855. *Monomethylation and Polymethylenation by Diazomethane in the Presence of Boron Compounds.*[1]

By Alwyn G. Davies, D. G. Hare, O. R. Khan, and J. Sikora.

Boron halides and boric esters (BX_3) react catalytically with diazomethane in ether to give only linear polymethylene and nitrogen, but organoboron compounds ($X =$ alkyl or aryl), particularly the boronic anhydrides, give also some product of methylenation ($X{\cdot}CH_2{\cdot}B{<}$) of the X–B bond. In the presence of a nucleophile, HA, little or no polymethylene is formed. With the first group of reagents diazomethane methylenates HA to CH_3A; with the organoboron compounds it is partitioned between forming CH_3A and an increased amount of $X{\cdot}CH_2B{<}$.

It is shown that polymethylene can be formed by repeated methylenation of the alkyl–boron bond, but a second route to polymethylene must operate, exclusively so in the case of boron trifluoride and boric esters. A full mechanistic analysis is presented, involving the following features:

The diazomethane co-ordinates to the boron to form a zwitterion. This can give polymethylene by a fast cationic chain process (i), and, when $X =$ alkyl or aryl, by a repeated 1,2-rearrangement of alkyl from boron to carbon. A nucleophilic reagent, HA, competes with diazomethane for reaction with the cationic centre, undergoing methylenation to CH_3A. This makes available for forming the zwitterion, 10^3—10^5 diazomethane molecules which would otherwise have been consumed in the fast reaction; any intrinsic migratory aptitude of the group X has therefore a much greater chance of being observed.

This picture implies that the propagating cations have a high selective reactivity for diazomethane as against alkanes, alkenes, and arenes. It is suggested that, in the non-polar solvent, the polar diazomethane molecules strongly solvate the diazonium ion, taking the place of the normal counter-ion. The primary carbonium ion is thus liberated in a local atmosphere of diazomethane molecules with which it reacts, to the exclusion of non-polar molecules which will be outside this solvation shell.

The Formation of Polymethylene.—The first report of the reaction of diazomethane with boron compounds was in 1948 by Meerwein,[2] who showed that a trace of a boric ester, boron halide, trialkylborane, or tetra-acetyl diborate gave polymethylene in practically quantitative yield:

$$nCH_2N_2 \xrightarrow{BX_3} nN_2 + -[CH_2]_n- \qquad (1)$$

The boron halides were much more effective than the boric esters, whose activity was parallel to the readiness with which they formed co-ordination compounds. The polymer was reported to have a m. p. of 370°, and a molecular weight (Rast) of 1800—2000, and to be swollen by pyridine and chloronaphthalene. Meerwein concluded that the polymer was cross-linked.

Buckley and Ray[3] found that the polymer prepared with methyl borate in ether or benzene was soluble in hot tetralin, and viscosity measurements indicated a molecular weight of 200,000: it was concluded that the polymer was linear. Homopolymers could not be formed from higher diazoalkanes, but these would copolymerise with diazomethane.

The first suggestion of the mechanism of polymerisation was by Kantor and Osthoff,[4] who reported that diazomethane and boron trifluoride in ether at 0° gave a polymer of

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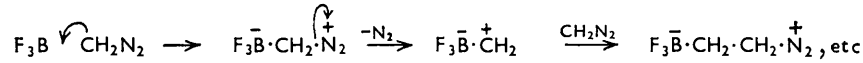
[1] This work was presented at the Chemical Society Symposium on Boron Compounds at Liverpool in April 1961, and summarised in *Proc. Chem. Soc.*, 1961, 172.

[2] Meerwein, *Angew. Chem.*, 1948, **60**, 78.

[3] Buckley and Ray, *J.*, 1952, 3701.

[4] Kantor and Osthoff, *J. Amer. Chem. Soc.*, 1953, **75**, 931.

molecular weight $3{\cdot}3 \times 10^6$, containing 0·26—0·1% of nitrogen. They suggested that the polymerisation occurred by a cationic chain mechanism, as illustrated in equation (2):



$$F_3B\;CH_2N_2 \longrightarrow F_3\bar{B}{\cdot}CH_2{\cdot}\overset{+}{N}_2 \xrightarrow{-N_2} F_3\bar{B}{\cdot}\overset{+}{C}H_2 \xrightarrow{CH_2N_2} F_3\bar{B}{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}_2\text{, etc.} \qquad (2)$$

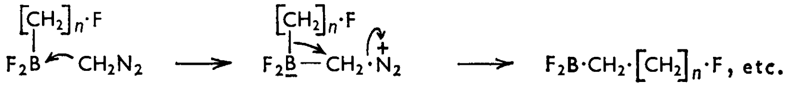
Feltzin, Restaino, and Mesrobian [5] proposed that adventitious water or alcohol acted as a co-catalyst and provided a counter-ion $(F_3B{\cdot}OR)^-$ for the extending cation, and Plesch [6] suggested that propagation occurred through the diazonium rather than the carbonium ion (*i.e.*, by an S_N2 rather than an S_N1 process).

An alternative mechanism for the polymerisation was put forward by Goubeau and Rohwedder,[7] who showed that, in the gas phase at —40° to —60°, diazomethane and boron trifluoride, diluted with nitrogen (molar ratios 1 : 200 : 60), gave a practically quantitative yield of difluorofluoromethylborane:

$$BF_3 + CH_2N_2 \longrightarrow F_2B{\cdot}CH_2F + N_2 \qquad (3)$$

This insertion of a methylene group between metal and halide is common with many other metal halides.[8]

By repetition of this process a linear polymer could be formed, each step involving nucleophilic attack of diazomethane at boron, and a nucleophilic 1,2-rearrangement of the $F{\cdot}[CH_2]_n$ group from boron to carbon (eqn. 4). We shall refer to this as the rearrangement mechanism.



$$\underset{F_2B\;CH_2N_2}{\overset{[CH_2]_n{\cdot}F}{|}} \longrightarrow \underset{F_2\underline{B}-CH_2{\cdot}\overset{+}{N}_2}{\overset{[CH_2]_n{\cdot}F}{|}} \longrightarrow F_2B{\cdot}CH_2{\cdot}[CH_2]_n{\cdot}F\text{, etc.} \qquad (4)$$

where $n = 0$ upwards.

