529. *The Reaction of Diborane with Some Alkene Oxides and Vinyl Compounds.*

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Diborane reacted rapidly with ethylene oxide at −80° forming diethoxyborine and a solid polymer containing *ca.* eight oxide units per molecule. Propylene oxide reacted similarly, forming di*iso*propoxyborine and a liquid polymer containing *ca.* six oxide units per molecule. Both polymers contained boron, and were shown to be of the type $H\cdot[CHR\cdot CH_2O]_n\cdot BH_2$. The reaction between boron trifluoride and ethylene oxide was studied under similar conditions. The mechanism of the reactions is discussed. Preliminary experiments showed that reactions of diborane with acrylonitrile, methyl methacrylate, and styrene were complex. The main product in each case appeared to be a trialkyl derivative of boron.

The electron-deficient nature of the so-called borine molecule is well known and its co-ordinating power is one of the characteristic features of diborane chemistry (Burg and Schlesinger, *J. Amer. Chem. Soc.*, 1937, **59**, 780). The reactions described below were studied in order to investigate the effect of diborane on molecules where co-ordination might be followed by molecular rearrangement, leading to further reaction, or where the transient existence of the borine molecule might initiate a reaction.

Diborane reacted rapidly with ethylene oxide and propylene oxide at −80°. At room temperature, in the gas phase, the reaction proceeded more slowly. From ethylene oxide, diethoxyborine was formed, together with a white polymeric solid. The latter contained, on the average, eight oxide units per molecule. Propylene oxide reacted in a similar manner, the products being di*iso*propoxyborine and a liquid polymer with an average of six oxide units per molecule. The polymers obtained from both alkene oxides contained boron. Infra-red analysis of these polymers has shown that they do not contain hydroxyl groups or olefinic double bonds. The infra-red spectra do, however, show the presence of B–H stretching frequencies identical with those of the terminal BH_2 groups in diborane (Stitt and Price, *J. Chem. Physics*, 1941, **9**, 780; 1947, **15**, 614). The spectrum of the polymer from ethylene oxide also shows an absorption band characteristic of a methyl group.

There is evidence, therefore, that the structure of the polymers is of the type $H\cdot[CHR\cdot CH_2\cdot O]_n\cdot BH_2$, where $R = H$ or CH_3 according to whether the polymer is derived from ethylene or propylene oxide. The wax-like polymer from ethylene oxide has a melting range of from 45° to 50° and, like its analogue derived from propylene oxide, is hygroscopic, insoluble in ether, and soluble in water or alcohol with the evolution of a small quantity of hydrogen. Depolymerisation occurs when the polymers are heated under a high vacuum.

Observations on the dialkoxyborines, produced simultaneously with the polymers, have confirmed those made by Brown, Schlesinger, and Burg (*J. Amer. Chem. Soc.*, 1939, **61**, 673).

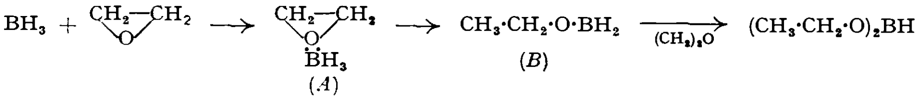
In order to correlate the reactivity of the borine molecule with that of boron trifluoride, a reaction between ethylene oxide and boron trifluoride at −80° was carried out in the high-vacuum apparatus, under the same conditions as were used for diborane.

Such a reaction is also of interest in the study of boron trifluoride-catalysed polymerisations in general, since, under the conditions used, any hydroxylic co-catalyst would be rigidly excluded. The presence of water vapour or other compounds containing a hydroxyl group has been shown to be necessary for the polymerisation of *iso*butene by boron trifluoride (Evans and Meadows, *J. Polymer Sci.*, 1949, **4**, 359; Symposium on Friedel–Crafts Catalysts, *Nature*, 1949, **164**, 655). It is possible, however, that in the reaction between boron trifluoride and ethylene oxide the latter itself acts as a co-catalyst. The reaction is highly exothermic; dioxan is formed together with liquid polymeric boron-containing material, which readily depolymerises at room temperature to give dioxan and less volatile material. A preliminary study of the infra-red spectra of the polymer has shown the absence of any absorption due to an olefinic double bond or hydroxyl group.

