutes the rubber septum was removed (and washed to remove traces of chloride) and the solution was refluxed overnight. The solution was neutralised with chlorine-free nitric acid (using phenolphthalein indicator) and titrated using silver nitrate solution ($0.01mol\ dm^{-3}$) with a potassium chromate indicator.

4.2.5 Standardisation of borane solutions by titration

Boric acid is a very weak acid and gives a poor end-point when treated with a base. The addition of a chelating agent such as mannitol causes boric acid to behave as a stonger acid. Thus it can be succesfully titrated with sodium hydroxide solution. BMS (borane dimethylsulphide complex, $1cm^3$) was hydrolysed in distilled water and left for 30 minutes to ensure complete hydrolysis. Excess mannitol was added (approximately 3g of mannitol for each 5×10^{-3}moles of boric acid) and the solution titrated with sodium hydroxide solution ($0.5mol\ dm^{-3}$) using phenolphthalein as the indicator.

4.2.6 Standardisation of borane solutions using the gas burette method

Borohydrides can be hydrolysed rapidly and quantitatively with suitable hydrolytic solvents releasing one mole of hydrogen gas per equivalent of metal hydride:



This property provides a convenient method for hydride analysis. The majority of BMS solutions were analysed using this method. The gas burette is shown in Fig.4.11.

Procedure

This was carried out according to the method described in the Aldrich Technical Bulletin, No.A 74. The hydrolysis flask was charged with glycerol ($50cm^3$), water ($50cm^3$) and methanol ($50cm^3$). Cooling water was run through the spiral condenser and the cold trap was cooled in a dry ice/acetone bath. Both stopcocks were opened and the levelling bulb was adjusted to give a zero reading for the level of distilled water (containing a little copper sulphate) in the gas burette. The burette tap was closed and the three-way tap was turned so that the hydrolysis flask and the gas burette formed a closed system. An accurately measured aliquot of BMS solution (usually $0.3cm^3$) was added slowly through the septum inlet using a syringe. Hydrolysis of the BMS was very rapid, being complete in about one minute. When the hydrolysis was complete the water level in the narrow glass tube (minus the height due to capillary action) was equalised by lowering the levelling bulb below the bottom of the burette. The process was repeated until consistent readings were obtained (usually 4 or 5 times).

The molarity of the BMS was calculated using the following equation:

$$\text{BMS molarity} = \frac{(P_1 - P_2)(273)(V_1 - V_2)}{(760)(T)(67.2)\ V_2}$$

Where,

P_1 = observed pressure (mm Hg)
P_2 = vapour pressure of water at T
V_1 = volume (cm^3) of hydrogen gas evolved
V_2 = volume (cm^3) of borane solution injected into hydrolysing solution
T = observed temperature (K)

The BMS used during the present work varied in concentration from 8.0 to 9.9 mol dm^{-3}. Quantities employed in the various preparations are quoted in moles rather than by volume.

4.2.7 Analysis of organoboranes by oxidation and GLC

The reaction of alkaline hydrogen peroxide with organoboranes is an essentially quantitative reaction:

$$R_3B + 3H_2O_2 + NaOH \longrightarrow 3ROH + NaB(OH)_4$$

Procedure

A dry $50cm^3$ round-bottomed flask was fitted with a reflux condenser, oil bubbler, septum-inlet adaptor and teflon follower, and flushed with nitrogen. The organoborane ($10cm^3$ of an approximately 0.5 mol dm^{-3} solution in THF) was placed in the flask by syringe. The flask was immersed in an ice bath and $2.0cm^3$ of 3 mol dm^{-3} sodium hydroxide was added. Hydrogen peroxide ($2cm^3$ of a 30% solution) was added at such a rate to keep the temperature below the reflux point of the THF (50°C). After the addition the reaction solution was stirred for an additional ten minutes at 50°C (water bath), and cooled to room temperature. The aqueous phase was saturated with potassium carbonate and an appropriate standard was added to the

THF layer (usually 5 x 10^{-3} moles of n-decane). The THF layer was then analysed for alcohols by GLC. Authentic samples of alcohols were used for comparison.

GLC conditions

The GLC analyses were carried out on a Pye-Unicam series 204 chromatograph equipped with a flame ionisation detector. An SP1000 column (8% SP1000 on Chromosorb W, 2m x 0.25 inch) was used. The alcohols were analysed using the following conditions: Column, detector and injector temperatures of 100, 250 and 200 °C respectively, and gas pressures of N_2, 1.5 ; H_2, 2.0 ; Air, 0.75 Kg cm^{-2}.

4.3 PURIFICATION OF REAGENTS AND SOLVENTS

Tetrachloromethane :- AR grade reagent (BDH) was used and stored over activated molecular sieves (3Å).

Dichloromethane :- Anhydrous reagent grade solvent (Koch Light) was used and stored over activated molecular sieves (5Å).

Tetrabromomethane :- Sublimed at 70°C (0.02 mm Hg) and stored under nitrogen.

Other Halogenoalkanes :- All compounds were used as supplied by the manufacturer and dried using 4 or 5Å molecular sieves.

Aldehydes :- All liquid aldehydes were distilled before use (benzaldehyde being first washed with sodium hydroxide solution).

Substituted Benzaldehydes :-

p-Cl :- Sublimed under vacuum (0.01 mm Hg) at 50°C.

p-NMe_2 :- Recrystallised from hexane.

p-NO_2 :- Recrystallised from ethanol/water, then sublimed under vacuum (2 mm Hg) at 30°C.

Benzene :- AR grade (Fisons) was used and dried using sodium wire.

Methanol :- Anhydrous grade reagent (Aldrich) was stored over 3Å molecular sieves.

Alkenes :- Pentene was used as supplied, and all other alkenes were distilled over lithium aluminium hydride prior to use.

All compounds mentioned were obtained from the Aldrich Chemical Co.(99%) unless otherwise stated.

EXPERIMENTAL DETAILS FOR CHAPTER TWO

4.4 BMS/TETRACHLOROMETHANE EXPERIMENTS

4.4.1 Preparation of monochloroborane dimethyl sulphide complex

A $50cm^3$ two necked round bottomed flask equipped with a tap with rubber septum, a teflon follower and double surface condenser was assembled while hot. The top of the condenser was fitted with an oil bubbler connected to a dry nitrogen source. The apparatus was flushed with nitrogen using a hypodermic needle inserted through the septum and left to cool. Deoxygenated tetrachloromethane ($10cm^3$, 0.10 mol) and BMS (0.10 mol) were introduced to the flask via the septum with the aid of dry hypodermic syringes. The flask was immersed in an oil bath and the solution was stirred and refluxed under a static pressure of nitrogen for a period of 20 hours. After cooling a sample of the solution was taken and analysed by ^{11}B n.m.r. spectroscopy.

4.4.2 The effects of additives and reaction conditions on the BMS/tetrachloromethane reaction

The procedure described above was followed for each of the experiments shown in Table 4.1. All solids were added to the flask in a nitrogen filled dry bag before assembly.

4.4.3 Experiment showing the effect of ultra violet irradiation upon a refluxing solution of BMS and tetrachloromethane

Table 4.1 The effect of additives and conditions on the BMS/tetrachloromethane reaction

Reaction	Additives and conditions
(i)	BMS (0.05 mol) and CCl_4 ($20cm^3$, 0.2 mol).
(ii)	Lauroyl peroxide (0.1g, BDH).
(iii)	Lauroyl peroxide (1.0g), with no heating[a].
(iv)	Lauroyl peroxide (0.1g) and purified CCl_4[b].
(v)	Hydroquinone (0.1g).
(vi)	Quinone (0.1g).
(vii)	Purified CCl_4[b].
(viii)	BMS (0.05 mol) and purified CCl_4[b] ($10cm^3$, 0.1mol).
(ix)	CCl_4 (AR grade, BDH) not stored over molecular sieves.
(x)	Solution refluxed for 4 days.
(xi)	Glassware covered with aluminium foil to exclude light.
(xii)	CCl_4 and $CHCl_3$ removed from the refluxed solution[c] and the borane complexes further refluxed with CCl_4 ($10cm^3$, 0.1 mol) for 20 hrs.

a - The reaction was very exothermic, self refluxing for 30 minutes.

b - Purified by distillation over phosphorus pentoxide.

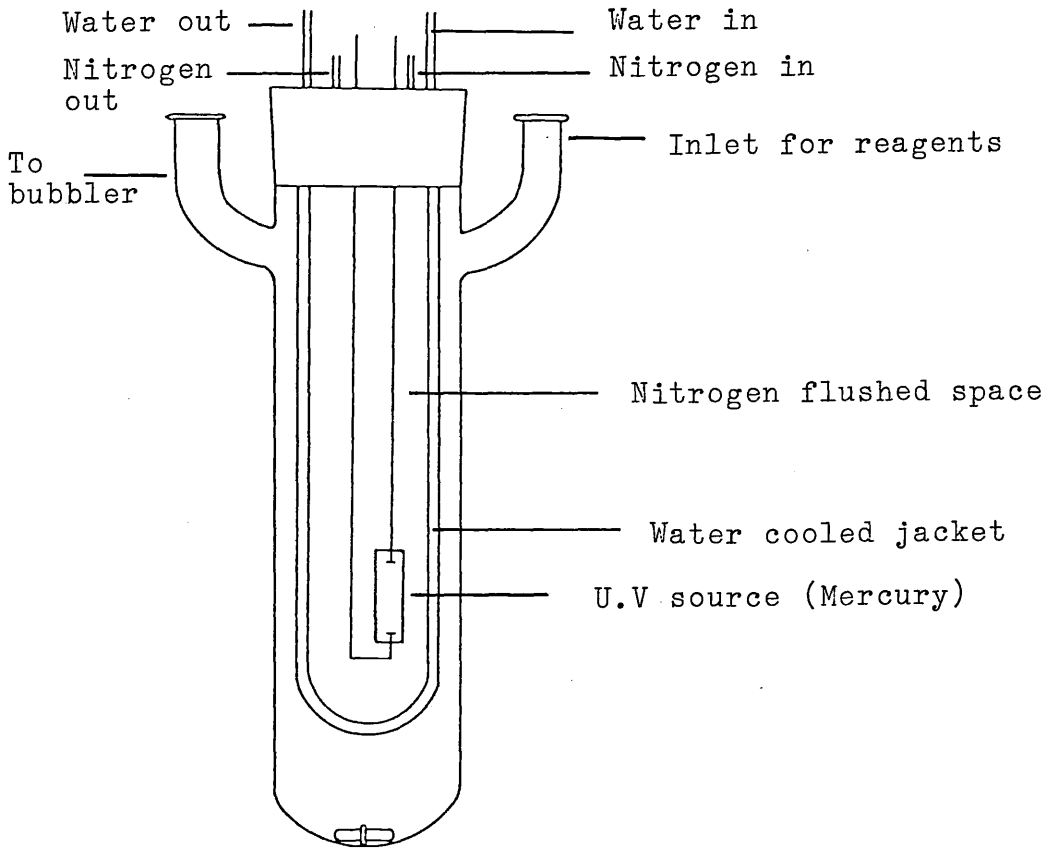
c - The volatile components were removed using a protected water aspirator.

The apparatus shown in Fig.4.12 was assembled hot and left to cool under a stream of nitrogen inserted through the rubber septum using a hypodermic needle. Deoxygenated tetrachloromethane (purified by distillation over phosphorus pentoxide, $10cm^3$, 0.10 mol) and BMS (0.1 mol) were introduced into the reaction vessel via the rubber septum using dry hypodermic syringes. The reaction vessel was lowered into an oil bath and brought to reflux temperature. The entire apparatus was covered in aluminium foil and the fume cupboard front covered in black paper. After starting the lamp, the solution was refluxed and irradiated for 17 hours under a static pressure of nitrogen. The experiment was repeated, irradiating the solution for 8.5 hours while refluxing it for only 4.5 hours of that time.

4.4.4 Experiment to show the effect of ultra violet light upon a solution of BMS and tetrachloromethane at room temperature

The procedure described in 4.4.3 was followed (using AR tetrachloromethane) using a beaker (5 Litre) containing water at room temperature (22°C) instead of the oil bath mentioned. The temperature was carefully maintained at 22°C and a sample was removed after 4.3 hours. The experiment was repeated using a soda glass insert (1mm thick) which replaced the quartz tube, in order to absorb the ultra violet light while keeping the heat output the same. The temperature of the water bath was carefully kept at 22°C and a sample was taken after 4.3 hours.

Figure 4.12 Ultra violet irradiation reaction vessel



4.4.5 Reaction between BMS and tetrachloromethane followed at the refluxing temperature in order to determine the rate constant and kinetic order

A 50cm^3 three necked round bottomed flask equipped with a tap with rubber septum, condenser fitted with oil bubbler, teflon follower and quickfit thermometer (0-100°C) was assembled hot and left to cool under a stream of nitrogen via a needle through the rubber septum. Deoxygenated tetrachloromethane (15cm^3, 0.15 mol) and BMS (0.15 mol) were introduced into the flask via the septum with the aid of hypodermic syringes. The flask was lowered into hot oil and the solution was refluxed under a static pressure of nitrogen. Samples were removed at regular intervals, introduced into nitrogen flushed, dry, 5mm n.m.r. tubes and placed in a refrigerator at 4°C. The refluxing temperature was recorded as 80°C.

4.4.6 Reaction between BMS and tetrachloromethane followed at 50°C in the presence of various solvents

The reactions shown in Table 4.2 were carried out at 50°C (internal temperature) in the presence of the stated solvents, using the procedure described in 4.4.5.