The only other example of the monomethylenation of a boron compound appears to be the reaction of trichloroborazole with an excess of diazomethane in ether at —65°, giving *BBB*-tri(chloromethyl)borazole in 60% yield.[9]

The principal criticisms [10] that have been levelled against the cationic mechanism are as follows. (i) The carbonium ion might be expected to undergo intramolecular hydride shift, producing methyl side-chains, whereas the polymer in fact appears to be linear. (ii) Intermolecular hydride transfer to the carbonium ion might be expected in a solvent such as " iso-octane," reducing the molecular weight of the polymer; this is not observed. (iii) In its original form the cationic mechanism involved the energetically unfavourable separation of opposite charges in a non-polar medium.

The rearrangement mechanism is free from these objections, and is compatible with the fact that the rate of the reaction is apparently of first order with respect to boron trifluoride and to diazomethane, and that the molecular weight of the polymer is proportional to the concentration of the diazomethane and inversely proportional to the concentration of boron trifluoride. Most recent workers in this field have assumed that this rearrangement mechanism is the only route to polymer, and that all the experimental facts could be accommodated on this basis.

The Methylenation of Alcohols and Amines.—Parallel but largely independent work has been carried out on the methylenation of nucleophiles, HA, particularly alcohols and amines, by diazomethane in the presence of boron compounds.

Alcohols are methylenated very slowly by diazomethane unless they contain a strongly

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[5] Feltzin, Restaino, and Mesrobian, *J. Amer. Chem. Soc.*, 1955, **77**, 206.

[6] Plesch, *Ricerca sci.*, 1955, **25**, 140.

[7] Goubeau and Rohwedder, *Annalen*, 1957, **604**, 168.

[8] Seyferth, *Chem. Rev.*, 1955, **55**, 1155.

[9] Turner, *Chem. and Ind.*, 1958, 1405.

[10] Reviewed by Bawn, Ledwith, and Matthies, *J. Polymer Sci.*, 1959, **34**, 93.

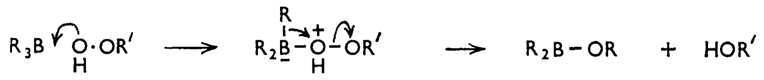
electron-attracting substituent, as in the structures R·CH(CN)·OH or $Cl\cdot CH_2\cdot CH_2\cdot OH$.[11] The reactions are catalysed by boron compounds such as fluoroboric acid[12] and boron trifluoride[13] (and Lewis acids derived from other metals); any deficiency in the yield of methyl ether can then be accounted for as polymethylene.

The relative rates of the methylenation of n-, s-, and t-butyl alcohol in the presence of fluoroboric acid are 2·2 : 1·3 : 1·0,[12a] and of n-, s-, and t-pentyl alcohol in the presence of boron trifluoride are 1·7 : 1·55 : 1·0.[14] Triphenylmethanol could not be methylenated.

Traces of higher ethers (*i.e.*, the products of dimethylenation, trimethylenation, etc.) have been reported. For example, butanol and diazomethane in the presence of triethylborane gave some butyl *ethyl* ether, and ethanol, tributyl borate, and diazomethane gave small amounts of the ethyl and the propyl ether of butanol.[15]

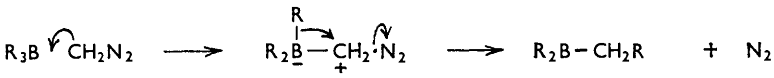
Similar considerations apply to methylenation at a nitrogen atom. In the absence of a catalyst, diazomethane reacts with the ammonium group in an amino-acid to give the quaternary ammonium zwitterion,[16] and ammonium hydroxide gives the primary and secondary compounds.[17] Ammonia and primary amines, on the other hand, are unreactive unless a Lewis acid such as boron trifluoride is present;[18] then, in ether, methylenation of the amine is accompanied by the formation of polymethylene unless an excess of amine is used. Fluoroboric acid can similarly serve as the catalyst.[19]

The Present Work.—Our interest in this reaction system arose from our work on the organoperoxyboranes where the nucleophilic 1,2-rearrangement of an alkyl group to oxygen occurs readily, *e.g.*:[20]



$$R_3B\ \underset{H}{O}\cdot OR' \longrightarrow R_2\overset{R}{\underset{-}{B}}-\overset{+}{\underset{H}{O}}-OR' \longrightarrow R_2B-OR + HOR' \qquad (5)$$

We hoped to establish the analogous insertion of a methylene group between alkyl and boron by the process:



$$R_3B\ CH_2N_2 \longrightarrow R_2\overset{R}{\underset{-}{B}}-\underset{+}{CH_2}\cdot N_2 \longrightarrow R_2B-CH_2R + N_2 \qquad (6)$$

Although this was generally accepted as being the route by which polymethylene was formed from diazomethane (eqn. 4), no example of this fundamental process had ever been observed.

RESULTS AND DISCUSSION

General Methods.—Various boron compounds in ether were treated with diazomethane (usually 0·3—3·0 mol.) under dry conditions, usually at −80°. If no reaction occurred, the mixture was allowed to warm: the onset of the reaction was shown by fading of the yellow colour of the diazomethane, and the appearance of a white cloud of polymethylene. When the reaction was complete, the product was treated with a peroxyacid or hydrogen peroxide to convert any R–B groups into the corresponding alcohols (or phenols) (eqn. 5). These were analysed by gas–liquid chromatography by comparison with authentic samples. Any polymer was filtered off and examined.

Under these conditions, the relative reactivity falls in the approximate sequence:

$$BF_3 > R_3B > (RBO)_3 > (R_2B)_2O > RB(OR)_2 > (RO)_3B.$$

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[11] Meerwein and Hinz, *Annalen*, 1930, **484**, 1.