The action of the boron trifluoride–ether complex on cyclic oxides in the presence of compounds containing a carbonyl group has been studied by Petrov (*J. Gen. Chem. Russia*, 1940, **10**, 981; 1944, **14**, 1038; 1946, **16**, 61), who found that considerable polymerisation of the oxides occurred as a side reaction even in the presence of a solvent. It is probable that the reaction between diborane and the cyclic oxides involves the intermediate formation of a borine complex, in which the boron atom of the borine molecule is co-ordinated to the oxygen atom of the oxide. This hypothesis is based on the recognised reactions of diborane with ethers, aldehydes, and ketones at −80° (Schlesinger and Burg, *J. Amer. Chem. Soc.*, 1938, **60**, 290; Brown, Schlesinger, and Burg, *ibid.*, 1939, **61**, 673). The formation of the dialkoxyborines by the action of diborane on the alkene oxides is of particular interest, since these compounds are also formed by the reaction of diborane with aldehydes and ketones. Indeed, a mechanism can be postulated to explain the formation of the dialkoxyborines from the alkene oxides similar to that suggested by Brown, Schlesinger, and Burg to explain their production from aldehydes and ketones. The mechanism suggested by the latter workers, taking acetaldehyde as the example, was :

$$CH_3\cdot CHO + BH_3 \longrightarrow \underset{(A)}{CH_3\cdot CHO{:}BH_3} \longrightarrow \underset{(B)}{CH_3\cdot CH_2\cdot O\cdot BH_2} \xrightarrow{CH_3\cdot CHO} (CH_3\cdot CH_2\cdot O)_2BH$$

Similarly for ethylene oxide, we have



Thus the action of diborane on both acetaldehyde and the isomeric ethylene oxide probably results in the formation of the monoalkoxyborine (*B*) which undergoes further reaction to give diethoxyborine. In both cases the step from (*A*) to (*B*) involves the transfer of a proton with a pair of electrons. In the case of the ethylene oxide–borine complex the breaking of the cyclic ring also takes place. The ethylene oxide molecule itself is subject to a considerable amount of internal strain, and it is likely that its borine complex is also unstable. This step would therefore require little energy.

It is possible for the borine–ethylene oxide complex to undergo ring fission without the transfer of a proton with a pair of electrons, and this would lead to the formation of the initiating unit $\overset{+}{C}H_2\cdot CH_2\cdot O\cdot\overset{-}{B}H_3$ and to the possibility of polymerisation by reaction with further ethylene oxide molecules. In order to achieve a neutral polymer molecule a chain termination of four steps is necessary. The evidence from the infra-red spectra that there is no double bond in the polymer molecule, together with the absence of the formation of significant amounts of hydrogen gas, excludes chain termination by the reaction :

$$\begin{aligned}&\overset{-}{B}H_3\cdot[O\cdot CH_2\cdot CH_2]_n\cdot O\cdot CH_2\cdot\overset{+}{C}H_2 + \overset{-}{B}H_3\cdot[O\cdot CH_2\cdot CH_2]_n\cdot O\cdot CH_2\cdot\overset{+}{C}H_2 \longrightarrow\\ &\qquad\overset{-}{B}H_3\cdot[O\cdot CH_2\cdot CH_2]_n\cdot O\cdot CH{=}CH_2 + H_2 + BH_2[O\cdot CH_2\cdot CH_2]_n\cdot O\cdot CH_2\cdot\overset{+}{C}H_2\end{aligned}$$

Any suggested mechanism for the polymerisation of alkene oxides by diborane must, however, await final confirmation from a study of the kinetics, in particular the effect of temperature change, diborane concentration, and monomer concentration.

Polymerisation reactions induced by diborane are not unknown. Brown, Schlesinger, and Burg report the formation of large amounts of paraldehyde together with a polymer of monoalkoxyborine $(CH_3\cdot CH_2\cdot O\cdot BH_2)_x$ in the reaction of diborane and acetaldehyde (*loc. cit.*). Hydrocarbons such as methane react with diborane at about 100°, and paraffin-chain synthesis and the formation of boron–carbon bonds occurs (Hurd, *J. Amer. Chem. Soc.*, 1948, **70**, 2053).