4.4.7 Experiment to determine the concentration of hexachloroethane in a typical monochloroborane solution

To a typical solution mentioned in 4.4.1 (after refluxing), 1,1,2,2-tetrachloroethane (4.00g, 0.024 mol) was added and the solution hydrolysed with distilled water (10cm^3, 0.56 mol). Chloroform, tetrachloromethane, dimethyl sulphide, tetrachloroethane and any hexachloroethane present were extracted with tetrachloromethane using a separating

Table 4.2 The reaction between BMS and tetrachloromethane followed at 50°C in different solvents

Reaction number	Reagents and solvents				
	BMS(mol)	CCl_4(mol)	PhH(cm^3)	CH_2Cl_2(cm^3)	$PhNO_2$(cm^3)[a]
(i)	0.046	0.046	—	—	—
(ii)	0.091	0.030	—	—	—
(iii)	0.033	0.100	—	—	—
(iv)	0.047	0.047	—	20.0	—
(v)	0.046	0.046	15.0	—	—
(vi)	0.091	0.030	15.0	—	—
(vii)	0.033	0.100	15.0	—	—
(ix)	0.046	0.046	—	—	15.0

a - Distilled over phosphorus pentoxide at 0.2mm Hg.

funnel. The extracted solution was analysed by GLC using the tetrachloroethane as the reference. Hexachloroethane was used as the standard. The GLC analysis was carried out with a Pye-Unicam series 204 chromatograph using a SE30 (5% on Celite) column. A column temperature of 120°C, injector temperature of 250°C and detector temperature of 300°C were used.

4.5 REACTION BETWEEN BMS AND HALOALKANES OTHER THAN TETRACHLOROMETHANE

4.5.1 Experiments to investigate the potential use of BMS/polyhalomethane reactions and to obtain their rate constants

The experiments shown in Table 4.3 were carried out at 90°C (internal temperature) using the general procedure described in section 4.4.5.

4.5.2 Reaction between tetrabromomethane and BMS

A 100cm^3 three necked round bottomed flask was equipped with a tap with rubber septum, teflon follower and two stoppers. After flushing with nitrogen, cooled and weighed it was placed in a nitrogen filled dry bag. Tetrabromomethane (30.15g, 0.091 mol) was added and the flask reweighed. The stoppers were replaced with a double surface condenser and Quickfit thermometer, while flushing the flask with nitrogen introduced via the septum. The top of the condenser was fitted with an oil bubbler and a static pressure of nitrogen maintained. BMS (0.091 mol) was added as well as a small quantity of of dimethyl sulphide (5cm^3) to help dissolve the solid. After lowering the flask into a hot oil bath, the solution was stirred and heated at 90°C for 20 hours taking samples at regular intervals. A white precipitate started to form after 1 hour and a large quantity of solid (8.5g when washed with dichloromethane and dried) formed overnight.

The solid produced from the reaction was dried in a nitrogen filled desiccator over phosphorus pentoxide.

Table 4.3 The reaction between polyhalomethanes and BMS followed at 90°C

Reaction No.	BMS (mol)	Polyhalomethane
(i)	0.038	$CFBr_3$ (10.25g, 0.038 mol, Lancaster Synthesis Ltd.)
(ii)	0.100	$CBrCl_3$ (9.9cm^3, 0.1 mol, Fluka Ltd.)
(iii)	0.100	$CBrCl_3$ (19.8cm^3, 0.20 mol)
(iv)	0.046	$CBrCl_3$ (4.5cm^3, 0.046 mol)[a]
(v)	0.022	CBr_2Cl_2 (5.28g, 0.022 mol, Lancaster Synthesis Ltd.)
(vi)	0.029	CBr_3Cl (8.25g, 0.029 mol)

a - The reaction was carried out using nitrobenzene (15.0cm^3) as solvent.

Bromide analysis was carried out using the Mohr titration method,[78] using the general technique described in section 4.2.3. The solid decomposed at 240°C and was only slightly soluble in water.

	Br(total)	Br^-	S	C	H	%
Calculated for $(CH_3)_2SCBr_4$:	81.2	20.3	8.1	9.1	1.5	
Found :	82.1	22.0	7.6	8.8	1.4	

4.5.3 Other haloalkane/BMS reactions

The reactions shown in Table 4.4 were carried out using the general procedure described in section 4.4.5. The solid produced from reaction (ii) analysed as follows;

	I	S	C	H	B	%
Calculated for $(CH_3)_3SI$:	62.2	15.7	17.6	4.4	0.0	
Found :	61.7	15.3	17.9	4.0	0.1	

4.5.4. BMS/triphenyl halomethane experiments

A $100cm^3$ three necked round bottomed flask equipped with a tap with septum, follower and stoppers was assembled hot and flushed with nitrogen. The weighed flask was transferred to a dry bag, the appropriate halide was added and the flask restoppered and reweighed. The flask was then fitted with a thermometer (with teflon seal) and condenser while flushing the flask through with nitrogen introduced via the septum. A static pressure of nitrogen was maintained by fitting an oil bubbler to the top of the condenser. The relevant solvent was added using the double-ended needle technique and the flask immersed in an ice bath. After cooling, BMS was added dropwise using a syringe,

keeping the stirred solution below 10°C. The reaction solution was then stirred for 2 hours in the ice bath. Table 4.5 summarises the reactions carried out using different halides and solvents.

Table 4.4 Haloalkane/BMS reactions

Reaction No.	T/°C	BMS(mol)	Haloalkane
(i)	22	0.0092	CI_4 (4.8g, 0.0092mol)[a]
(ii)	22	0.100	MeI (6.2cm^3, 0.100mol)[b]
(iii)	70	0.100	$SiCl_4$ (11.5cm^3, 0.100mol)
(iv)	90	0.093	$CHBr_3$ (8.1cm^3, 0.093mol)[c]
(v)	90	0.091	CH_2Br_2 (6.4cm^3, 0.091mol)[d]
(vi)	70	0.092	CH_2BrCl (6.0cm^3, 0.092mol)[d]
(vii)	50	0.100	$(CH_3)_3CCl$ (10.9cm^3, 0.100mol)
(viii)	75	0.100	$(CH_3)_3CBr$ (11.5cm^3, 0.100mol)
(ix)	75	0.100	$(CH_3)_2CHBr$ (9.4cm^3, 0.100mol)[d]
(x)	75	0.100	$CH_3(CH_2)_4Br$ (12.4cm^3, 0.100mol)[d]
(xi)	90	0.020	Pentabromotoluene (9.67g, 0.020mol)
(xii)	70	0.048	$(CH_3)_2CBrCl$ (5.0cm^3, 0.048mol)[d]
(xiii)	50	0.047	$CF_3CHBrCl$ (9.29g, 0.047mol)
(xiv)	90	0.036	$CBrCl_2CBrCl_2$ (11.82g, 0.036mol)
(xv)	90	0.100	CCl_3CCl_3 (24.4g, 0.100mol)[e]
(xvi)	90	0.100	As (xv) + 0.1g lauroyl peroxide
(xvii)	90	0.085	$CHCl_2CHCl_2$ (9.0cm^3, 0.085mol)
(xviii)	90	0.085	As (xvii) + 0.1g lauroyl peroxide

a - 10°C temperature rise, 1g of brown solid formed.

b - 30°C temperature rise, 5g of white solid formed.

c - Stabilised with diphenylamine.

d - Small amount of solid formed overnight (less than 0.5g)

e - Dimethyl Sulphide (10cm^3) added in order to dissolve solid.

Table 4.5 BMS/triphenyl halomethane experiments

Reaction No.	BMS(mol)	Halomethane		Solvent/cm^3	
		Ph_3CCl	Ph_3CBr	CH_2Cl_2	PhH
(i)	0.048	13.40g, 0.048mol	—	—	25[a]
(ii)	0.017	9.70g, 0.035mol	—	—	25[a]
(iii)	0.036	10.10g, 0.036mol	—	25[b]	—
(iv)	0.035	19.37g, 0.070mol	—	25	—
(v)	0.028	—	8.91g,0.028mol	25	—
(vi)	0.011	—	7.23g,0.022mol	25	—

a - Boron trichloride dimethyl sulphide complex formed was dissolved using CH_2Cl_2 ($15cm^3$).

b - Reaction also carried out allowing the temperature of the solution to rise to 40°C.

4.6 PREPARATION OF DIALKYL AND CYCLIC ALKYL CHLOROBORANES

4.6.1 Hydroboration of alkenes using monochloroborane dimethyl sulphide complex, prepared using BMS and tetrachloromethane

A 500cm^3 two-necked round-bottomed flask equipped with a 250cm^3 pressure equalising dropping funnel with rubber septum, teflon follower and condenser fitted with an oil bubbler was assembled hot and left to cool under nitrogen. A slight positive pressure of nitrogen was maintained to prevent suck-backs during the hydroboration. The flask was lowered in an ice bath and charged with monochloroborane solution (prepared from 0.10 moles of BMS and tetrachloromethane as described in section 4.4.1) introduced via the septum and funnel using the double-ended needle technique. Using the same method, deoxygenated dichloromethane (150cm^3) was introduced into the flask and left for 15 minutes to cool. The appropriate liquid alkene (sufficient for hydroboration by all boranes present in the mixture) was introduced into the dropping funnel using a measuring cylinder and double-ended needle. The solution was stirred and the alkene added slowly over a period of 15 minutes. After removing the ice bath the solution was stirred at room temperature for 2 hours to ensure completion of the reaction. The solvent and dimethyl sulphide were removed under vacuum using a protected water aspirator after replacing the condenser and dropping funnel with a tap and stopper. The crude dialkyl chloroborane was transferred to a dry vacuum distillation apparatus (equipped with a tap with septum)

using a double-ended needle. The distillations were carried out using a protected manostat connected to a rotary oil vacuum pump equipped with two cold traps. The hydroborations are summarised in Table 4.6.

4.6.2 Hydroboration of 1,5 cyclooctadiene

A 500cm^3 two-necked round-bottomed flask equipped with a 100cm^3 pressure equalising dropping funnel (with rubber septum) , teflon follower and condenser (fitted with and oil bubbler) was assembled hot and cooled under nitrogen. Monochloroborane solution (0.10mol) was added to 200cm^3 of deoxygenated dichloromethane and the solution was cooled to 0 °C in an ice bath. Cyclooctadiene (21.0cm^3, 0.17mol, distilled at 36mm Hg over lithium aluminium hydride) was added dropwise over a period of 15 minutes. The ice bath was removed and the solution stirred for 2 hours at room temperature. After pumping off the solvent, the resulting viscous liquid was heated to 140 °C (using a condenser to prevent the loss of dimethyl sulphide) for 1 hour in an oil bath. The crude product was recrystallised twice from hexane containing dimethyl sulphide (5cm^3 in 200cm^3 of hexane) giving 16.6g (76% yield) of crystalline B-Cl-9-borabicyclo[3.3.1] nonane dimethyl sulphide complex.

Table 4.6 Preparation of dialkyl and cyclic alkyl chloroboranes

Reaction No.	BH_2Cl (mol)	Alkene
(i)	0.07[a]	Pent-1-ene ($30cm^3$, 0.27mol)
(ii)	0.07	2-methyl-pent-1-ene($33cm^3$, 0.27mol)
(iii)	0.04	4,4-dimethyl pent-1-ene (Fluka, 14.7g, 0.15mol)
(iv)	0.07	Oct-1-ene ($42cm^3$, 0.27mol)
(v)	0.07	2-methyl-1,3-butadiene ($12.3cm^3$, 0.12mol)

a - A typical monochloroborane solution prepared from 0.1 mol of BMS and tetrachloromethane contains 0.07mol of monochloroborane.

EXPERIMENTAL DETAILS FOR CHAPTER THREE

4.7 DIALKYLCHLOROBORANE/ALDEHYDE EXPERIMENTS

4.7.1 Experiments investigating the reaction between dialkylchloroboranes and aldehydes/ketones

A $100cm^3$ two-necked round-bottomed flask equipped with a rubber septum, teflon follower and condenser (fitted with an oil bubbler) was assembled hot and left to cool under nitrogen. The dialkylchloroborane (prepared as described in section 4.6.1) and dichloromethane ($30cm^3$) were introduced into the flask and the contents were cooled in an ice bath. The appropiate aldehyde was added dropwise using a syringe over a period of 15 minutes. After removing the ice bath the contents of the flask were stirred at room temperature for 2 hours. Samples for infra-red and n.m.r. spectroscopy were taken at regular intervals during the reactions. The solvent and volatiles were removed under vacuum using a protected water pump. These experiments are summarised in Table 4.7.

4.7.2 Methanolysis of reaction products from various dipentylchloroborane/aldehyde reactions

The procedure described in section 4.7.1 was followed for the aldehydes shown in Table 4.8. After removal of the solvent and volatiles the product(s) was transferred to an apparatus similar to that described in section 4.7.1. Dichloromethane ($30cm^3$) was added and the contents brought to $0\,^{\circ}C$ in an ice bath. Methanol (enough to esterify all hydrolysable chlorine) was added dropwise using a syringe

Table 4.7 Reactions between dialkylchloroboranes and aldehydes/ketones.