[12] (*a*) Caserio, Roberts, Neeman, and Johnson, *J. Amer. Chem. Soc.*, 1958, **80**, 2584; (*b*) Neeman, Caserio, Roberts, and Johnson, *Tetrahedron*, 1959, **6**, 36.

[13] Müller and Rundel, *Angew. Chem.*, 1958, **70**, 105.

[14] Müller, Bauer, and Rundel, *Z. Naturforsch.*, 1959, **14**b, 209.

[15] Bawn and Ledwith, *Chem. and Ind.*, 1958, 1329.

[16] Kuhn and Brydowna, *Ber.*, 1937, **70**, 1333.

[17] Wieland and Peil, *Chem. Ber.*, 1956, **89**, 2408.

[18] Müller, Huber-Emden, and Rundel, *Annalen*, 1959, **623**, 34.

[19] Daniels and Kormendy, *J. Org. Chem.*, 1962, **27**, 1860.

[20] (*a*) Davies, Hare, and Khan, *J.*, 1963, 1125; (*b*) Davies, Hare, and White, *J.*, 1961, 341, and previous papers.

Thus, in dilute solution, the reaction catalysed by boron trifluoride is complete in less than 1 minute, whereas that with methyl borate under similar conditions requires 2 hours.

All these reactions gave polymethylene, though in low yield in the case of the boronic anhydrides.

Similar studies were carried out on systems containing a nucleophile such as an amine as an additional component. The rate of disappearance of the colour of the diazomethane was now much slower, and little or no polymethylene was formed. The products were examined as before, and any amines analysed by gas–liquid chromatography.

The results are summarised in the Table.

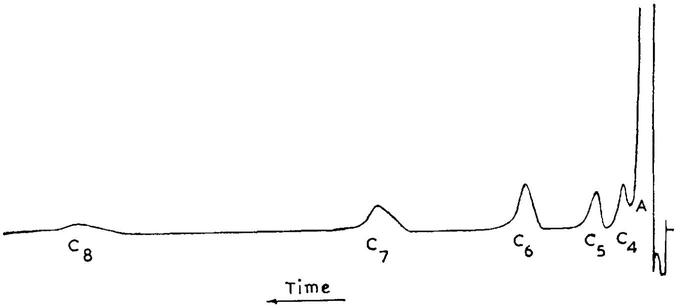
The reaction of diazomethane with boron compounds.

Expt.	BX_3	CH_2N_2 (mol.)	Mol. HA	Reaction temp.[c]	Time [e]	Poly-methylene, yield (%) [g]	Other products identified [h]
1	$F_3B\cdot OEt_2$	1	0	−65°	inst.	100	
2	$F_3B\cdot OEt_2$	2·2	1·25 $Bu\cdot NH_2$	−5	>2 hr.	25	
3	$(MeO)_3B$	1	0	R.T.	100 min.	90	No CH_2O
4	$(MeO)_3B$	1	1 $Ph\cdot CH_2\cdot NH_2$	R.T.	>3 hr.	0	No CH_2O; p-, s-, and t-amines detected
5	$(MeO)_3B$	3	1 $Ph\cdot CH_2\cdot NH_2$	R.T.	120 min.	15	$Ph\cdot CH_2\cdot NH_2$ 24, $Ph\cdot CH_2\cdot NHMe$ 48, $Ph\cdot CH_2\cdot NMe_2$ 28%
6	$(EtO)_3B$	1	0	<R.T.		+	
7	Bu_3B	<1 [b]	0	−65		100	
8	Bu_3B	5	2·5 Bu_2NH	−75	*f*	+	
9	Bu_3B	6	0·2 $Bu\cdot NH_2$	−75	inst.	+	
10	$Bu^s{}_3B$	1·5	0	−118	fast	+	$Bu^s\cdot CH_2\cdot OH$ *ca.* 1%
11	$Bu^s{}_3B$	1	3 $Ph\cdot CH_2\cdot NH_2$	−50 to −45 [d]	fast	0	$Bu^s\cdot CH_2\cdot OH$ 30%
12	$Bu^s{}_3B$	1	3 Bu_3N	−75	v. fast	+	$Bu\cdot CH_2\cdot OH$ *ca.* 1%
13	$Bu^i{}_2BBu^t$	0·75	0 0	−75 or R.T.	v. fast	+	No $Bu^i\cdot CH_2\cdot OH$ or $Bu^t\cdot CH_2\cdot OH$
14	$Bu^i{}_2BBu^t$	1·5	3 $Ph\cdot CH_2\cdot NH_2$	−55 to −50 [d]	fast	0	Bu^tOH 28, Bu^iOH 48, $Bu^t\cdot CH_2\cdot OH$ 4, $Bu^i\cdot CH_2\cdot OH$ 20%
15	Ph_3B	1·2	3 Bu_3N	R.T.	inst.	46	
16	Ph_3B	1·2	3 Bu_2NH	R.T.	2 min.	58	
17	Ph_3B	1·2	3 $Bu\cdot NH_2$	R.T.	3 hr.	+	
18	Ph_3B	1·2	3 $Ph\cdot CH_2\cdot NH_2$	R.T.	2 hr.	16	
19	$(Bu^s{}_2B)_2O$	2	0	R.T.	inst.	+	
20	$(Bu^s{}_2B)_2O$	2	6 $Ph\cdot CH_2\cdot NH_2$	R.T.	30 min.	+	$Bu^s\cdot CH_2\cdot OH$ 24%
21	$Bu^s\cdot B(OBu)_2$	2	0	R.T.	1 min.	101	
22	$Bu\cdot B(OBu)_2$	3	0	<R.T.[d]		+	No $Bu\cdot CH_2\cdot OH$
23	$Ph\cdot B(OH)_2$	1	0	<R.T.[d]		*ca.* 100	$Ph\cdot CH_2\cdot OH$ *ca.* 1%; no MeOH
24	$Ph\cdot B(OH)_2$	1	3 Bu_3N	R.T.		85	$Ph\cdot CH_2\cdot OH$ 2%; no MeOH
25	$Ph\cdot B(OH)_2$	1	3 $Ph\cdot CH_2\cdot NH_2$	R.T.		0	$Ph\cdot CH_2\cdot OH$ 20%; no MeOH
26	$Bu^i\cdot B(OC_2H_4)_2NH$	1	0	R.T.	1 hr.	+	No $Bu^i\cdot CH_2\cdot OH$
27	$(Bu^s\cdot BO)_3$	3	0	−50 to −40 [d]	fast	slight	$Bu^s\cdot CH_2\cdot OH$ 30%
28	$(Bu\cdot BO)_3$	22·5	0	<R.T.[d]		+	See Figure
29	B_2H_6 [a]	1	0	R.T.	1 min.	+	
30	$NaBH_4$	Excess	0	R.T.	2 hr.	slight	