These reactions suggested that diborane might polymerise vinyl compounds. It was found that acrylonitrile, methyl methacrylate, and styrene reacted slowly with diborane at room temperature. The main product in each case appeared to be a trialkyl derivative of boron. The action of diborane on vinyl compounds thus appears to be parallel to that of diborane on olefins, a reaction which also gives boron trialkyls (*idem, ibid.*), *viz.*

$$B_2H_6 + 6R\cdot CH{=}CH_2 = 2(R\cdot CH_2\cdot CH_2)_3B$$

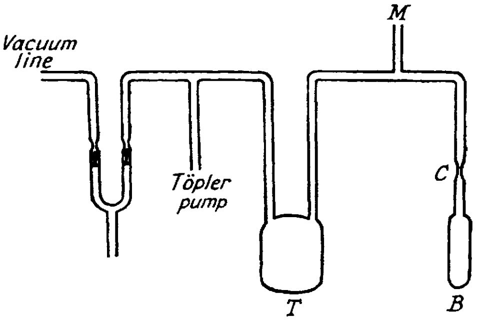
For the reactions between diborane and styrene, and diborane and methyl methacrylate, the reaction ratio of diborane to vinyl compound was close to 1 : 6. Acrylonitrile and diborane, however, reacted to give at least three products, and the ratio of reactants varied considerably with each experiment as the proportion of the products changed. All the latter were non-volatile *in vacuo* even at temperatures as high as 70°. The main product was a red solid, insoluble in all common solvents, but which could be hydrolysed by boiling hydrochloric acid to give its boron content as boric acid. A pale yellow solid was also formed together with a non-volatile oil. Mixtures of products are highly probable because of the possibility of co-ordination of borine molecules to any nitrogen atom capable of donating a pair of electrons. The reaction products deserve further study.

The products from styrene and methyl methacrylate were viscous liquids easily oxidised by air, that from styrene being oxidised with the evolution of a considerable amount of heat.

EXPERIMENTAL.

Apparatus and Technique.—The experimental work was carried out in a high-vacuum apparatus of the type used by Stock and his co-workers (Stock, " Hydrides of Boron and Silicon," Cornell Univ. Press; *Ber.*, 1921, **54**, 142). The reaction vessel is shown in the figure. A small bulb *B*, fitted with a capillary *C*, was attached to the vacuum line by means of a Stock valve. The manometer *M* allowed pressure changes to be followed, and the U-trap *T* was used to condense volatile compounds of the reaction before any non-condensable gas was taken off with the Töpler pump. A known weight of the organic compound was distilled into *B*, followed by a known volume of diborane. The Dewar flask of liquid nitrogen surrounding *B* was then removed, and the diborane allowed to vaporise and react with the organic liquid. In the case of the cyclic oxides, the bulb was cooled in a solid carbon dioxide–alcohol bath during the experiment. At the end of a reaction, after any non-condensable gas had been removed by the Töpler pump, unreacted diborane and organic compound, together with any volatile products, were taken into the vacuum apparatus for separation by trap-to-trap distillation and fractional condensation. Any non-volatile reaction product formed in *B* could be removed for analysis by sealing off the capillary.

The diborane used in the experiments was prepared by reduction of boron trichloride with lithium aluminium hydride (Finholt, Bond, and Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69**, 1199). Boron trifluoride, obtained from a commercial cylinder, was purified by distillation in the high-vacuum system. The organic compounds, also obtained commercially, were purified in a similar manner.



All boron analyses were carried out by titration of boric acid in the presence of mannitol.

Reaction between Diborane and the Alkene Oxides.—In a typical experiment 29·8 millimoles of ethylene oxide (Found: *M*, 44·4) were treated with 3·68 millimoles of diborane (v. p. 158 mm. at $-117°$) at $-80°$. After 20 hours the volatile compounds in the reaction vessel were removed and separated by distillation. 3·4 Millimoles of ethylene oxide (Found: C, 54·5; H, 9·1%; *M*, 44·5. Calc. for C_2H_4O: C, 54·6; H, 9·1%; *M*, 44) were condensed at $-123°$ and 0·43 millimole of diborane (v. p., 166 mm. at $-116°$) were trapped at $-196°$. 3·25 Millimoles of diborane and 26·4 millimoles of ethylene oxide had, therefore, reacted, giving a ratio of reactants B_2H_6 : $(CH_2)_2O$ of 1 : 8·14. Besides the unreacted diborane and ethylene oxide, 0·416 g. of a volatile liquid was condensed at $-65°$ and 0·681 g. of a non-volatile white solid remained in the reaction bulb.