Reaction No.	R_2BCl R(mol)	Aldehyde/ketone
(i)	n-C_5H_{11} (0.043)	PhCHO ($4.3cm^3$, 0.043mol)
(ii)	n-C_5H_{11} (0.038)	PhCHO ($7.7cm^3$, 0.076mol)
(iii)	n-C_5H_{11} (0.045)	p-NO_2-PhCHO(6.8g, 0.045mol)
(iv)	n-C_5H_{11} (0.040)	p-NMe_2-PhCHO(5.97g,0.040mol)
(v)	n-C_5H_{11} (0.046)	CH_3CHO (2.0g, 0.046mol)
(vi)	n-C_5H_{11} (0.046)	CCl_3CHO ($4.4cm^3$, 0.046mol)
(vii)	n-C_5H_{11} (0.046)	CBr_3CHO ($4.8cm^3$, 0.046mol)
(viii)	n-C_5H_{11} (0.044)	$(CH_3)_3CCHO$ ($4.8cm^3$,0.044mol)
(ix)	n-C_5H_{11} (0.046)	$(CH_3)_2CHCHO$ ($4.2cm^3$,0.046mol)
(x)	n-C_5H_{11} (0.044)	$CH_3(CH_2)_6CHO$($6.9cm^3$,0.044mol)
(xi)	n-C_5H_{11} (0.044)	$CH_3(CH_2)_2CHO$($3.9cm^3$,0.044mol)
(xii)	n-C_5H_{11} (0.045)	$CH_3CH{=}CHCHO$ ($3.7cm^3$,0.045mol)
(xiii)	n-C_5H_{11} (0.014)	$C_6H_{11}CHO$ (cyclohexylcarboxaldehyde, $1.7cm^3$, 0.014mol)
(xiv)	n-C_5H_{11} (0.036)	Ph_2CO (6.63g, 0.036mol)
(xv)	n-C_5H_{11} (0.040)	$(CH_3)_2CO$ ($2.9cm^3$, 0.040mol)
(xvi)	$CH_3(CH_2)_2CH(CH_3)$-CH_2 (0.040)	$CH_3(CH_2)_6CHO$($6.3cm^3$,0.040mol)
(xvii)	n-C_8H_{17} (0.042)	PhCHO ($4.3cm^3$, 0.042mol)
(xviii)	Cl (i.e.BCl_3,0.05)	PhCHO ($7.6cm^3$, 0.075mol)

Table 4.8 Methanolysis of reaction products from the dipentylchloroborane/aldehyde experiments

Reaction No.	$(n\text{-}C_5H_{11})_2BCl$ /mol	Aldehyde (mol)	Methanol
(i)	0.043	PhCHO (0.043)	$1.7cm^3$, 0.043mol
(ii)	0.043 [a]	PhCHO (0.043)	$1.7cm^3$, 0.043mol
(iii)	0.043 [b]	PhCHO (0.043)	$1.7cm^3$, 0.043mol
(iv)	0.044	$(CH_3)_3CCHO$ (0.044)	$1.8cm^3$, 0.044mol
(v)	0.046	CCl_3CHO (0.046)	$1.9cm^3$, 0.046mol

a - Initial reaction mixture left to react for 20 hours before methanolysis.

b - Initial reaction mixture left to react for 40 minutes before methanolysis. After removal of solvent the reaction products were distilled at 0.1 mm Hg.

over a period of 10 minutes. After stirring for fifteen minutes the hydrogen chloride, excess methanol and dichloromethane were removed under vacuum using a protected water pump.

4.7.3 Analysis of alkenes from the dialkylchloroborane/aldehyde reactions using ^{1}H n.m.r. spectroscopy

To the reaction mixture described in section 4.7.1 before solvent removal, benzene ($1.0cm^3$) or dichloromethane ($2.0cm^3$) was added to act as an internal standard. By comparison of the integrals from the standard and alkene, the yield of alkene was obtained. The methylene group adjacent to the olefinic protons (allylic) which appears as a quartet proved suitable for this purpose.

4.7.4 Volumetric analysis of alkenes from the dialkylchloroborane/aldehyde reactions

The solvent and alkene stripped from the dialkylchloroborane/aldehyde reaction were treated with bromine ($4.0cm^3$) . Excess bromine (not reacted with the alkene) was converted to bromide by the addition of potassium iodide (25g) thus liberating iodine. The iodine was titrated with a solution of sodium thiosulphate (2.00 mol dm^{-3}), using starch solution as an indicator. The amount of pentene contained in the cold trap (removed from the reaction solution) was then calculated.

4.8 REACTIONS BETWEEN SUBSTITUTED BENZALDEHYDES AND DIALKYLCHLOROBORANES FOLLOWED USING VARIABLE TEMPERATURE N.M.R. SPECTROSCOPY

All experiments were performed using a Jeol FX90Q fourier transform n.m.r. spectrometer with Jeol software and variable temperature accessories. The operating frequencies were 89.56 MHz for ^{1}H and 28.7 MHz for ^{11}B. The operating temperatures were checked using a 10mm n.m.r. tube containing an alcohol thermometer (-50 to +30°C) in deuterated chloroform, leaving the sample in the nitrogen stream for 5 minutes to reach thermal equilibrium.

4.8.1 General procedure

The apparatus shown in Fig.4.9 was assembled hot, evacuated and then filled with nitrogen. The dialkyl chloroborane was introduced using a weighed syringe with a 12 inch needle, the syringe being reweighed after the addition. After addition of the solvent and replacement of the septum (under positive pressure of nitrogen) the solution was deoxygenated using the freeze-thaw technique. The aldehyde was added to the frozen solution using a precision gas-tight syringe ($0.5cm^3$) equipped with a 12 inch needle. After freezing the aldehyde, the septum was replaced and the tube evacuated. After sealing the tube it was stored in dry ice until needed. After checking the temperature of the probe, the contents of the tube were allowed to liquefy and after briefly shaking the tube it was inserted into the probe. The n.m.r. spectrum was recorded every 2 minutes and the sample was left at each temperature for at

4.8.2 The reaction between benzaldehyde and dipentylchloroborane

The procedure described above was followed using dipentylchloroborane (0.99g, 5.3×10^{-3}mol), benzaldehyde ($0.53cm^3$, 5.3×10^{-3}mol) and deuterated chloroform ($1.0cm^3$, Aldrich 99.8%). The temperature stages at which the reaction was observed were -40, -10, 0, 10, 17, 30, 40, and 50°C. The experiment was performed for both ^{1}H and ^{11}B nuclei.

4.8.3 The reaction between excess benzaldehyde and dipentylchloroborane

The procedure described in section 4.8.2 was followed using dipentylchloroborane (0.86g, 4.6×10^{-3}mol), benzaldehyde ($0.94cm^3$, 9.2×10^{-3}mol) and deuterated chloroform ($1.0cm^3$).

4.8.4 Kinetic order and rate constants of aldehyde/dialkylchloroborane reactions determined using ^{1}H n.m.r. spectroscopy

The general procedure described earlier was followed, but before placing the tube inside the probe it was brought to 0°C in an ice bath. After placing the tube inside the probe (the temperature of which being carefully checked) the stopclock was started and ^{1}H n.m.r. spectra were recorded at regular intervals. It was found that a 10mm tube containing deuterated chloroform ($3cm^3$) and a thermometer at 0°C took 3 minutes to reach 16°C in the probe. Thus only spectra recorded after three minutes were used in subsequent calculations. The concentration of alkene was determined by comparing the integral heights of the aromatic protons to the allylic alkene protons. Table 4.9

shows the various reagents and conditions used. The infinity value for the pentene concentration was obtained by warming the sample at room temperature for 5 minutes then replacing the sample back into the probe.

Table 4.9 Dialkylchloroborane/aldehyde kinetic experiments

Reaction No.	R_2BCl R, alkyl group	Aldehyde	$CDCl_3$ /cm^3	T/°C
(i)	n-C_5H_{11} (0.98g, 5.2×10^{-3}mol)	PhCHO (0.53cm^3, 5.2×10^{-3}mol)	1.00	9.0
(ii)	n-C_5H_{11} (0.91g, 4.9×10^{-3}mol)	PhCHO (0.49cm^3, 4.9×10^{-3}mol)	1.00	9.0
(iii)	n-C_5H_{11} (1.34g, 7.1×10^{-3}mol)	PhCHO (0.25cm^3, 2.5×10^{-3}mol)	1.50	9.0
(iv)	n-C_5H_{11} (1.00g, 5.3×10^{-3}mol)	PhCHO (0.18g, 1.8×10^{-3}mol)	1.40	9.0
(v)	n-C_5H_{11} (0.91g, 4.9×10^{-3}mol)	PhCHO (0.49cm^3, 4.9×10^{-3}mol)	1.00	7.0
(vi)	n-C_5H_{11} (0.89g, 4.7×10^{-3}mol)	PhCHO (0.48cm^3, 4.7×10^{-3}mol)	2.00	16.0
(vii)	n-C_5H_{11} (0.90g, 4.8×10^{-3}mol)	p-MeO-PhCHO (0.58cm^3, 4.8×10^{-3}mol)	1.00	9.0
(viii)	n-C_5H_{11} (0.42g, 2.2×10^{-3}mol)	p-NO_2-PhCHO [a] (2.2×10^{-3}mol)	—	9.0

cont.

a - 2.46cm^3 of aldehyde solution (0.900 mol Lit^{-1} in $CDCl_3$)

Table 4.9 continued.

Reaction No.	R_2BCl R, alkyl group	Aldehyde	$CDCl_3$ /cm^3	T/°C
(ix)	n-C_5H_{11} (0.76g, $4.0x10^{-3}$mol)	p-Cl-PhCHO [b] ($4.0x10^{-3}$mol)	—	9.0
(x)	$CH_3(CH_2)_2CH(CH_3)CH_2$ (0.92g, $4.2x10^{-3}$mol)	PhCHO ($0.43cm^3$, $4.2x10^{-3}$mol)	1.00	9.0
(xi)	n-C_8H_{17} (1.37g, $5.0x10^{-3}$mol)	PhCHO ($0.51cm^3$, $5.0x10^{-3}$mol)	1.00	9.0
(xii)	n-C_5H_{11} (1.00g, $5.3x10^{-3}$mol)	PhCHO ($0.54cm^3$, $5.3x10^{-3}$mol)	1.00[c]	9.0

b - $1.96cm^3$ of aldehyde solution (2.050 mol Lit^{-1} in $CDCl_3$).

c - CD_2Cl_2 used instead of $CDCl_3$.

APPENDIX I

A.I DETAILS OF KINETIC INVESTIGATION OF THE BMS / TETRACHLOROMETHANE REACTION

A.I.1 Reaction between BMS and tetrachloromethane at 50°C

Each kinetic run was performed three times and the results from three typical runs are shown on Table A.I.1. The concentration of the borane species were derived using the ^{11}B n.m.r ratios and initial BMS concentratios. Figure A.I.1 shows the MCBS growth curve for the equimolar reaction (no added solvent). Figures A.I.2, A.I.3 and A.I.4 show the plots of data according to second order and pseudo first order reactions.

A.I.2 Reaction between BMS and tetrachloromethane at 80°C

The reaction was carried out using neat conditions and the results are shown on Table A.I.2. Figure A.I.5 shows the growth curves for MCBS and DCBS for the first seven hours of reaction.

Initial inspection of the results suggests that the rate of formation of DCBS cannot be greater than 0.037/1.77 that of MCBS. Therefore the reaction sequence,

$$BH_3 \xrightarrow{k_1} BH_2Cl \xrightarrow{k_2} BHCl_2 \xrightarrow{k_3} BCl_3$$

has rate constants $k_1 > k_2 > k_3$.

(i) Determination of k_1-

Since the initial reactant concentrations are equal, then we can estimate k_1 for the proposed second order react-

Table A.I.1 Typical results of the kinetic investigation into the reaction between BMS and tetrachloromethane at 50°C.