[a] Prepared from sodium borohydride and boron trifluoride, and washed through diethylene glycol dimethyl ether. [b] The diazomethane solution was injected through a 20-gauge syringe needle into the stirred solution of the borane to ensure rapid mixing. Polymethylene was formed at once, the internal temperature rising to about −55°. [c] R.T. = room temperature. [d] The reagents were mixed at a lower temperature, but reacted only at the temperature indicated. [e] Inst. = instantaneously: reaction occurred before the reagents were homogeneously mixed. V. fast: reaction took place within a few sec. of components being mixed. Fast: reaction complete within about 30 sec. (Small differences in time are not significant because the concentrations of reagents varied.) [f] Fast after an induction period of a few sec. [g] +: a substantial amount of the polymer was formed, but its quantity was not determined. [h] Apart from ROH from organoboranes, $R\cdot B\!<$. Yields are expressed as percentages of total hydroxy-compound or total amine recovered.

Proof of the Methylenation of the R–B *Group.*—In the absence of an added nucleophile, boron trifluoride and boric esters gave only polymethylene of very high molecular weight, and no insertion of methylene between boron and fluoride or boron and alkoxide could be detected.

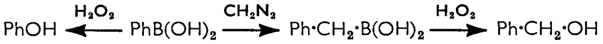
Trialkylboranes and alkylboronic esters gave polymer of relatively low molecular weight, together with traces of monomethylenation products. For example, phenylboronic acid and diazomethane gave polymethylene in high yield but, after oxidation of the product with hydrogen peroxide, the gas–liquid chromatogram showed the presence of a small amount of benzyl alcohol in the phenol (Expt. 23) (eqn. 7).



Gas–liquid chromatogram of alcohols from the reaction of diazomethane with n-butylboronic anhydride (Table, Expt. 28). Glycerol on Celite, 8 ft., at 100°; 1·6 l. of N_2/hr. C_4–C_8 denote normal alcohol of the stated C content. A = Et_2O.

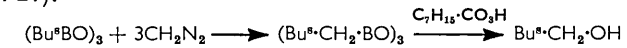
Molar ratios of alcohols: $C_4 : C_5 : C_6 : C_7 : C_8 = 1{\cdot}0 : 2{\cdot}0 : 3{\cdot}9 : 2{\cdot}9 : 2{\cdot}5$.

Boronic anhydrides gave the monomethylenation products in much better yield. For example, s-butylboronic anhydride reacted with diazomethane (3 mol.) at —40° to —50°,



$$\mathrm{PhOH} \xleftarrow{\mathrm{H_2O_2}} \mathrm{PhB(OH)_2} \xrightarrow{\mathrm{CH_2N_2}} \mathrm{Ph{\cdot}CH_2{\cdot}B(OH)_2} \xrightarrow{\mathrm{H_2O_2}} \mathrm{Ph{\cdot}CH_2{\cdot}OH} \qquad (7)$$

giving some polymethylene; oxidation of the product gave 2-methylbutan-1-ol in about 30% yield (Expt. 27).



$$\mathrm{(Bu^sBO)_3} + \mathrm{3CH_2N_2} \longrightarrow \mathrm{(Bu^s{\cdot}CH_2{\cdot}BO)_3} \xrightarrow{\mathrm{C_7H_{15}{\cdot}CO_3H}} \mathrm{Bu^s{\cdot}CH_2{\cdot}OH} \qquad (8)$$

In reactions of this type we have demonstrated the methylenation of the n-butyl, isobutyl, s-butyl, t-butyl, and phenyl groups bonded to boron. This established for the first time the reality of the monomethylenation of an R–B group, and the feasibility of this as the prototype for the formation of polymethylene.*

If an excess of diazomethane is used, methylene units can be repeatedly inserted between the boron atom and the growing alkyl group, and the homologous series of organoboranes which are formed can be identified by gas–liquid chromatography of the alcohols liberated on oxidation. The Figure shows the chromatogram of the alcohols, $\mathrm{Bu{\cdot}[CH_2]}_n\mathrm{{\cdot}OH}$ (n = 0—4), obtained by reaction between n-butylboronic anhydride and 22·5 mol. of diazomethane (*i.e.*, 7·5 molecules of CH_2N_2 per R–B group; Expt. 28 in the Table). This proves that a polymethylene chain can be built up by replication of the insertion reaction.

If a nucleophile such as water or a primary amine is present in the reaction system, the

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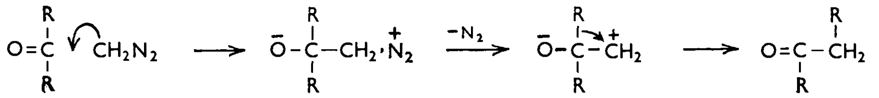
* Leffler and Ramsey [21] have independently reported the methylenation and diphenylmethylenation of triphenylborane and have shown that the polymethylene obtained on using triphenylborane or tri-1-naphthylborane carries an aryl group. It does not necessarily follow that the polymer has been formed by repeated insertion of methylene between the organic group and boron. For example, an aryl group might be transferred in the termination of the cationic mechanism which is discussed below: $^{-}\mathrm{Ar_3B{\cdot}[CH_2]}_n\mathrm{{\cdot}CH_2{\cdot}N_2}^{+} \longrightarrow \mathrm{Ar_2B{\cdot}[CH_2]}_n\mathrm{{\cdot}CH_2Ar} + \mathrm{N_2}$.