The volatile liquid trapped at $-65°$ was diethoxyborine [Found: B, 10·6, 10·8%; *M*, 100, 102; v. p. 35·5 mm. at 0°. Calc. for $(C_2H_5O)_2BH$: B, 10·6%; *M*, 101·9; lit. value for v. p. at 0°, 37·5 mm. (Brown, Schlesinger, and Burg, *loc. cit.*)]. As reported by the latter workers diethoxyborine decomposes above 0° to give diborane and ethyl borate. The diethoxyborine was kept at room temperature for a week; it was then fractionated to give diborane, diethoxyborine, and ethyl borate [Found: C, 50·0; H, 10·7; B, 7·4, 7·6%;. Calc. for $(C_2H_5O)_3B$: C, 49·4; H, 10·3; B, 7·4%], n_D^{20} 1·3798 (lit., 1·3808).

The *polymer* in the reaction bulb was found to have an average composition corresponding to eight $\cdot CH_2\cdot CH_2\cdot O\cdot$ units per molecule of borine, *viz.*, $H\cdot[CH_2\cdot CH_2\cdot O]_8\cdot BH_2$ [Found: C, 51·3, 53·1; H, 9·8, 9·5; B, 2·1, 2·5%; *M* (Rast), 373. $H\cdot[CH_2\cdot CH_2\cdot O]_8\cdot BH_2$ requires C, 52·5; H, 9·6; B, 2·9%; *M*, 366]. It was hygroscopic. A specimen exposed to the atmosphere for one hour before analysis was found to have C, 47·3; H, 8·8%. $H\cdot[CH_2\cdot CH_2\cdot O]_8\cdot B(OH)_2$ requires C, 48·2; H, 8·8%.

Other experiments with diborane and ethylene oxide were carried out, and the ratio of reactants, together with the approximate yields of product, are shown in the following table. In an experiment using excess of diborane the reaction ratio of diborane to ethylene oxide was reduced to 1 : 5·08, and in a vapour-phase reaction the ratio was 1 : 5·35.

B_2H_6 used (millimoles).	$(CH_2)_2O$ used (millimoles).	Ratio.	$BH(OEt)_2$ formed (g.).	Polymer formed (g.).	B_2H_6 used (millimoles).	$(CH_2)_2O$ used (millimoles).	Ratio.	$BH(OEt)_2$ formed (g.).	Polymer formed (g.).
3·28	28·4	1 : 8·66	0·268	0·794	2·13	14·79	1 : 6·95	0·227	0·462
2·26	22·45	1 : 9·94	0·301	0·724	1·68	12·5	1 : 7·45	0·280	0·341

The reaction between diborane and excess of propylene oxide at $-80°$ was similar to that with ethylene oxide. The polymeric material produced was liquid and the di*iso*propoxyborine formed was characterised by molecular weight, boron analysis [Found: B, 8·35, 8·6%; *M*, 128·3, 130. Calc. for $(C_3H_7O)_2BH$: B, 8·3%; *M*, 129·9], and v. p. at 0° (10·1 mm. Lit. value, *loc. cit.*, 10·0 mm.). After storage for one week at room temperature, it was fractionated to give diborane, a little unchanged dialkoxyborine, and a less volatile liquid [Found, for the last: C, 58·4; H, 11·5; B, 6·05, 5·55. Calc. for $(C_3H_7O)_3B$: C, 57·6; H, 11·2; B, 5·75%].

The liquid *polymer* formed in the reaction was analysed [Found : C, 59·3, 60·9; H, 10·6, 10·6; B, 3·0, 2·9, 2·8%; *M* (Rast), 308, 324. $H\cdot[CH(CH_3)\cdot CH_2\cdot O]_6\cdot BH_2$ requires C, 59·8; H, 10·8; B, 3·0%; *M*, 362].

Further experimental data for the reaction between diborane and propylene oxide are given below. Diborane used in the reaction was tensimetrically pure. The propylene oxide had C, 61·9; H, 10·1%; *M*, 58·9 (Calc. for C_3H_6O : C, 62·1; H, 10·35%; *M*, 58).