(i) Equimolar reaction $(BMS)_o = 4.84$ mol dm^{-3}
$(CCl_4)_o = 4.84$ mol dm^{-3}

Time x10^{-2}/s	$(BMS)_t$/ mol dm^{-3}	$(MCBS)_t$/ mol dm^{-3}	$((BMS)_t^{-1} - (BMS)_o^{-1}) \times 10^3$ / dm^{3}mol^{-1}
0	4.84	0.00	0.0
36	4.77	0.07	3.0
72	4.68	0.16	7.1
144	4.45	0.38	18.1
210	4.28	0.56	27.0
264	4.17	0.67	33.2
318	4.06	0.78	39.7

(ii) Excess tetrachloromethane reaction

$(BMS)_o = 2.51$ mol dm^{-3}
$(CCl_4)_o = 7.51$ mol dm^{-3}

Time x10^{-1}/s	$(BMS)_t$/ mol dm^{-3}	$(MCBS)_t$/ mol dm^{-3}	ln $(BMS)_t$
0	2.51	0.00	0.92
498	2.47	0.05	0.90
1698	2.34	0.17	0.85
2718	2.14	0.37	0.76
7238	1.55	0.96	0.44
9048	1.37	1.14	0.32

Table A.I.1 (continued)

(iii) Excess BMS reaction $(BMS)_o = 7.05$ mol dm^{-3}
$(CCl_4)_o = 2.33$ mol dm^{-3}

Time x 10^{-1}/s	$(BMS)_t$/ mol dm^{-3}	$(MCBS)_t$/ mol dm^{-3}	$\ln((CCl_4)_o - (MCBS)_t)$
0	7.05	0.00	0.85
498	6.91	0.14	0.78
1698	6.49	0.56	0.57
2718	6.31	0.74	0.46
8238	5.33	1.72	-0.49
9948	5.21	1.84	-0.71

Figure A.I.1 Plot showing growth of MCBS during the equimolar reaction between BMS and tetrachloromethane at 50°C

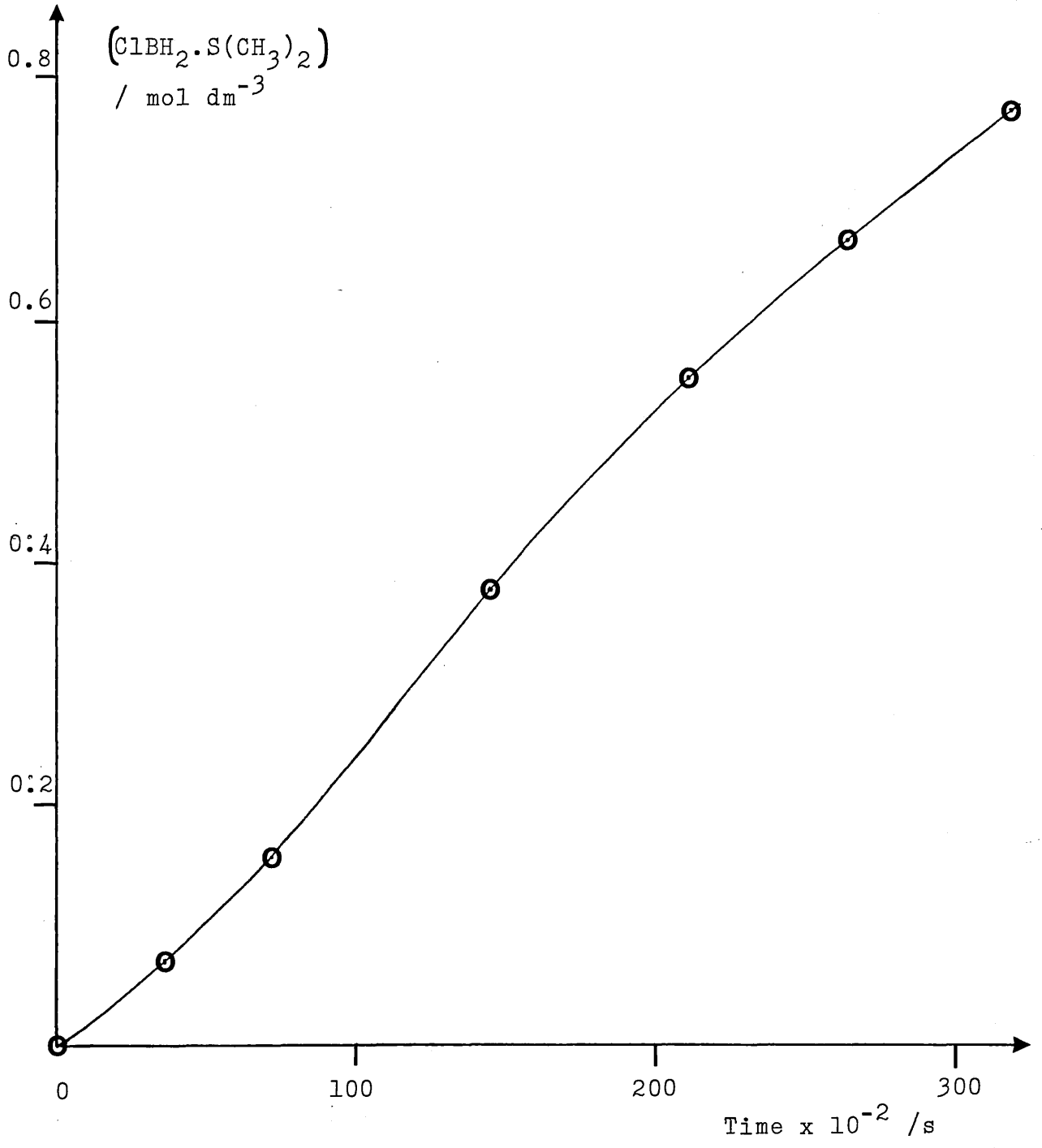


Figure A.I.2 Second order plot for the equimolar BMS / tetrachloromethane reaction at 50°C

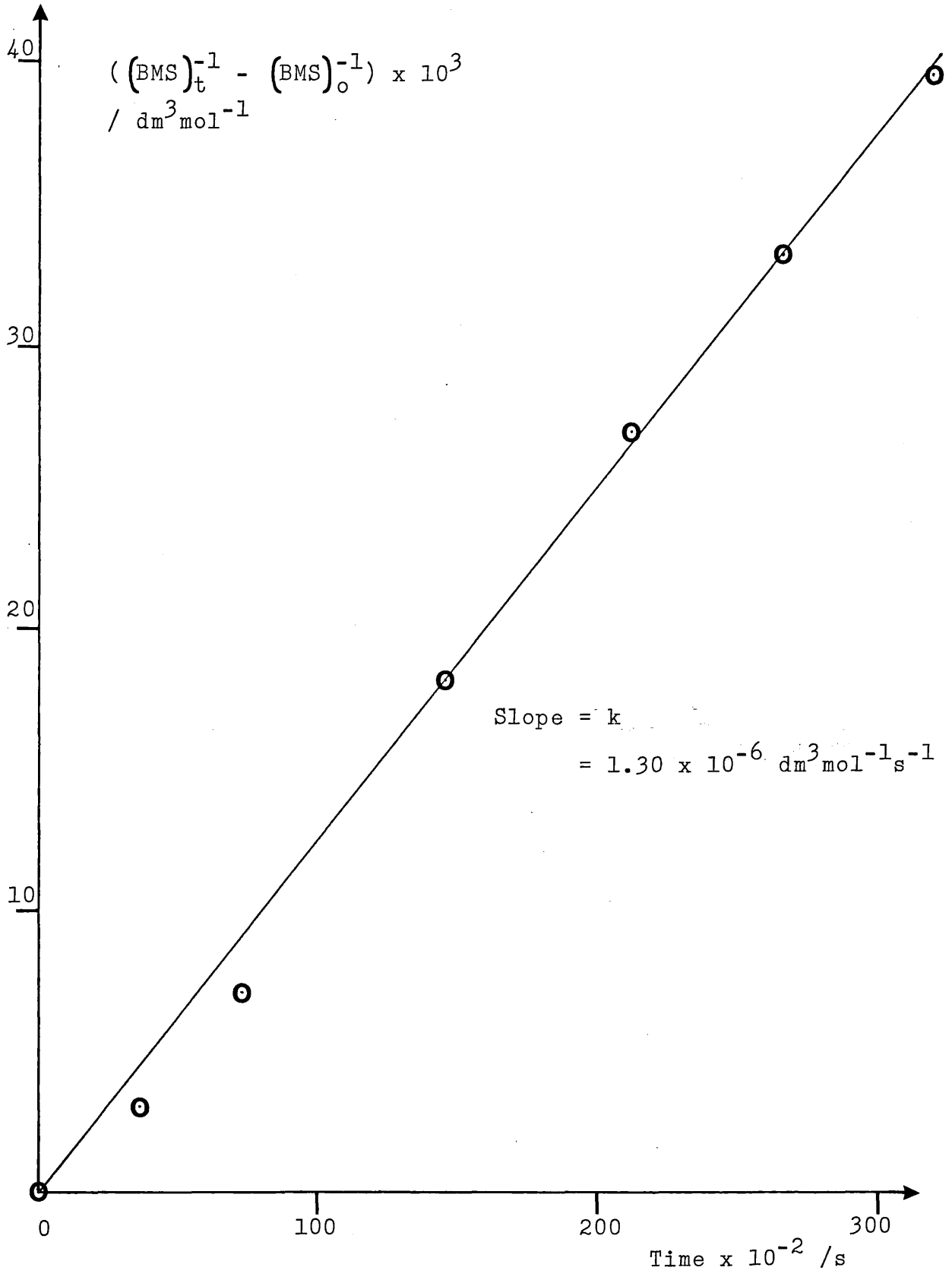


Figure A.I.3 Pseudo first order plot for the reaction between BMS and excess tetrachloromethane at 50 °C

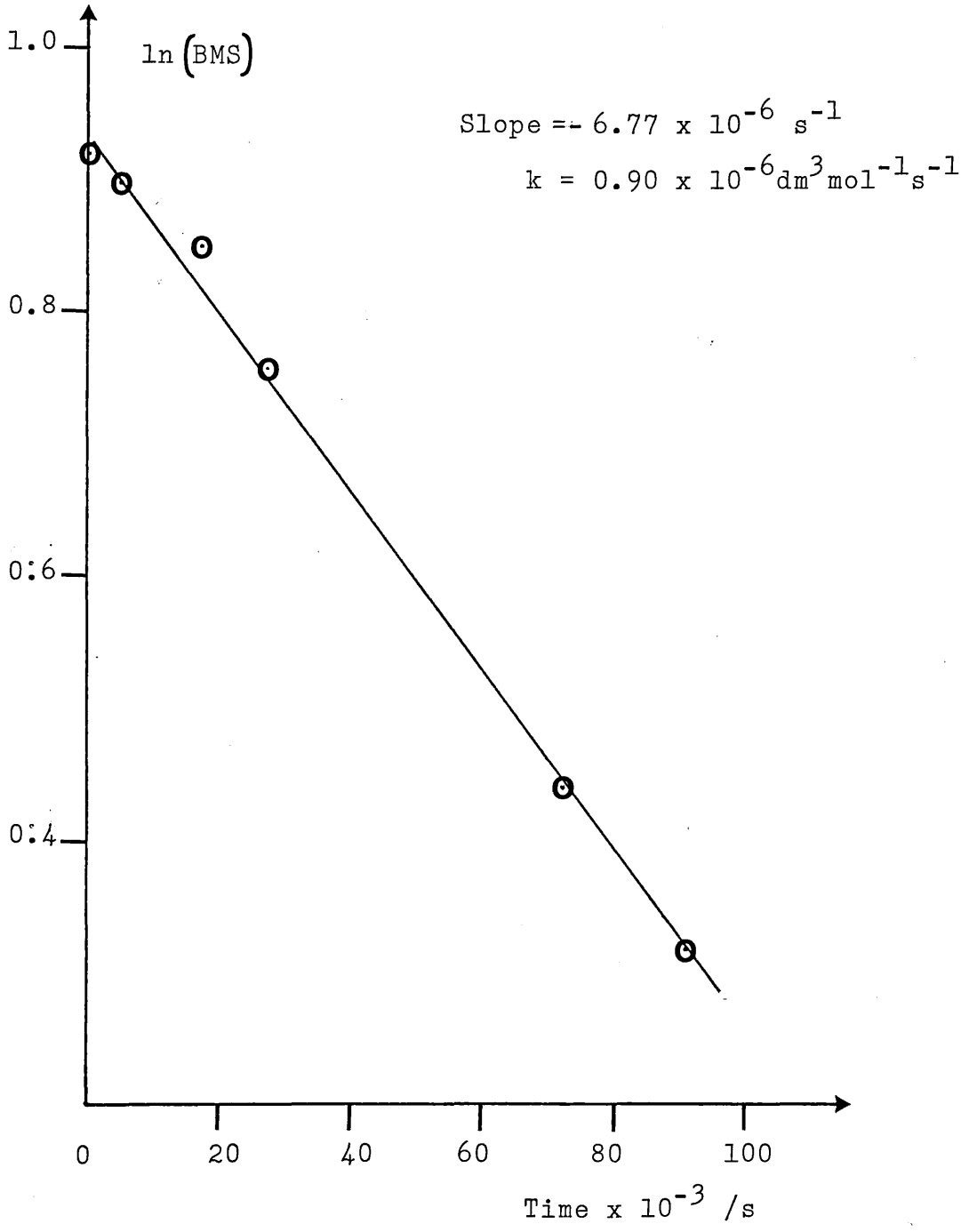


Figure A.I.4 Pseudo first order plot for the reaction between tetrachloromethane and excess BMS at 50 °C