[21] Leffler and Ramsey, *Proc. Chem. Soc.*, 1961, 117.

insertion of methylene between R and B becomes much more prominent. The organoboron compounds gave little or no polymethylene; some of the diazomethane was consumed in methylenating the nucleophile, and the rest in converting RB into $R{\cdot}CH_2B$. For example, tri-s-butylborane and diazomethane at −120° gave an almost quantitative yield of polymethylene, and the presence of 2-methylbutan-1-ol could only just be detected on the chromatogram (Expt. 10). In the presence of benzylamine (Expt. 11), no reaction occurred below −50°; then no polymethylene was formed, but 30% of the diazomethane methylenated the Bu^s–B group, and the rest methylenated the amine.

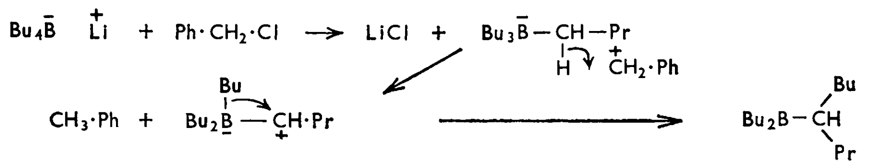
Mechanism of the Methylenation of the RB *Group*.—The mechanism of the process by which a methylene group is inserted between alkyl and boron or between aryl and boron is in all probability the nucleophilic 1,2-rearrangement as shown in equation (6), the loss of nitrogen preceding migration of the alkyl group. This migration would be expected to occur most readily in a pseudo-aromatic system such as a borazole or boronic anhydride, as is observed, because the cyclic electron delocalisation which was interrupted by the addition of the diazomethane would thereby be restored.

This mechanism is a logical extension of the homologation of ketones with diazomethane:



$$O{=}\overset{R}{\underset{R}{C}}\;CH_2N_2 \longrightarrow \bar{O}{-}\overset{R}{\underset{R}{C}}{-}CH_2{\cdot}\overset{+}{N_2} \xrightarrow{-N_2} \bar{O}{-}\overset{R}{\underset{R}{C}}{-}\overset{+}{C}H_2 \longrightarrow O{=}\underset{R}{C}{-}\overset{R}{CH_2} \qquad (9)$$

This is supported by Jäger and Hesse's recent demonstration [22] that the boron ylide can be generated by an alternative route, and observed to rearrange, as shown in equation (10).



$$Bu_4\bar{B}\;\overset{+}{Li} + Ph{\cdot}CH_2{\cdot}Cl \longrightarrow LiCl + Bu_3\bar{B}{-}\underset{H}{CH}{-}\underset{\overset{+}{C}H_2\cdot Ph}{Pr}$$

$$CH_3{\cdot}Ph + Bu_2\overset{Bu}{\underset{-}{B}}{-}\underset{+}{C}H{\cdot}Pr \longrightarrow Bu_2B{-}CH\begin{smallmatrix}Bu\\Pr\end{smallmatrix} \qquad (10)$$

We examined the reaction of di-isobutyl-t-butylborane with diazomethane (1·5 mol.) in the presence of benzylamine (3 mol.). After oxidation of the product, gas–liquid chromatography of the alcohols showed the presence of t-butyl alcohol (0·84 mol.), isobutyl alcohol (1·44 mol.), neopentyl alcohol (0·11 mol.), and isopentyl alcohol (0·61 mol.), and the absence of t-pentyl alcohol (Expt. 14). The structure of the alcohols is that which would be expected, but their relative amount is surprising in that it implies that an isobutyl group migrates 2—3 times more readily than a t-butyl group, whereas the converse applied in the migration to oxygen (eqn. 5).[20b] The interpretation of the methylenation, however, might be obscured by rapid disproportionation of the methylenation product, di-isobutylneopentylborane, in the early stages of the reaction, to give tri-isobutylborane; and this compound, for steric reasons, might be more reactive than di-isobutyl-t-butylborane.

The Evidence for a Second Mechanism.—We have established above the validity of the rearrangement route to polymethylene. Since Goubeau and Rohwedder's work,[7] most authors have accepted this as the only polymerisation mechanism available.

We believe, on the other hand, that this rearrangement mechanism has, in fact, a severely limited field of application and that it is the exceptional rather than the usual process. The evidence for this is as follows.

(i) *Trialkylboranes*. Equimolar amounts of tributylborane or tripentylborane and diazomethane in ether give polymer in high yield. If polymerisation occurred by repetition of the rearrangement process, this would demand that the reactivity of each homologue

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[22] Jäger and Hesse, *Chem. Ber.*, 1962, **95**, 345.

should be much greater than that of its predecessor (*e.g.*, $\mathrm{PrB}\langle \gg \mathrm{BuB}\langle$). This is unreasonable; and under the conditions where we *can* observe insertion (*i.e.*, the reaction of butylboronic anhydride), we find that the reactivity does not increase with chain length.

(ii) *Boronic esters.* Likewise, approximately equimolar amounts of boronic esters and diazomethane in homogeneous ethereal solution give polymer in very good yield. By the same argument, this polymer cannot be formed by the rearrangement process.

(iii) *Boric esters.* Equimolar boric esters and diazomethane give only polymethylene of high molecular weight. If the reaction occurred by the rearrangement reaction, the compound $\mathrm{RO{\cdot}[CH_2]_n{\cdot}B(OR)_2}$, *i.e.*, a boronic ester, would be an intermediate, and we have shown in section (ii) above that boronic esters do not react by this mechanism. Again, the polymer cannot be formed by the rearrangement process.