B_2H_6 used (milli-moles).	$(CHMe\cdot CH_2)O$ used (milli-moles).	Ratio.	$BH(OPr)_2$ formed (g.).	Polymer formed (g.).	B_2H_6 used (milli-moles).	$(CHMe\cdot CH_2)O$ used (milli-moles).	Ratio.	$BH(OPr)_2$ formed (g.).	Polymer formed (g.).
2·91	14·5	1 : 4·98	—	—	3·34	16·19	1 : 4·85	0·740	0·166
3·79	18·38	1 : 4·86	0·875	0·181	2·88	14·5	1 : 5·03	0·679	0·224

The absorption of diborane by the alkene oxides at −80° proceeds rapidly at first but after an hour the absorption takes place more slowly (see table). The reaction was continued, however, in order to increase the yield of products. The rate at which ethylene oxide reacts with diborane in the vapour phase at room temperature is shown in a further table.

Reaction between diborane and ethylene oxide at —80.°

Time, hours	0	0·25	0·5	1	2	6	15	20
Pressure of B_2H_6, mm.	208	137	131	126	121	105	86	80·5

Reaction between diborane and ethylene oxide in the vapour phase.

Time, hours	0	0·5	1	1·5	2	2·5	3
Total pressure of gas, mm.	332	326	316	305	297	293	287

Reaction between Boron Trifluoride and Ethylene Oxide at −80°.—In a typical experiment, 22·3 millimoles of ethylene oxide were treated with 3·07 millimoles of boron trifluoride. The reaction appeared to be complete in a few minutes. After an hour the volatile compounds were removed from the reaction vessel. 0·42 Millimole of ethylene oxide was recovered together with 0·159 g. of a volatile liquid trapped at —45°. 0·98 G. of non-volatile polymeric material remained in the trap. No boron trifluoride was recovered. The reaction ratio boron trifluoride to ethylene oxide was, therefore, 1 : 7·1. The volatile liquid trapped at —45° was dioxan (Found : C, 54·5; H, 8·9%; *M*, 88·4. Calc. for $C_4H_8O_2$: C, 54·5; H, 9·1%; *M*, 88); n_D^{20} 1·4226 (lit., 1·4224). In other experiments the reaction ratio of boron trifluoride to ethylene oxide was 1 : 6·46, 1 : 6·23, 1 : 6·23, and 1 : 7·23.

The non-volatile polymeric material was a liquid which depolymerised at room temperature. This depolymerisation was accelerated by gentle warming, under high vacuum, at approximately 40°. The main product of depolymerisation was impure dioxan : *M*, 87·2; n_D^{20} 1·431 (cf. above). A black liquid residue remained in the reaction trap after several hours' pumping and gentle warming (Found : B, 8·8%).

Measurement of the Spectra.—The spectra were measured on a Standard Perkin Elmer Model 12B infra-red spectrometer fitted with a rock-salt prism. Two thicknesses of liquid polymer were used, the thicker layer being 160 μ. and the thinner one 20 μ.

In the case of the solid polymer prepared from ethylene oxide and diborane, a liquid film was produced by gently warming the rock-salt plates of the cell to approximately the m. p. of the polymer before the latter was placed between them. The samples were sealed *in vacuo* for transportation, and the spectra were taken immediately after the samples had been unsealed.

Neither the polymer from ethylene oxide nor that from propylene oxide showed any absorption in the double-bond region 1600—1700 cm.$^{-1}$. There was no absorption band corresponding to a hydroxyl group on freshly opened samples of the polymers, but a sample which had been exposed to the air for a short time showed a weak band at 3300 cm.$^{-1}$.

The polymer from ethylene oxide showed weak absorption bands at 2520 cm.$^{-1}$ and 2620 cm.$^{-1}$, corresponding to the stretching of B–H bonds. These bands were stronger, however, in the lower molecular-weight polymer from propylene oxide. A strong absorption band at 1375 cm.$^{-1}$ in the polymer from ethylene oxide probably indicates a methyl group. A preliminary investigation of the spectra of the polymeric material obtained from boron trifluoride and ethylene oxide also showed no bands at 1600—1700 cm.$^{-1}$ and 3300 cm.$^{-1}$.