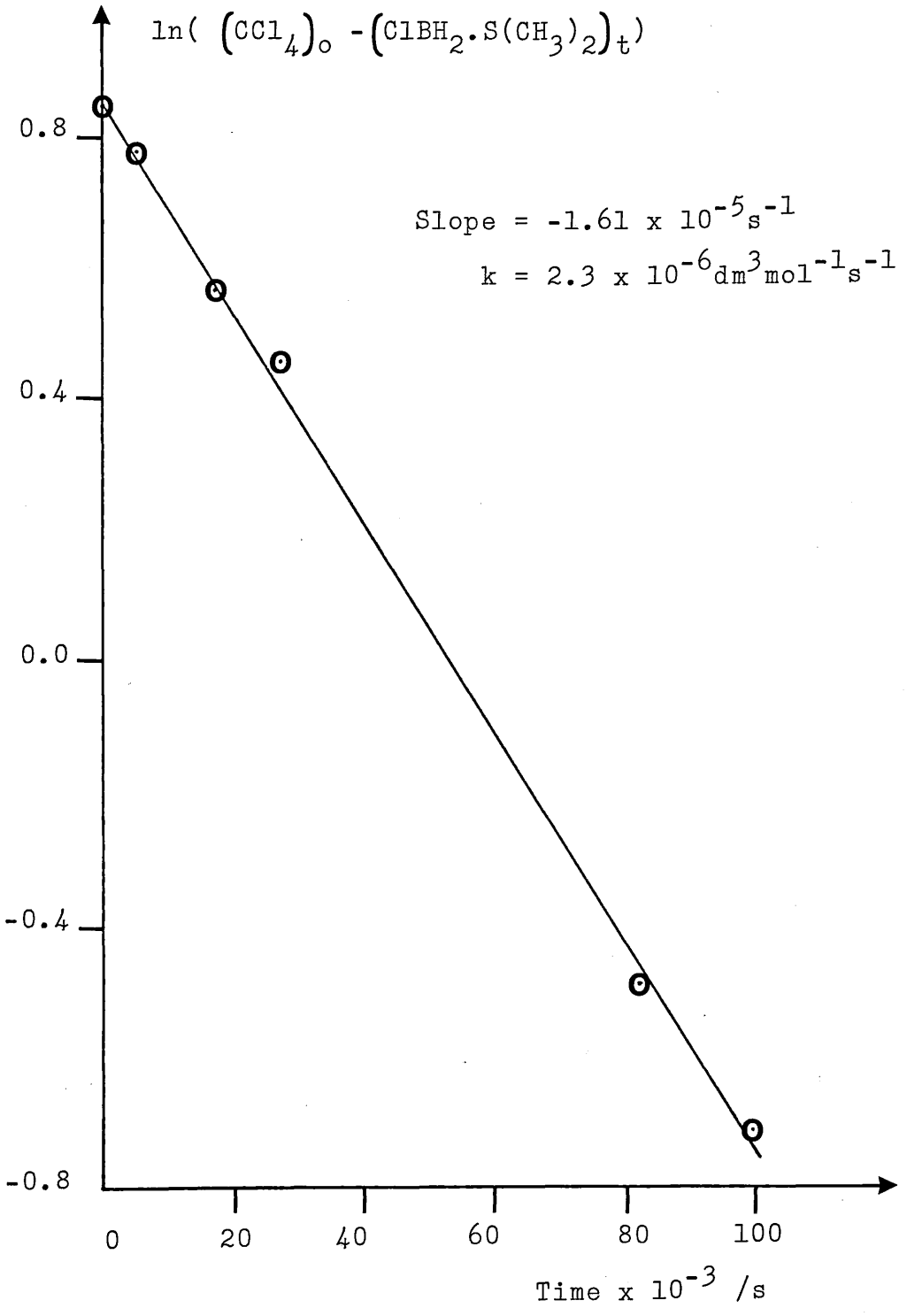
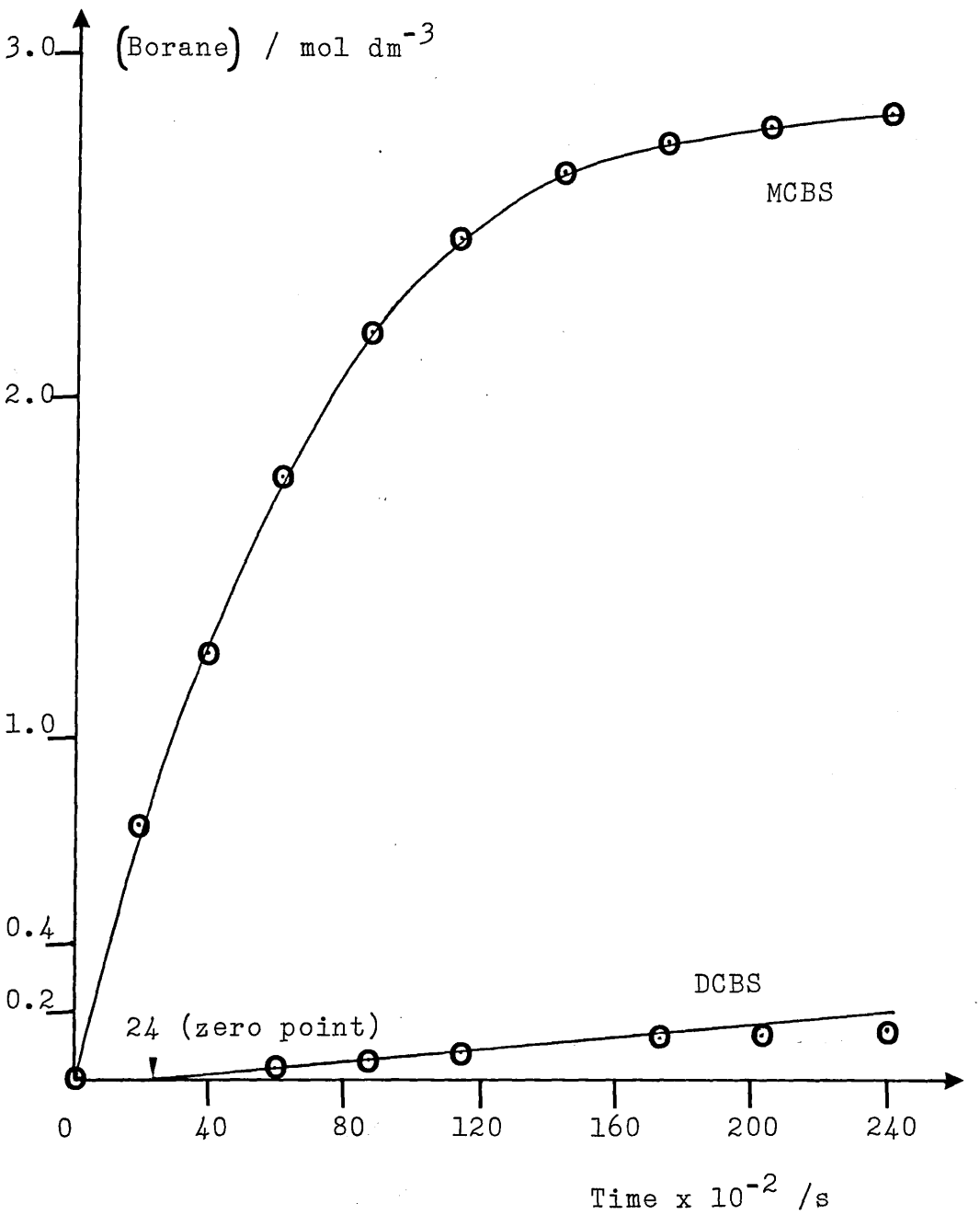


Table A.I.2 Results of kinetic investigation of BMS /tetrachloromethane reaction at 80°C

Time x 10^{-2} s	$(BMS)_t$/ mol dm^{-3}	$(MCBS)_t$/ mol dm^{-3}	$(DCBS)_t$/ mol dm^{-3}
0	4.66	0.00	0.00
18	3.91	0.75	0.00
39	3.40	1.26	0.00
60	2.89	1.77	0.037
87	2.42	2.19	0.065
114	2.10	2.47	0.093
144	1.86	2.66	0.121
174	1.82	2.75	0.126
204	1.72	2.80	0.140
240	1.68	2.84	0.145
720	1.12	3.26	0.280
3480	0.42	3.45	0.792

$$(BMS)_o = (CCl_4)_o = 4.66 \text{ mol } dm^{-3}$$

Figure A.I.5 Graph showing the growth of chloroboranes during the BMS / tetrachloromethane reaction at 80°C



ion using the initial rates.

Time x 10^{-2}/s	$(BMS)_t^{-1} - (BMS)_o^{-1} = k_1 t$	k_1/dm^{3}mol^{-1}s^{-1}
18	1/3.91 - 1/4.66	2.3 x 10^{-5}
39	1/3.40 - 1/4.66	2.0 x 10^{-5}
60	1/2.89 - 1/4.66	2.2 x 10^{-5}

The rate constants are fairly close and give 2.2 ± 0.1 x 10^{-5} dm^{3}mol^{-1}s^{-1} as a good value of k_1.

(ii) Determination of k_2-

Figure A.I.5 shows the graph of $(DCBS)_t$ against time and the initial points are extrapolated back to the time where the concentration appears to become zero. This gives a time of 2400 seconds. The first few points of the graph follow a shallow straight line. Therefore over small portions of the growth curves from 2400 seconds we can make the following approximation,

$$\frac{d(BHCl_2)}{dt} = k_2 (BH_2Cl)(CCl_4) \approx \frac{\Delta(BHCl_2)}{\Delta t}$$

This is valid if DCBS is formed only from MCBS and that none is produced when the BMS concentration is at a maximum. Between t = 2400 and 6000 seconds,

$$(BH_2Cl)_{average} = \frac{0.90 + 1.77}{2} = 1.34 \text{ mol dm}^{-3}$$

$$(CCl_4)_{average} = (CCl_4)_o - (BH_2Cl)_{av.} - (BHCl_2)_{av.}$$

$$= 4.66 - 1.34 - 0.02 = 3.30 \text{ mol dm}^{-3}$$

$$\frac{\Delta(BHCl_2)}{\Delta t} = \frac{0.037}{3600} = k_2 \times 1.34 \times 3.3$$

$$k_2 = 2.3 \times 10^{-6}\ dm^3 mol^{-1} s^{-1}.$$

Using the same method;

between 6000 and 8700 s , $k_2 = 2.0 \times 10^{-6}\ dm^3 mol^{-1} s^{-1}$

8700 and 11400 s, $k_2 = 2.0 \times 10^{-6}$

11400 and 14400 s, $k_2 = 1.8 \times 10^{-6}$

14400 and 17400 s, $k_2 = 0.3 \times 10^{-6}$

17400 and 20400 s, $k_2 = 1.0 \times 10^{-6}$

The first four values for k_2 are fairly close and these give us a mean k_2 of $2.0 \pm 0.2 \times 10^{-6}\ dm^3 mol^{-1} s^{-1}$. To test the validity of the rate constants, they were inserted into the original kinetic equations in order to generate borane concentrations and then compared with the observed values. The results are shown on Table A.I.3. The calculated yields of DCBS assumes no consumption of MCBS in the calculations. This will also effect the final yield of MCBS. More refined calculations would provide a closer match. The calculated and observed yields are displayed graphically on Figures A.I.6, A.I.7, and A.I.8 for easier comparison. The same time scale is used for convenience (up to 24000 s). The MCBS growth curves are very similar, and while the calculated curve diverges slightly after 18000 s, the calculated concentration after 348000 s (4 days) heating is only 9% lower than the observed value of MCBS. The DCBS growth curves match well initially but diverge after 14000 s. However even after four days, the concentration remains at a reasonable level (observed 0.8, calculated 1.4 mol dm^{-3}).

The consistency of the initial results and sensible long term values using fairly unsophisticated calculations

Figure A.I.6 Graph showing observed and calculated MCBS concentrations during the BMS / tetrachloromethane reaction at 80°C

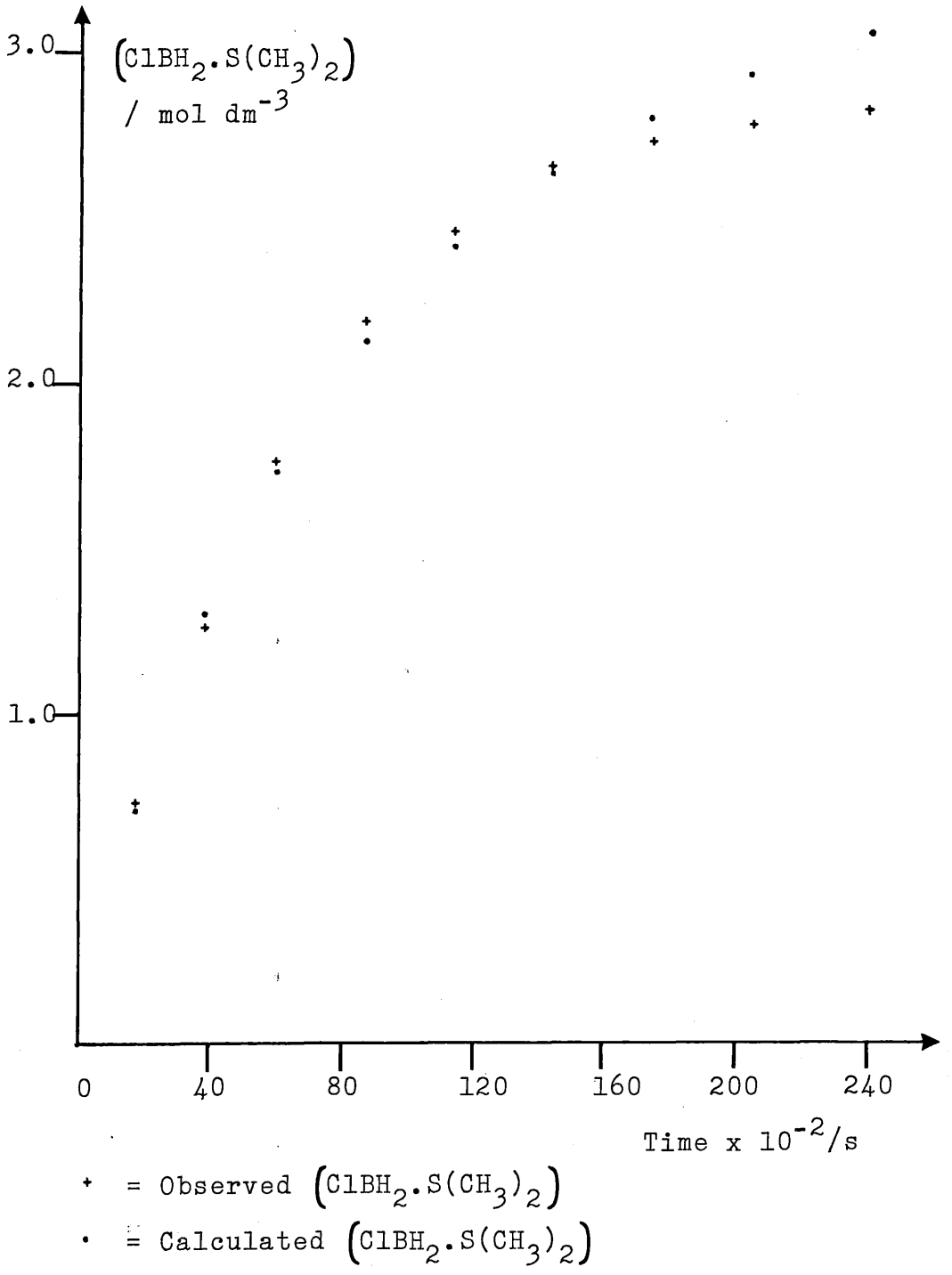


Figure A.I.7 Graph showing observed and calculated DCBS concentrations during the BMS / tetrachloromethane reaction at 80°C