(iv) *Boronic anhydrides.* Boronic anhydrides react with an equimolar amount of diazomethane to give some product of monomethylenation of the R–B bond, and some high polymer, but no detectable oligomer. This again suggests that the two products are the result of independent processes.

(v) *Boron trifluoride.* Again, a molar deficiency of diazomethane gives only polymer. If boron trifluoride gave polymethylene by the rearrangement route, difluorofluoromethylborane, $\mathrm{F_2B{\cdot}CH_2F}$, would have to be much more reactive than boron trifluoride, and by the rearrangement of $\mathrm{F{\cdot}CH_2}$, not F. We have no direct evidence on this point, but it seems unlikely; Goubeau and Rohwedder[7] obtained only the product of monomethylenation and report no higher homologues. Turner[9] showed that the methylenation of trichloroborazole stopped at the stage of the tri(chloromethyl) compound, and Al'mashi, Fel'meri, and Gants[23] found that aluminium trichloride and aluminium tribromide gave the products $\mathrm{Al(CH_2X)_3}$ ($\mathrm{X = Cl}$ or Br) even when a three-fold deficiency of diazomethane was used. All these point to the fact that the halogen–metal bond is more reactive than the halogenomethyl–metal bond.

We conclude that, in the absence of a nucleophile, there must be at least two independent routes to polymer. In the series of compounds which we have investigated the rearrangement route is important under our conditions only with the boronic anhydrides, is barely detectable with the boronic esters and trialkylboranes, and is inoperative with the boric esters and boron trifluoride.

In the presence of a nucleophile such as an amine, this second route to polymer is blocked. With the organoboron compounds, the two routes to polymer are normally in competition: this blocking of the second route permits the rearrangement reaction to be more prominent, and the diazomethane is partitioned between this reaction and the methylenation of the nucleophile. Where no R–B bonds are present, the rearrangement reaction still does not occur, and all the diazomethane is now used in methylenating the nucleophile, HA, to MeA.

The Mechanism of the Second Route to Polymer.—In the first place, the reaction shows none of the characteristics of a free-radical reaction. Other workers have shown that quinol, t-butylcatechol, and αα-diphenyl-β-picrylhydrazyl have no effect on the rate of polymerisation or the yield of polymer.[5] No chain-branching of the polymethylene occurs, as is observed in the homolytic polymerisation of ethylene. Cyclohexene, which might be expected to inhibit the polymerisation by chain transfer, has no effect on the rate, and styrene and 4-methoxystyrene, which might be expected to inhibit the decomposition of diazomethane and to give an olefin homopolymer or an olefin–methylene copolymer, again have no effect on the rate of the reaction and can be recovered. There appears to be little precedent for a chain reaction of diazomethane which involves free radicals, and compounds of boron would hardly be expected to induce homolysis.

Likewise, there seems to be little support for a process involving carbene. When it is generated by photolysis or pyrolysis of diazomethane in the gas phase, polymethylene of high molecular weight is not produced, and in solution the carbene would not be expected

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[23] Al'mashi, Fel'meri, and Gants, *Doklady Akad. Nauk S.S.S.R.*, 1958, **118**, 1121.

to show the highly discriminating reactivity that the formation of polymethylene requires. Cyclohexene, which traps carbene, forming norcarane, had no effect on the polymerisation, and could be recovered from the reaction system.*

We believe, on the other hand, that this second and more widely operating route to polymethylene is basically the cationic chain reaction (eqn. 2) which was originally proposed by Kantor and Osthoff [4] but has been rejected by most recent authors in favour of the rearrangement process. The conclusion that the polymerisation can be propagated by a diazonium or carbonium ion indeed seems inescapable, because Hammond and Williams have recently shown that a simple protic acid, toluene-*p*-sulphonic acid, catalyses the formation of polymethylene while undergoing concomitant methylenation.[25] The variety of mechanisms which can be postulated are now much more restricted than in the case of the reactions catalysed by boron compounds, and there seems no reasonable alternative to the process shown in equation (11).

$$CH_2N_2 \xrightarrow{H^+} CH_3N_2^+ \xrightarrow[-N_2]{CH_2N_2} CH_3{\cdot}CH_2{\cdot}N_2^+ \xrightarrow[-N_2]{CH_2N_2^+} CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}N_2^+, \text{ etc.} \qquad (11)$$

In the following sections, the experimental results are interpreted in terms of this hypothesis of a cationic mechanism.

(i) *The effect of added nucleophiles.* We have explained previously how added nucleophiles, HA, can be methylenated by the $^-X_3B{\cdot}CH_2^+$ zwitterion. Each methylenation of this type frees, say 10^3—10^5 diazomethane molecules which would otherwise have been consumed in the fast cationic polymerisation and are now available for forming new $^-X_3B{\cdot}CH_2^+$ zwitterions. The number of these being formed is now 10^3—10^5 times as great as in the absence of the nucleophile. Any intrinsic aptitude of the group X to migrate from boron to carbon has now a much greater chance of being detected, and we find that the rearrangement reaction is much more prominent.

As might be expected, some of the " first " carbonium ions escape capture at this stage, and react with diazomethane to give the " second " or even " third " carbonium ions, $^-X_3B{\cdot}CH_2{\cdot}CH_2^+$ and $^-X_3B{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2^+$, along the route to polymer. These may now be captured by HA which is thereby converted into $CH_3{\cdot}CH_2A$ and $CH_3{\cdot}CH_2{\cdot}CH_2A$. The traces of product resulting from di- and tri-methylenation of HA [15] can thus be accounted for.