Acrylonitrile and Diborane.—In a typical experiment 4·24 millimoles of tensimetrically pure diborane remained in contact with 41·8 millimoles of acrylonitrile for 20 hours at room temperature. All volatile compounds were then removed from the reaction vessel. After fractionation, 1·62 millimoles of diborane and 26·9 millimoles of acrylonitrile were recovered, giving a reaction ratio diborane : acrylonitrile of 1 : 5·7. The solid *product* was analysed [Found : C, 61·9; H, 6·8; N, 23·85; B, 6·6, 6·3. $B_2H_6(CH_2\cdot CH\cdot CN)_{5\cdot 7}$ requires C, 62·1; H, 7·0; N, 24·2; B, 6·55%]. In this experiment the product was almost entirely a red solid and there was little formation of yellow solid and oil. In other experiments, however, the proportion of the latter in the reaction product increased. The red and yellow solid reaction products were insoluble in water, alcohol, acetone, ether, chloroform, and benzene, but freely soluble in formodimethylamide.

In other experiments the ratio of reactants diborane : acrylonitrile was 1 : 3·52, 1 : 4·56, 1 : 5·12 The products of this reaction were far more stable in air than those from styrene and methyl methacrylate the latter being rapidly oxidised.

Methyl Methacrylate and Diborane.—In a typical experiment 19·12 millimoles of methyl methacrylate were treated with 4·10 millimoles of diborane. After approximately 20 hours the volatile compounds were taken into the high-vacuum system for separation by distillation: 2·72 millimoles of diborane and 10·47 millimoles of methyl methacrylate were recovered. Thus the ratio of reactants diborane : methyl methacrylate was 1 : 6·26. In a second experiment it was 1 : 5·6. The reaction *product* was a highly viscous liquid, soluble in acetone and benzene. Boron analysis carried out on the products of the two experiments gave B, 3·6 and 3·9% {$[CH_2{\cdot}CH(CH_3){\cdot}CO_2CH_3]_3B$ requires B, 3·45%}. In this preliminary study no evidence for the cleavage of the ester by the borine molecule was observed (Brown, Schlesinger, and Burg, *loc. cit.*).

Styrene and Diborane.—In a typical reaction between excess of styrene and diborane, 0·504 g. of styrene reacted with 0·0207 g. of diborane, giving a ratio of reactants of 6·46 : 1. The *product*, soluble in benzene, had B, 2·7, 3·15% [$(C_6H_5{\cdot}CH_2{\cdot}CH_2)_3B$ requires B, 3·3%].

Rapid oxidation by the atmosphere of the liquid products of the above two reactions prevented accurate values of carbon and hydrogen analysis and molecular weight from being obtained. Values of 260 and 292 were obtained for the two liquids, respectively, by the cryoscopic method, benzene being used as solvent: $[CH_2{\cdot}CH(CH_3){\cdot}CO_2CH_3]_3B$ requires *M*, 314, and $(C_6H_5{\cdot}CH_2{\cdot}CH_2)_3B$ requires *M*, 326.

In the reactions described above diborane was allowed to remain in contact with the organic compounds for approximately 20 hours, small quantities of hydrogen being formed. This gas formation was not connected with the main reaction but was due to a reaction between the surface of the reaction system and the diborane. This was shown by carrying out two blank experiments in which diborane alone was placed in the apparatus for a few hours, during which time 6·2 and 8·9 c.c. of hydrogen were formed. The volume of hydrogen formed in any one experiment depended entirely on the type of pre-treatment given to the glass. In three reactions in which the reaction bulb was merely pumped to a hard vacuum for several hours before an experiment, the volumes of hydrogen formed were 6·85, 6·1, and 7·0 c.c. Before two other experiments the reaction bulb was baked during evacuation; the volumes of hydrogen formed in these reactions were 4·8 and 5·6 c.c. Formation of hydrogen gas was reduced to a minimum by evacuating the reaction system while heating it and then allowing diborane to remain in the apparatus for a few hours before an experiment. Such pre-treatment of the glass of the system reduced the volume of hydrogen formed in two reactions to 2·8 and 2·88 c.c. All the glass used in the apparatus was subjected to a uniform pre-treatment of washing with chromic acid and distilled water, followed by air-drying.

One of the authors (F. G. A. S.) is indebted to the Department of Scientific and Industrial Research for a Maintenance Grant. The authors also thank Dr. N. Sheppard for photographing and interpreting the infra-red spectra.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, June 3rd*, 1950.]