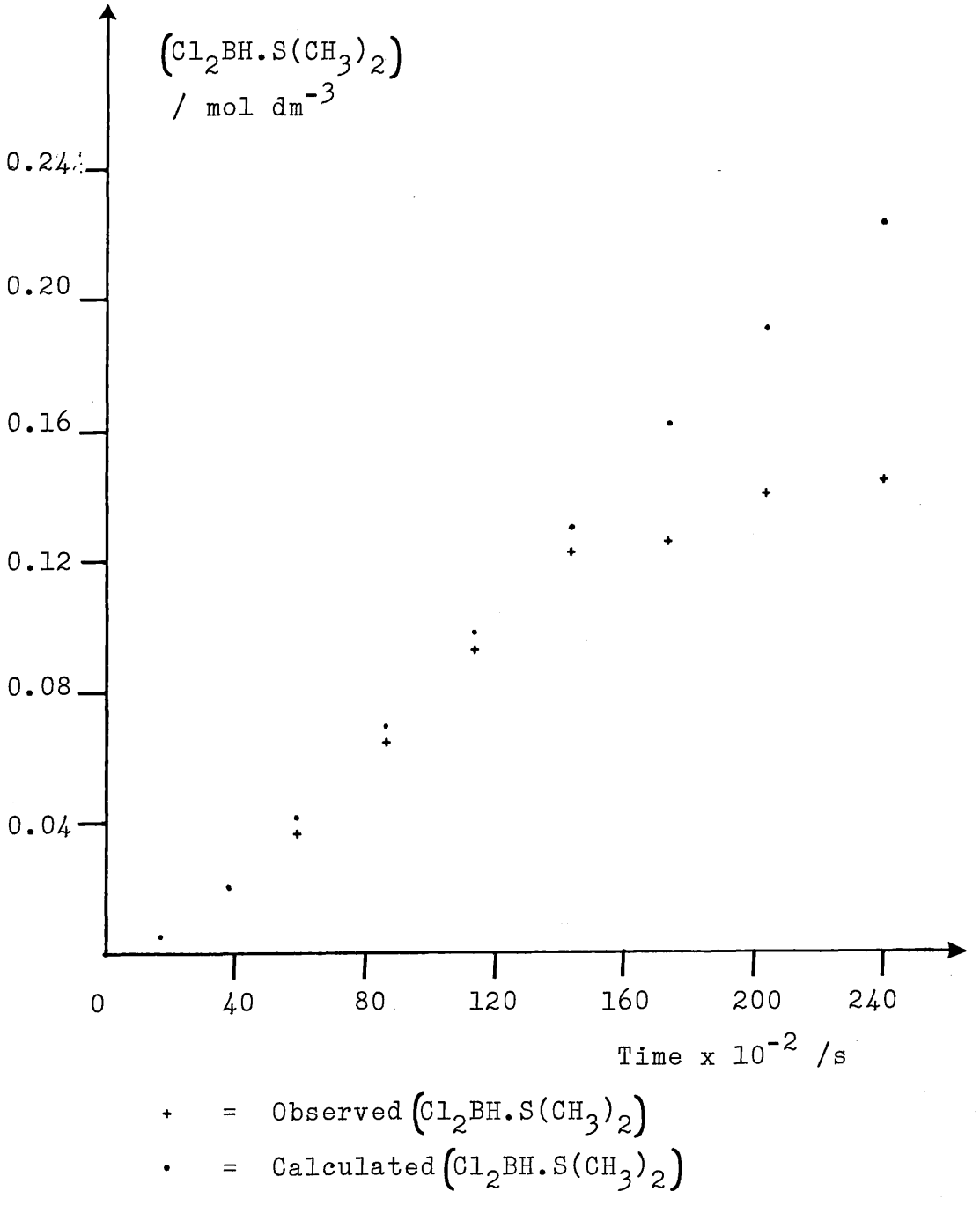


Figure A.I.8 Graph showing the observed and calculated BMS concentrations during the BMS / tetrachloromethane reaction at 80°C

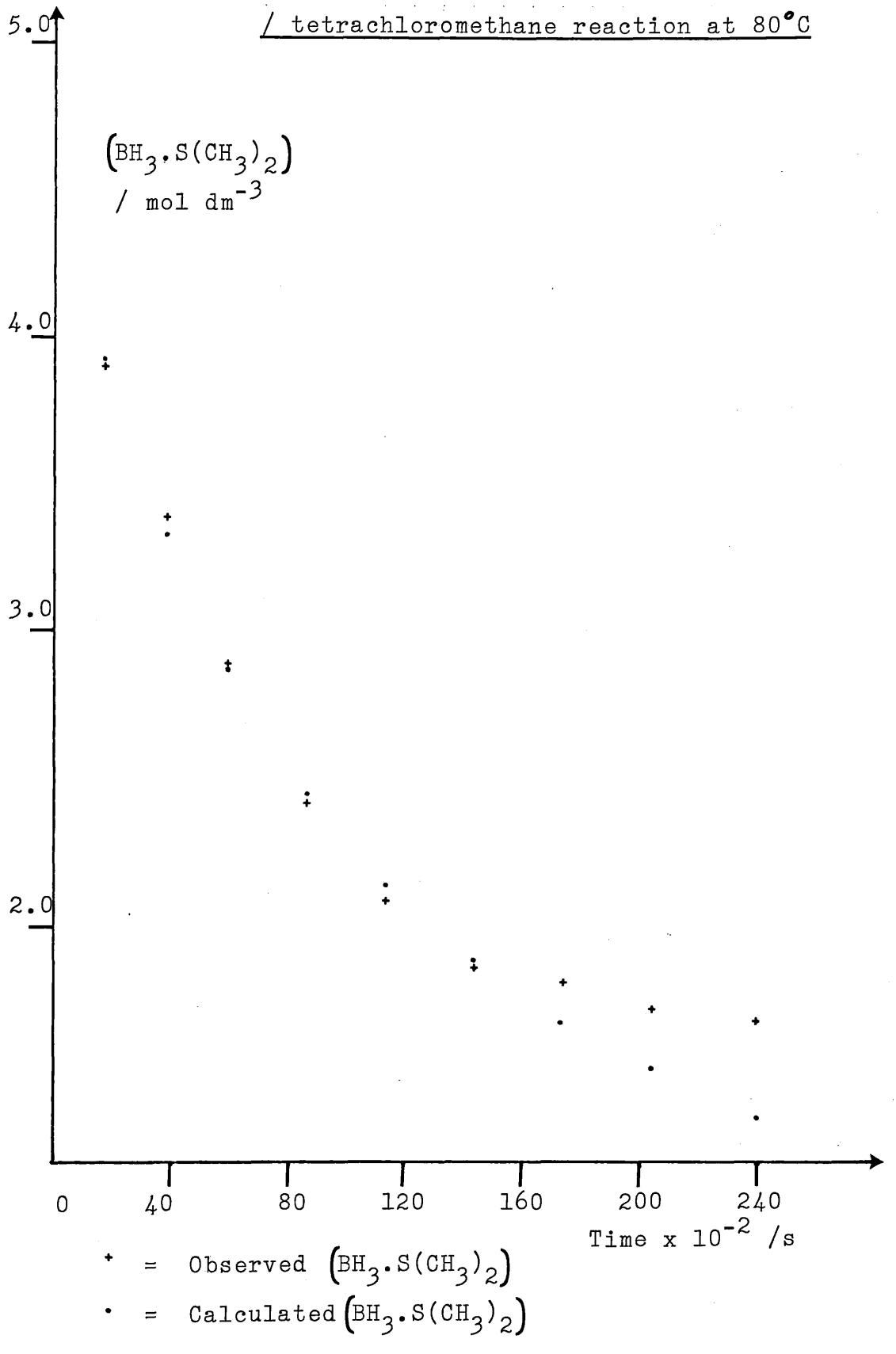


Table A.I.3 Observed and calculated concentrations of boranes produced during the BMS / tetrachloromethane reaction

Time x 10^{-2}/s	$(BMS)_t$ Found	$(BMS)_t$ Calc.	$(MCBS)_t$ Found	$(MCBS)_t$ Calc.	$(DCBS)_t$/mol dm^{-3} Found	$(DCBS)_t$/mol dm^{-3} Calc.
0	4.66	4.66	0.00	0.00	0.00	0.00
18	3.91	3.93	0.75	0.72(0.73)[a]	0.00	0.006
39	3.40	3.33	1.26	1.31(1.33)	0.00	0.021
60	2.89	2.88	1.77	1.74(1.78)	0.037	0.042
87	2.42	2.46	2.19	2.13(2.20)	0.065	0.070
114	2.10	2.15	2.47	2.41(2.51)	0.093	0.099
144	1.86	1.88	2.66	2.65(2.78)	o.121	0.131
174	1.82	1.67	2.75	2.83(2.99)	0.126	0.162
204	1.72	1.51	2.80	2.96(3.15)	0.140	0.191
240	1.68	1.35	2.84	3.09(3.31)	0.145	0.224
720	1.12	0.56	3.26	3.54(4.10)	0.280	0.564
3480	0.42	0.13	3.45	3.14(4.53)	0.792	1.386

a-- The figures in brackets do not take subsequent loss of MCBS by forming DCBS into account.

imply that the values for k_1 and k_2 are reasonable.

APPENDIX II

A.II ^{11}B N.M.R SPECTROSCOPIC DATA

Of the different spectroscopic methods used during this work, ^{11}B n.m.r has proved to be the most informative. While not providing unambiguous identification of new compounds by itself, it is the only method for analysing haloborane mixtures. The spectra were recorded mainly at Kings College, London using a Bruker SM250 spectrometer operating at 80.25 MHz. The variable temperature ^{11}B n.m.r experiments were recorded at Royal Holloway College, Egham using a Jeol FX90Q spectrometer operating at 28.7 MHz.

There appears to be some confusion over the signs of chemical shift values for non-proton n.m.r work. This arises because the term 'Chemical Shift' can refer to either changes in shielding or in the resonance frequency. At constant applied field, B_o ; $(\nu_A - \nu_B) \propto -(\sigma_A - \sigma_B)$, where ν_x is the resonance frequency for species x, and σ_x is the shielding constant for species x. IUPAC are in favour of chemical shift signs relating to resonance frequencies (expressed in ppm).[76,77] Therefore higher frequencies compared to the reference are given positive values.

Various compounds have been used in the past as references in boron work, but boron trifluoride-diethyl etherate complex appears to be currently accepted as the standard external reference. Shift values using the other references can be easily converted. Two useful conversions are (i) For shift values using trimethyl borate as a reference,

δ(relative to $BF_3.OEt_2$) = δ(relative to $B(OCH_3)_3$) + 18.3 ppm and (ii) using boron trichloride as a reference, δ(relative to $BF_3.OEt_2$) = δ(relative to BCl_3) + 47.0 ppm.

The chart (Figure A.II.1) shows some representative chemical shifts for compounds of interest in this field. It proved to be a valuable aid for fast reference and is included as such. The shift values are taken mainly from a compilation of such data by G.Eaton and N.Lipscomb[58] along with more modern sources.[40]

The dimethyl sulphide complexes prepared in this work showed the following chemical shifts (50% in tetrachloromethane, relative to $BF_3.OEt_2$) and coupling constants(B—H), the figures in brackets being the literature values[40]; BH_3, δ -19.6 (19.8), J 105 ; BH_2Cl, δ -6.9 (6.7), J 130(131); $BHCl_2$, δ 2.4(2.2), J 158(157); BCl_3, δ 7.7 ; BH_2Br, δ -10.9 (-10.5), J 132(132) ; $BHBr_2$, δ -7.9(-7.3), J 160(160) ; BHBrCl, δ -2.6, J 161. δ and J being expressed in ppm and Hz respectively. Figure A.II.2 shows a ^{11}B n.m.r spectrum (from a reaction between BMS and triphenylchloromethane) which contains the following species as the dimethyl sulphide complexes ; (1) BH_3 (quartet), (2) BH_2Cl (triplet), (3) $BHCl_2$ (doublet) and (4) BCl_3 (singlet).

Broad-band decoupling of such spectra (both for chloro- and bromoboranes) collapses the signals and gives identical relative integral values for the corresponding peaks. This technique proved necessary with the mixed haloborane (bromine and chlorine) studies where the coupled signals overlapped. Decoupling resolved the signals sufficiently to determine the ratio of species.