(ii) *Chain-transfer experiments.* Solvents such as " iso-octane " [10] are essentially without effect on the molecular weight of the polymethylene which is formed: it must be concluded that chain-transfer by the process shown in equation (12) does not occur.

$$\sim\!\sim\!\sim CH_2^+ + HCR_3 \longrightarrow \sim\!\sim\!\sim CH_3 + CR_3^+ \qquad (12)$$

We attempted to use 4-methoxystyrene, which readily undergoes cationic polymerisation,[26] as a chain-transfer agent, but no homopolymer of 4-methoxystyrene or copolymer of methylene with 4-methoxystyrene was formed. Diethyl ether obviously does not capture the chain, but a patent [27] reports that tetrahydrofuran, which is not polymerised by boron trifluoride or diazomethane separately, undergoes cationic polymerisation with these mixed reagents.† It appears then that alkanes, alkenes, arenes, and ethers, even

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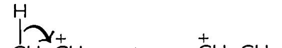
* Nasini, Saini, and Trossarelli [24] have tentatively interpreted the polymerisation of diazoalkanes on metallic surfaces in terms of a carbene bonded to the metal; this is equivalent to the metallomethylium ion, $^-M{-}CH_2^+$, which we accept as the key intermediate.

† Müller and Huber-Emden [28] have recently reported the analogous polymerisation of tetrahydrofuran, tetrapyran, and dioxan, using ethyl diazoacetate.

[24] Nasini, Saini, and Trossarelli, *Pure Appl. Chem.*, 1962, **4**, 255.
[25] Hammond and Williams, *J. Org. Chem.*, 1962, **27**, 3775, and personal communication.
[26] Mayo and Walling, *Chem. Rev.*, 1950, **46**, 191.
[27] du Pont de Nemours, U.S.P. 2,691,038/1954.
[28] Müller and Huber-Emden, *Annalen*, 1961, **649**, 70.

when present in large amount, are surprisingly inefficient in competing with diazomethane for what we believe to be a primary carbonium ion.

(iii) *The structure of the polymer.* It is generally agreed that the polymethylene obtained by treating diazomethane with boron compounds is unbranched, and indeed it is used as a model straight-chain polymer. Nucleophilic rearrangement of hydride in a primary carbonium ion (eqn. 13) therefore does not occur.



$$\sim\!\sim\overset{\overset{H}{|}}{C}H-\overset{+}{C}H_2 \longrightarrow \sim\!\sim\overset{+}{C}H-CH_3 \qquad (13)$$

If we are to accept the picture of cationic polymerisation, we must again assume that the attack of the diazomethane is a relatively fast process.

(iv) *The question of counter-ions: solvation of the cation by diazomethane.* The question of co-catalysts and counter-ions in cationic polymerisation is notoriously intractable both experimentally and theoretically. In the present case, it might be suggested [5,6] that adventitious water or alcohol acts as a co-catalyst, and provides a counter-ion, by the process:

$$H_2O + BX_3 + CH_2N_2 \longrightarrow CH_3\cdot\overset{+}{N_2}\ \ X_3\overset{-}{B}\cdot OH \xrightarrow[-N_2]{CH_2N_2} CH_3\cdot CH_2\cdot\overset{+}{N_2}\ \ X_3\overset{-}{B}\cdot OH, \text{ etc.} \qquad (14)$$

Although gross amounts of water inhibit the polymerisation, we could not deny that, despite our precautions, much smaller amounts of water or other impurities are present which act as a co-catalyst. Bawn and Ledwith and their co-workers, however, have established that this process is most unlikely.[10]

Secondly, a counter-ion could be provided by the process:

$$2BX_3 + CH_2N_2 \longrightarrow X_2B\cdot CH_2\cdot N_2^+\ \ BX_4^- \xrightarrow[-N_2]{CH_2N_2} X_2B\cdot CH_2\cdot CH_2\cdot N_2^+\ \ BX_4^-, \text{ etc.} \qquad (15$$

This remains a formal possibility, but we believe that it is an unnecessary assumption, and that a more consistent and satisfactory picture can be based on interaction between the cationic pole and the dipolar diazomethane, as follows.

In the non-polar solvent ether, the positive diazonium pole will attract around itself a shell of polar, polarisable, diazomethane molecules. These will solvate strongly, and (with a similar solvation of the negative pole) will take the place of the counter-ion which is usually postulated. If this is accepted, the apparently anomalous behaviour of the primary carbonium ion and the diazomethane nucleophile is recognisable as the established behaviour [29] of a strongly solvated diazonium ion in a non-polar medium.

The very reactive primary carbonium ion, when liberated, finds itself surrounded by orientated diazomethane molecules, while the hydrogen on the β-position is predominantly in an unfavourable conformation for migration.[30] Reaction therefore occurs very rapidly with the diazomethane, and no migration of hydride is observed. In the same way, it has been shown that if the n-propyl cation is generated from its diazonium ion in ether in the presence of acetate ion, the product is overwhelmingly n-propyl acetate.[31]

Non-polar molecules such as " iso-octane " and 4-methoxystyrene will be outside the solvating shell of diazomethane molecules and will have no chance of capturing the carbonium ion. Only a relatively polar molecule, such as water or an alcohol or amine, can be present in the shell and compete on more equal terms.

Conclusion.—Our analysis of these interdependent reactions is summarised in the abstract at the beginning of this paper and in the annexed scheme.

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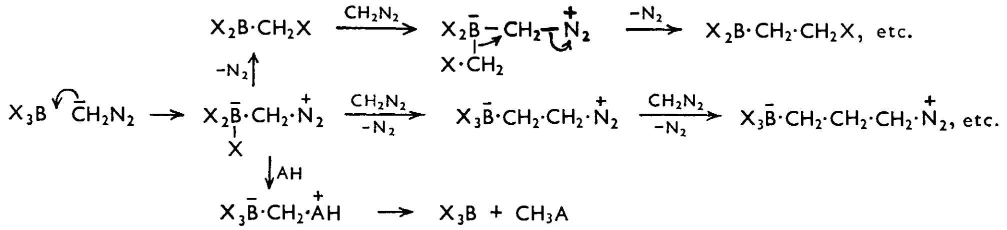
[29] Reviewed by Ridd, *Quart. Rev.*, 1961, **15**, 418, and by Zollinger, " Azo and Diazo Chemistry," Interscience Publ., Inc., New York, 1961, pp. 123—136.

[30] Cram and McCarty, *J. Amer. Chem. Soc.*, 1957, **79**, 2866.