Figure A.II.1 Some representative chemical shifts for compounds of interest in the study of hydroboration using chloroborane-dimethyl sulphide complexes

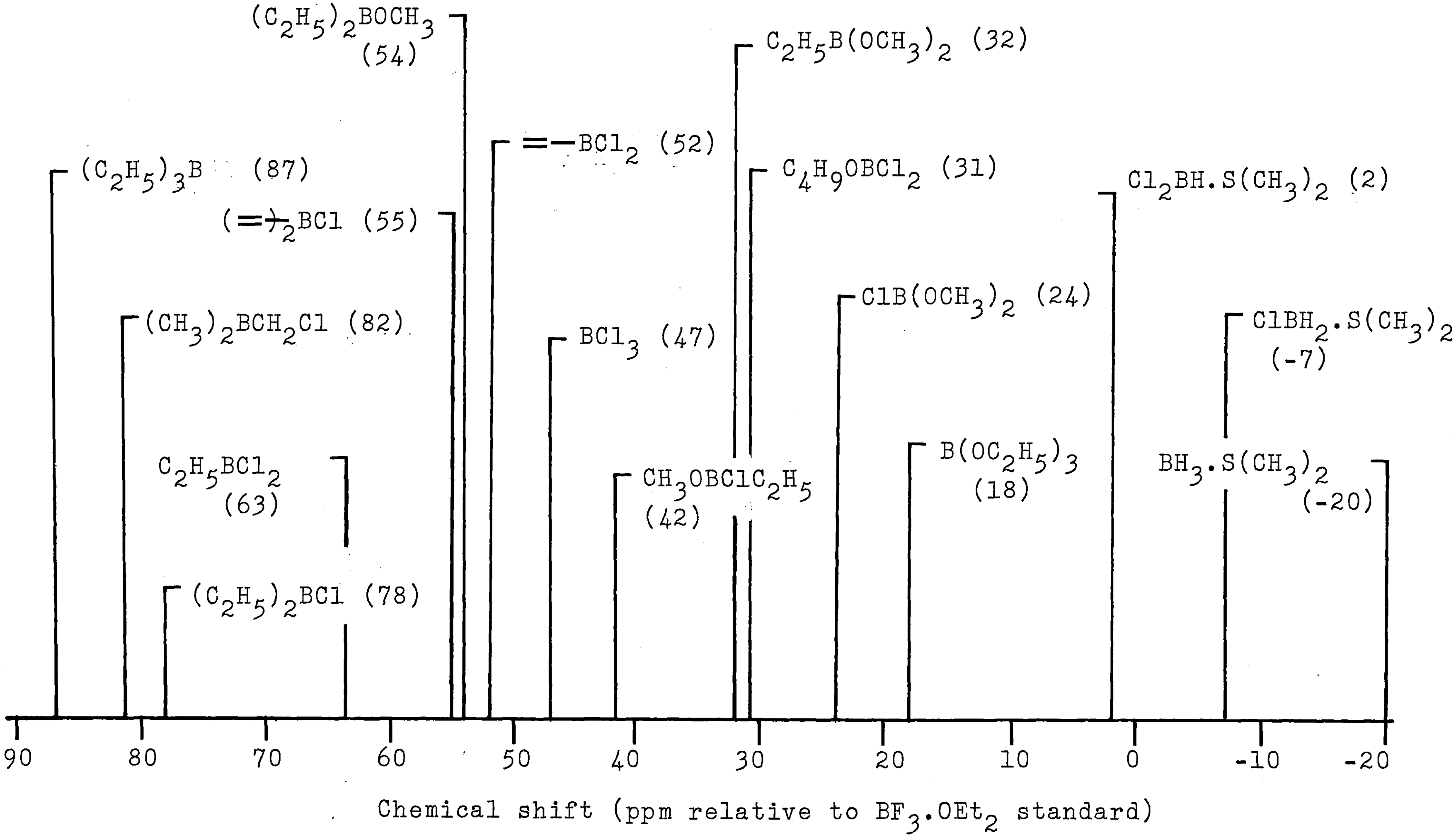
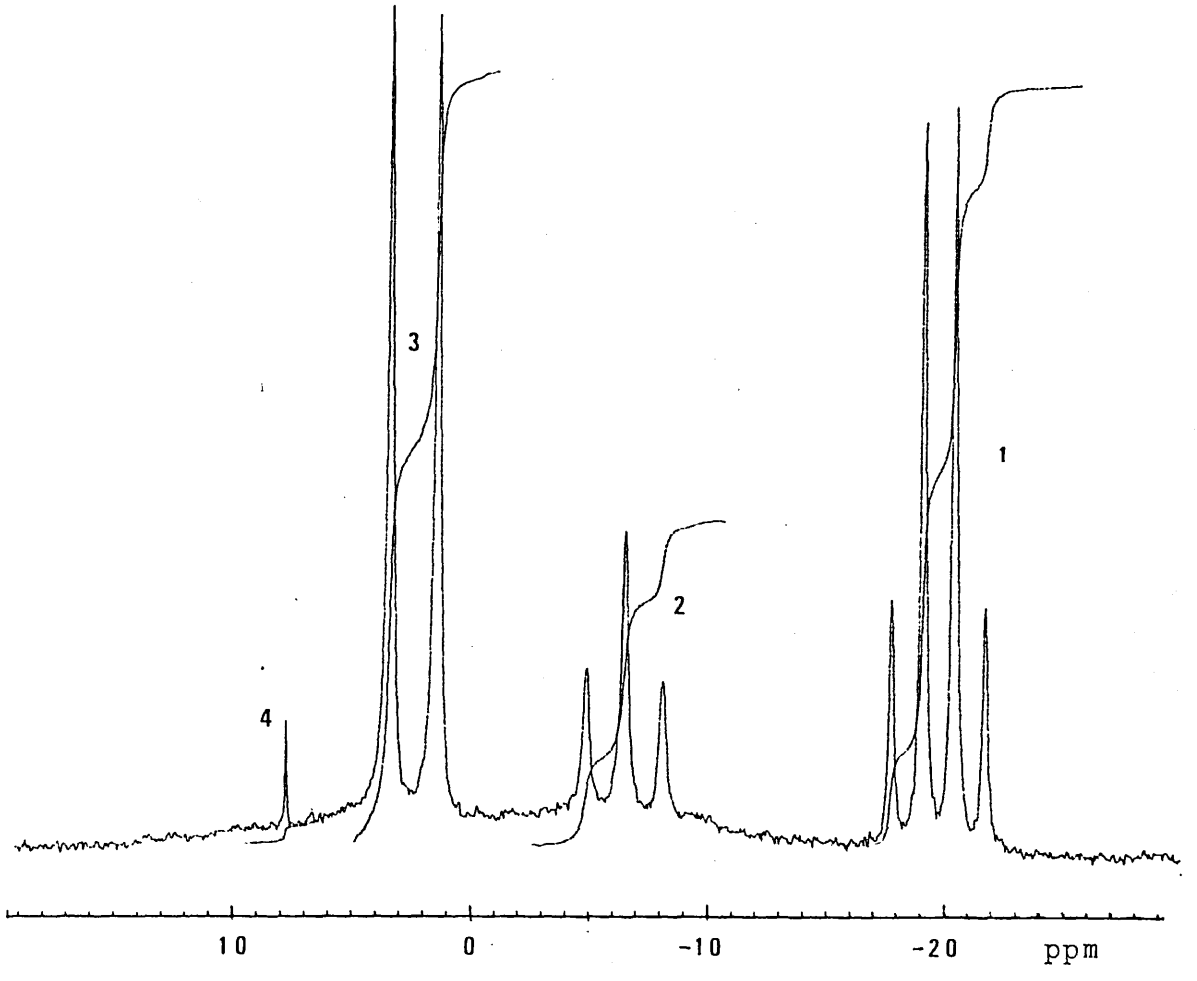


Figure A.II.2 80 MHz ^{11}B n.m.r spectrum showing BMS, MCBS, DCBS and boron trichloride-dimethyl sulphide complexes



APPENDIX III

A.III DETAILS OF KINETIC INVESTIGATION OF THE REACTION BETWEEN DIALKYLCHLOROBORANES AND SUBSTITUTED BENZALDEHYDES

The results of two typical reactions using equimolar and excess dialkylchloroborane are shown on Table A.III.1 treating the data for second order kinetics. The relevant plots of $\left(\left(\text{Pentene}\right)_{\infty} - \left(\text{Pentene}\right)_t \right)^{-1}$ and $\ln \frac{\left(R_2BCl\right)_t}{\left(PhCHO\right)_t}$ against time are shown in Figures A.III.1 and A.III.2, and give good fits for the data.

Table A.III.2 shows the half lives for the consumption of aldehyde for three different reactions having similar borane concentrations. Substituting the values into the Noyes equation,

$$\text{Reaction order for given reactant (PhCHO)} = n = 1 + \frac{\log t_{\frac{1}{2}} - \log t'_{\frac{1}{2}}}{\log\left(PhCHO\right)'_o - \log\left(PhCHO\right)_o}$$

gives the following values of n. Comparing reaction 1 with reaction 2 and 3 gives n as 0.7 and 0.8. Comparing reaction 1 with 3 gives n as 0.6. These values are similar and give a value of n close to 1.

Table A.III.1 Results of reaction between benzaldehyde and dipentylchloroborane at 9°C

(i) $(PhCHO)_o = (R_2BCl)_o = 1.93$ mol dm^{-3}

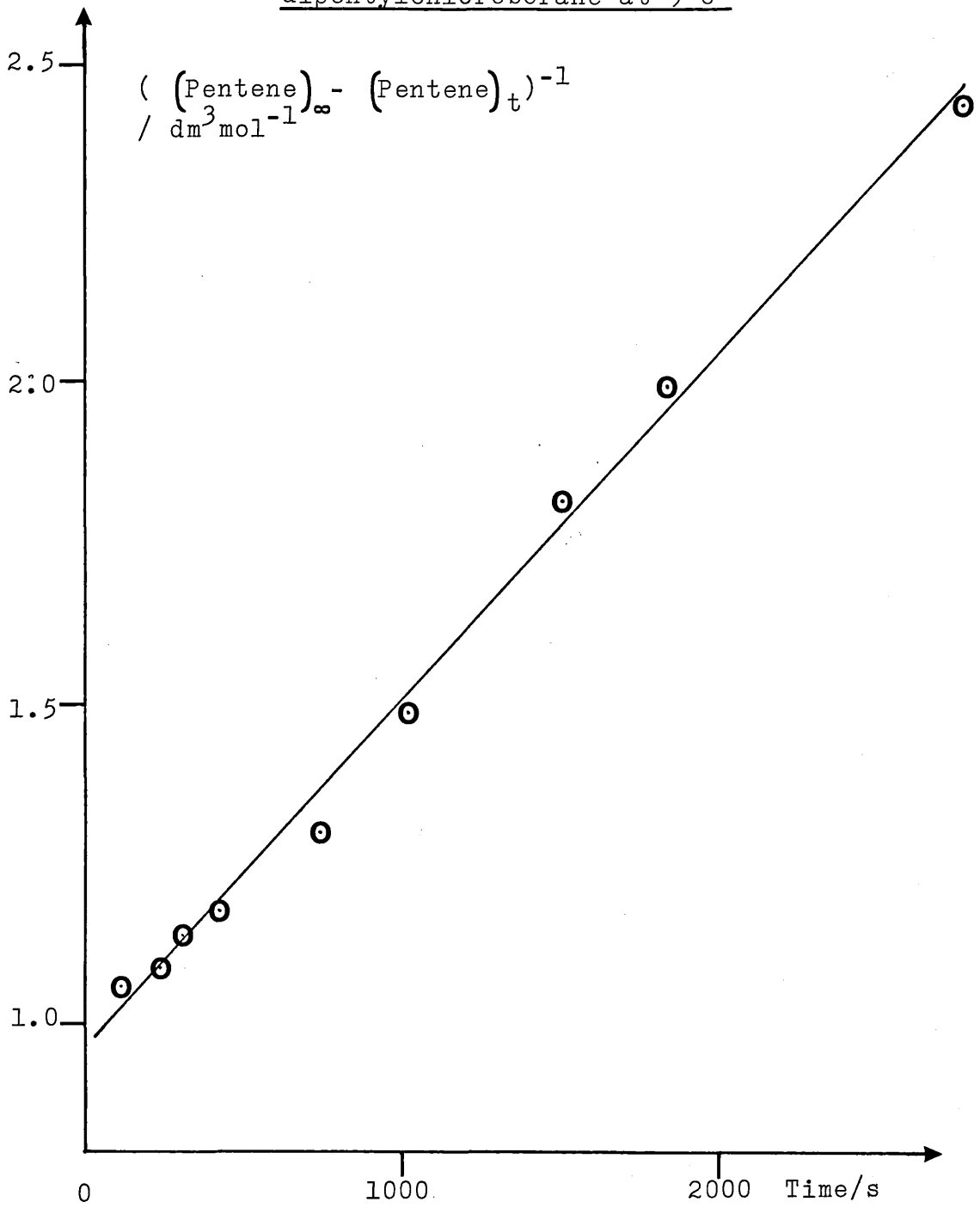
Time/s	$(Pentene)_t$ /mol dm^{-3}	$((Pentene)_\infty - (Pentene)_t)^{-1} \times 10^4$ /dm^{3}mol^{-1}
120	0.22	1.06
240	0.24	1.09
315	0.28	1.14
420	0.31	1.18
750	0.39	1.30
1020	0.49	1.49
1500	0.61	1.82
1830	0.66	2.00
2760	0.75	2.44
	1.16 (=60% yield)	