[31] (*a*) Adamson and Kenner, *J.*, 1935, 286; (*b*) Huisgen and Rüchardt, *Annalen*, 1956, **601**, 1, 121.



Much work has also been reported on similar reaction systems involving other diazoalkanes,[3,5,21,24,32] and other metal catalysts [8,24,33] (especially compounds of copper [5,32a,32d,34] and of gold [24,32c,32f]), where olefins or azines may be major products. The analysis suggested here, with appropriate modifications, appears to be applicable also to these systems.

EXPERIMENTAL

Reagents.—Ethereal diazomethane (*ca.* 0·5M), prepared by hydrolysing methylnitrosourea, was filtered through glass wool at −80° to remove ice, dried thoroughly over potassium hydroxide pellets, and stored at −80°. Borosilicate glass (powdered " Pyrex ") had no significant effect on the stability of the solution at room temperature. The diazomethane was estimated before use by adding an excess of benzoic acid and back-titrating the excess with sodium hydroxide solution. By this method, and by following the optical density at 4500 mμ, it was shown that no reaction occurred between diazomethane and benzylamine during 12 hr.

Boron trifluoride–ether complex (Eastman Kodak) was redistilled and a middle fraction collected. Triphenylborane (L. Light & Co.) was recrystallised three times from benzene under nitrogen. Phenylboronic acid, m. p. 215°, was obtained by treating n-butyl borate with phenylmagnesium bromide. The preparation of the other organoboron compounds has been described previously.[20]

Reaction of Diazomethane with Boron Compounds.—The reaction of diazomethane with tri-s-butylborane in the presence of benzylamine (Expt. 11) is described in detail to illustrate most of the experimental points. The other significant experiments are summarised in the Table.

The apparatus consisted of a 500 c.c. three-necked flask fitted with a jacketed dropping-funnel, stirrer, nitrogen inlet and outlet, and a plunger for breaking the encapsulated borane.[35] All solvents and solutions were outgassed before use.

The apparatus containing the capsule of tri-s-butylborane (0·3358 g.) was flushed with oxygen-free nitrogen for 1 hr. Either (31 c.c.) containing benzylamine (0·5928 g.) was then added, the capsule was broken, and the solution cooled to −75°. Diazomethane (0·0775 g.) in ether (92 c.c.) at −75° was then added during 0·5 hr.; no reaction was apparent. The mixture was allowed to warm slowly: the colour of the diazomethane disappeared between −50° and −45°, and some polymethylene was formed.

At room temperature, the mixture was oxidised with peroxyoctanoic acid (1·775 g., 6·0 mol.) and after 1 hr. was hydrolysed with water (0·2 g., 6 mol.), for 2 hr. Most of the ether was distilled off. The remaining material which was volatile at −75°/0·03 mm. was analysed by gas–liquid chromatography (Silicone oil on Celite at 101°; 1·00 l. of N_2/hr.), and shown by comparison with the authentic compounds to contain only s-butyl alcohol and 2-methylbutan-1-ol (*ca.* 30% yield on diazomethane).

The involatile residue was basified. extracted with ether, and analysed similarly (at 170°); benzylamine, methylbenzylamine, and dimethylbenzylamine were detected. Amines were also sometimes analysed by Wagner, Brown, and Peters's method.[36]

In some experiments, the infrared spectrum of the polymethylene was determined as follows.

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[32] (*a*) Buckley, Cross, and Ray, *J.*, 1950, 2714; (*b*) Yakubovich and Ginsberg, *Doklady Akad. Nauk S.S.S.R.*, 1950, **73**, 957; (*c*) Ledwith, *Chem. and Ind.*, 1956, 2714; (*d*) Korshak and Sergeev, *Doklady Akad. Nauk S.S.S.R.*, 1957, **115**, 308; (*e*) Bawn, Ledwith, and Matthies, *J. Polymer Sci.*, 1958, **33**, 21; (*f*) Nasini, *J. Polymer Sci.*, 1959, **34**, 93.

[33] Wittig and Schwarzenbach, *Annalen*, 1961, **650**, 1.

[34] Bawn and Rhodes, *Trans. Faraday Soc.*, 1954, **50**, 934.

[35] Abraham and Davies, *J.*, 1959, 429.

[36] Wagner, Brown, and Peters, *J. Amer. Chem. Soc.*, 1947, **69**, 2609.

The polymer, freshly recrystallised or reprecipitated if possible, was triturated to a smooth paste with ether, and applied to a potassium bromide plate. After the solvent had evaporated, the even layer of polymethylene powder was covered with the second plate. The cell was mounted in a holder and heated under an infrared lamp until the polymer fused. These samples gave spectra of low background. The plates could be separated with a thin spatula after they had been boiled in xylene.

The standard Dumas analysis for nitrogen is unreliable on polymethylene: a sample of Ziegler-type polyethylene which was recrystallised from xylene showed an apparent content of 1% of nitrogen. The report[4] that some samples of polymethylene which were obtained from diazomethane contained a trace of nitrogen should therefore be treated with reserve.

Attempts to Trap Intermediates.—(i) *With 4-methoxystyrene.* Methyl borate (1 c.c.) was added at 0° to diazomethane (0·62 g.) and 4-methoxystyrene (1·3488 g.) in ether (20 c.c.). Nitrogen was evolved, and the colour of the diazomethane was discharged in 2 min. The polymer was filtered off and found to have an infrared spectrum identical with that of pure polymethylene. 4-Methoxystyrene was recovered from the filtrate.

(ii) *With cyclohexene.* Diazomethane (2·1 g.) in ether (85 c.c.) at −70° was added under nitrogen to a stirred solution of cyclohexene (5 c.c.) and boron trifluoride–ether complex (3·5 c.c.) in ether at −70°. After 30 min., the mixture was allowed to warm to room temperature. Polymethylene (85%) and boron trifluoride–ether complex were recovered, but no norcarane could be detected.

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William Ramsay and Ralph Forster Laboratories,
University College, Gower Street, London, W.C.1.
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