(ii) $(PhCHO)_o = 0.64$ mol dm^{-3}, $(R_2BCl)_o = 1.93$ mol dm^{-3}

Time/s	$(Pentene)_t$ /mol dm^{-3}	$(Pentene)_t$ /0.58[a] = x /mol dm^{-3}	$\ln \frac{(R_2BCl)_o - x}{(PhCHO)_o - x}$
1920	0.11	0.19	1.35
2640	0.17	0.29	1.55
3180	0.24	0.41	1.90
3600	0.25	0.43	1.97
4200	0.29	0.50	2.32
4920	0.31	0.53	2.54
	0.37 (= 58% yield)		

a-- This factor reflects the non-stoichiometric yield of alkene

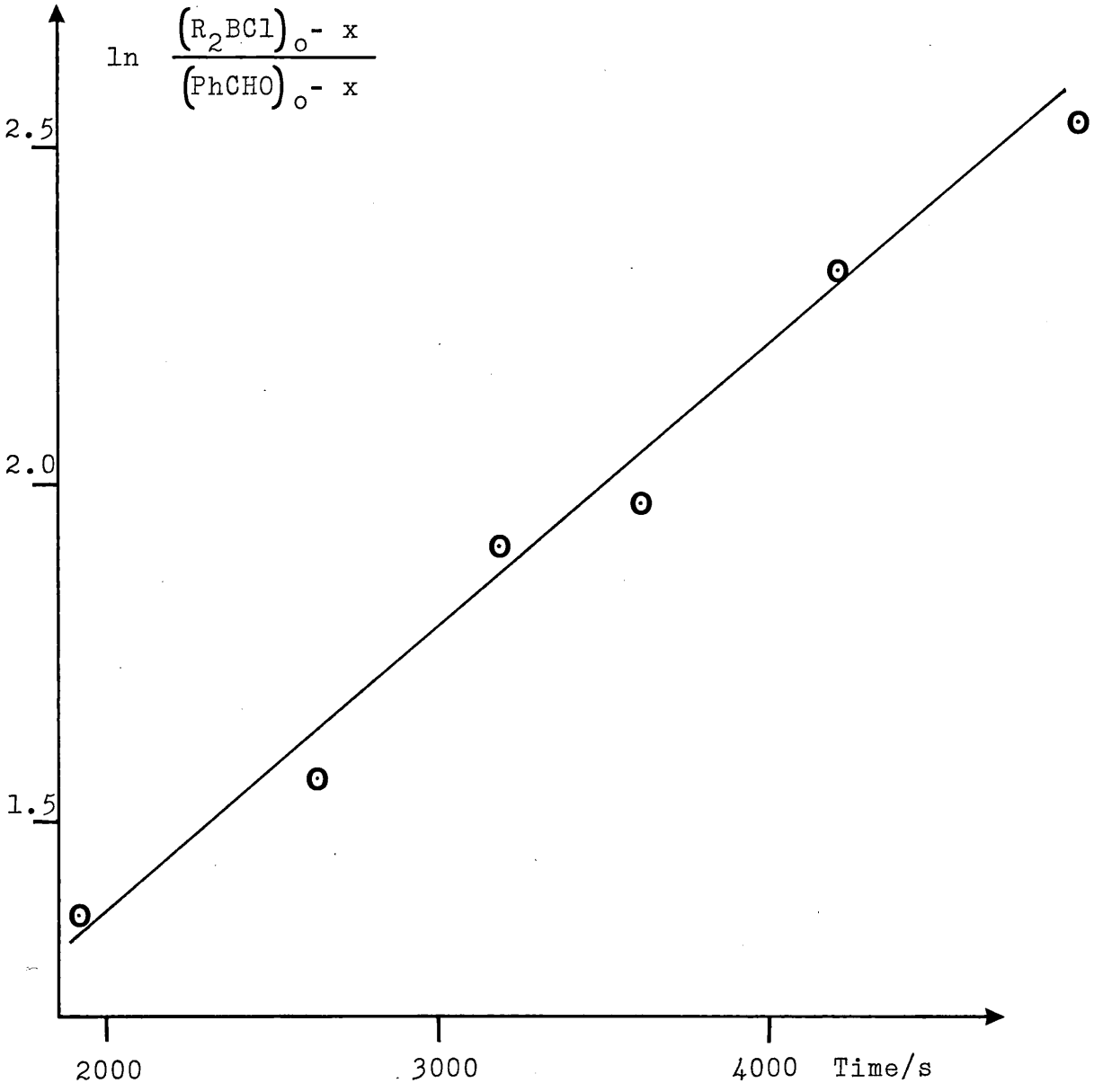
Figure A.III.1 Second order kinetic plot for the equimolar reaction between benzaldehyde and dipentylchloroborane at 9°C



Slope = 5.45×10^{-4}, k = slope x 0.60 (yield of alkene 60%)

= $3.3 \times 10^{-4} dm^3 mol^{-1} s^{-1}$

Figure A.III.2 Second order plot for the reaction between benzaldehyde and excess dipentylchloroborane at 9 °C



k = Slope / ($(R_2BCl)_o - (PhCHO)_o$) = $4.0 \times 10^{-3} / 1.29$

= $3.1 \times 10^{-4} dm^3 mol^{-1} s^{-1}$

Table A.III.2 Aldehyde consumption half lives for the reaction between dipentylchloroborane and benzaldehyde at 9 °C

Reaction number	$(PhCHO)_o$ /mol dm^{-3}	$(R_2BCl)_o$ /mol dm^{-3}	$t_{\frac{1}{2}}$ /s
1	1.93	1.93	2000
2	0.64	1.93	1500
3	0.99	1.85	1800

REFERENCES

1 P.Dittmar, E.Krause and R.Nitsche, Ber. dtsch. chem. Ges.,1921, 54, 2784.

2 H.C.Brown, J.Am.Chem. Soc., 1956, 78, 1248.

3 H.C.Brown, 'Organic synthesis via boranes', Wiley -Interscience, 1975.

4 C.Cragy, 'Organoboranes in organic synthesis', Ed. Marcel Dekker, New York ,1973.

5 H.C.Brown and G.Zweifel, Org. Reactions, 1963, 1, 13.

6 D.T.Hurd, J. Org. Chem., 1948, 13, 711.

7 T.C.Cheng, B.Lepeska and D.J.Pasto, J. Am. Chem. Soc. 1972, 94, 6083.

8 L.Rosenblum, J. Am. Chem. Soc., 1955, 77, 5016.

9 M.V.Bhatt and H.C.Brown, J. Am. Chem. Soc., 1966, 88, 1440.

10 H.C.Brown and G.Zweifel, J. Am. Chem. Soc., 1963, 85, 2066.

11 H.C.Brown and E.Negeshi, Synthesis, 1974,77.

12 H.C.Brown and E.Negeshi, J. Am. Chem. Soc., 1967, 89, 5477.

13 H.C.Brown and G.Zweifel, J. Am. Chem. Soc., 1960, 82, 4708.

14 H.C.Brown and R.L.Sharp, J. Am. Chem. Soc., 1966, 88, 5851.

15 H.Arzoumanian and G.Zweifel, J. Am. Chem. Soc., 1967, 89, 291.

16 A.M.Hurdlik and P.F.Hurdlik, 'The chemistry of the

carbon-carbon triple bond', Part 1, Ed. S.Patai, Wiley, New York, 1978.

17 H.C.Brown and R.L.Sharp, J. Am. Chem. Soc., 1968, 90, 2915.

18 P.M.Aronovich and B.M.Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 1968, 2745.

19 D.J.Pasto and S.R.Snyder, J. Org. Chem., 1966, 31, 2773.

20 H.Toi and Y.Yamamoto, Chem. Lett., 1974, 485.

21 H.C.Brown and R.M.Gallivan Jr., J. Am. Chem. Soc., 1968, 90, 2906.

22 Y.N.Bubvov et al., Zh. Obshch. Khim., 1972,42.

23 H.C.Brown and G.Zweifel, J.Am. Chem. Soc., 1959, 81, 247.

24 H.C.Brown and G.Zweifel, J. Am. Chem. Soc., 1961, 83, 2544.

25 G.W.Kabalka et al., J.Org. Chem., 1978, 43, 1567.

26 H.C.Brown and J.H.Kawakami, J. Am. Chem. Soc., 1970, 92, 1990.

27 W.J.Wechter, Chem. Ind.(London), 1959, 294.

28 A.Streitwieser et al., J. Org. Chem., 1967, 32, 1530.

29 D.J.Pasto, 'Boron hydride chemistry', Academic Press, New York, 1975.

30 H.C.Brown and A.W.Moerikofer, J. Am. Chem. Soc., 1963, 85, 2063.

31 P.Sykes, 'A guidebook to mechanism in organic chemistry', Longman Group Ltd., 1978.

32 G.D.Graham et al., J. Am. Chem. Soc., 1979, 101, 2863.

33 S.Nagase et al., J. Am. Chem. Soc., 1980, 102, 4536.

34 A.B.Burg, J. Am. Chem. Soc., 1934,56, 499.

35 H.C.Brown, J. Inorg. Nucl. Chem., 1959, 9, 51.

36 D.J.Pasto, J Am. Chem. Soc., 1967, 89, 295.

37 G.Zweifel, J .Organomet. Chem., 1967,9, 215.

38 H.C.Brown, J. Am. Chem. Soc., 1976, 98, 1785.

39 A.Arase and M.Hoshi, Bull. Chem. Soc. Jpn., 1981, 54, 299.

40 H.C.Brown and N.Ravindran, Inorg. Chem., 1977, 16, 2938.

41 H.C.Brown and N.Ravindran, J. Org. Chem., 1977, 42, 2533.

42 V.R.Miller and G.E.Ryschkewitsch, J Am. Chem. Soc., 1973, 95, 2836.

43 W.Paget and K.Smith, J.C.S Chem. Comm., 1980, 1169.

44 H.C.Brown, J. Org. Chem. 1979, 44, 2417.

45 H.C.Brown and M.Zaidlewicz, J. Am. Chem. Soc., 1976, 98, 4917.

46 H.C.Brown and S.Kulkarni, J. Org. Chem., 1979, 44, 2422.

47 H.C. Brown, J.Org. Chem., 1973, 38, 1617.

48 H.C.Brown, J. Am. Chem. Soc., 1972, 94, 2114.

49 K.Kinberger and W.Siebert, Z. Naturforsch.Teil B, 1975, 30, 55.

50 H.C.Brown, J. Am. Chem. Soc., 1976, 98, 1798.

51 H.C.Brown, J. Org. Chem., 1980, 45, 384.

52 H.C.Brown, J. Org. Chem., 1980, 45, 389.

53 H.C.Brown et al., J. Am. Chem. Soc., 1973, 95, 2394.

54 M.Midland et al., J. Am. Chem. Soc., 1973, 95, 4069.

55 P.S.Jones and P.N.Gates - unpublished work, Royal Holloway College, Egham, Surrey, England.

56 F.Cotton and G.Wilkinson 'Advanced Inorganic Chemistry'. 3rd edition, page 113, John Wiley and Sons Inc.

57 J.A. Kerr and A.F.Trotman-Dickenson, 'Handbook of Chemistry and Physics',63rd edition, 1982-3, CRC Press, Boca Raton, Florida.

58 G.Eaton and W.Lipscomb 'NMR Studies of Boron Hydrides and Related Compunds', 1969, New York, W.A.Benjamin Inc.

59 M.Frazer et al. J. Chem. Soc., 1957, 739.

60 H.Meerwein et al., J. prakt. Chem., 1936, 147, 226.

61 B.Mikhailov et al., Izv. AN SSSR, Ser. Khim., 1965, 8.

62 B.Mikhailov et al., J. Gen. Chem. USSR, 1966, 36, 65.

63 M.Midland et al., J. Am. Chem. Soc., 1977, 99, 5211.

64 M.Midland et al., J. Organomet. Chem., 1978, 156, 203.

65 M.Midland and S.Zedric, J. Am. Chem. Soc., 1982,104, 528.

66 M.Midland et al., J. Am. Chem. Soc., 1979,101, 2352.

67 M.Midland and S.Zedric, J. Am. Chem. Soc., 1982, 104, 525.

68 W.Gerrard 'The organic chemistry of boron', 1961, John Wright and Sons Ltd., page 223.

69 W.Gerrard 'The organic chemistry of boron', 1961, John Wright and Sons Ltd., page 71.

70 R.Stewart and K.Yates, Can. J. Chem., 1959, 37, 664.

71 K.Bowden and M.Hardy, Tetrahedron 1966, 22, 1169.

72 R.Burnett and D.Kirk, J. Chem. Soc., Perkin Trans.2, 1976, 1523.

73 Asahi Chemical Industry Co., Ltd., Patent. Brit., 959,320, May 27th, 1964.

74 Asahi Chemical Industry Co., Ltd., Patent, Japan 18,962, Sept. 4th, 1964.

75 Summitono Chemical Co., Patent. Japan, 68,153, 1st August, 1968.

76 "Recommendations for the presentation of NMR data for publication in chemical journals", Pure Appl. Chem. 1972, 29, 627.

77 "Recommendations for the presentation of NMR data for publication in chemical journals", Pure Appl. Chem. 1976, 45, 217.

78 A.I.Vogel 'A textbook of quantitative inorganic analysis', Third edition, 1961, Longman.