The polymerisation of epoxides by metal halide catalysts

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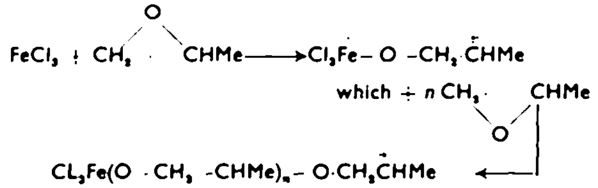
AT the Nottingham Conference on High Polymers (July, 1958) Professor G. Gee and his colleagues[1] advanced a mechanism for the polymerisation of propylene oxide in the presence of ferric chloride which included both (a) a cationic mechanism using carbonium ions terminally, and in a distinct second stage (b) a complex-formation and migration mechanism.

(a)

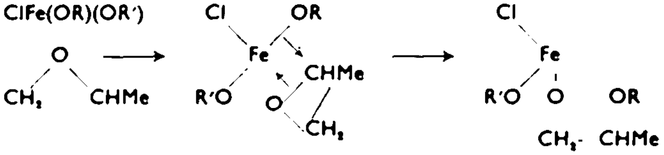


with termination by formation of $Cl_2Fe(O{\cdot}CH_2{\cdot}CHMe)_n{\cdot}O{\cdot}CH_2{\cdot}CHMeCl$
A second similar process affords ClFe(OR)(OR′)

where R = $(O{\cdot}CH_2CHMe)_xCl$

and R′ = R or is $(O{\cdot}CH_2{\cdot}CHMe)_{x\,.\,.\,y}Cl$

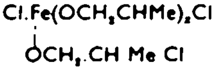
(b)



As the product remains of the form $ClFe(OR)_2$ the process can be continued with formation of a high polymer.

This latter idea amounts to insertion of the polymerising unit between the metal atom and the first oxygen atom of the chain. It is fully analogous to Professor C. E. H. Bawn's view[2] of the formation of polymethylene and substituted polymethylene chains from diazoalkanes and trivalent boron catalysts, and also to the present writer's conception of the formation of polyethylene using Ziegler catalysts.[3] It seems, however, unnecessary to postulate a different type of mechanism as in (a); the complex migration process of (b) may be used from the beginning and throughout the sequence of reactions. The assumption must be made that the migratory aptitude of –OR is superior to that of –Cl and also that the latter decreases in the series Cl_3Fe, Cl_2Fe, ClFe. This is in complete agreement with Bawn's conclusion that all the products from BF_3 and nCH_2N_2 are $F_2B(CH_2)_nF$.

The first product is then $Cl_2Fe{\cdot}O{\cdot}CH_2{\cdot}CHMeCl$ and this is rapidly changed by further union with C_3H_6O and OR migration to $Cl_2Fe(OCH_2{\cdot}CHMe)_xCl$ (where x is a small number). At this stage the slower Cl from Cl_2Fe attacks the complexing unit and we get



$$\begin{array}{l}Cl.Fe(OCH_2CHMe)_xCl\\ \,|\\ OCH_2.CH\,Me\,Cl\end{array}$$

There can be little doubt but that when the metal carries *two* chains the rate of complex formation will be drastically reduced; transition from Fe–O– to ·O–Fe–O could have a similar effect. Naturally the shorter chain could include more than one $-O-C_3$ unit, in fact just as many as are needed to produce the steric hindrance contemplated. Probably only one group, as above, would suffice. It may be anticipated, therefore, that the two chains produced in the first rapid phase of the polymerisation will not be even approximately equal in length.

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[1] *Technical Press reports*, e.g. R. O. Colclough, E. Gee, W. C. E. Higginson, S. B. Jackson and M. Litt; *Plastics* October (1958).

[2] Communication to the Nottingham Conference on High Polymer Technology, July (1958).

[3] R. Robinson, *The Chemical Age* May 5th (1956); lecture to joint meeting of the Italian Chemical Society and the Society of Chemical Industry, Turin, Nov (1957). (In the press).

The writer's interest in what may be thought a point of minor importance is mainly that he sees no necessity for the assumption of fully developed carbonium ions as intermediates in reactions. The processes so illustrated in terms of current dogma, can always be considered as concerted and the cationic charge can be dissipated before it reaches its maximum possible value.

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The reductive coupling of triphenylchlorosilane: evidence for the triphenylsilyl Grignard reagent*

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We wish to report a new reaction in organosilicon chemistry, the coupling of two molecules of a chlorosilane by a Grignard reagent to produce the Si-Si linkage. The nature of the reaction products indicates that probably an organosilylmagnesium compound is formed as an intermediate. This intermediate would constitute the first known example of a "silyl Grignard reagent".

When 0·05 mole of triphenylchlorosilane was refluxed for 18 hours or longer with 0·10 mole of *cyclo*hexylmagnesium bromide in 250 ml of tetrahydrofuran, hexaphenyldisilane, m.p. 365-366°, was produced in 67 per cent yield. One mole each of *cyclo*hexene and *cyclo*hexane are produced for each mole of $Ph_3SiSiPh_3$ formed in this coupling reaction. Phenyl and 2-methyl*cyclo*hexyl Grignard reagents gave 51 per cent and 62 per cent yields respectively of $Ph_3SiSiPh_3$ under the same conditions. The solvent has an important influence on the course of the reaction since no disilane is obtained when tetrahydrofuran is replaced by the less basic solvent diethyl ether.

The nature of the reaction suggests that a silylmetallic intermediate may be involved. Indeed, other investigators have shown that organosilylmetallic compounds R_3SiM (M Na, K, Li) will couple with chlorosilanes to produce the Si-Si linkage,[1,2] and Gilman has noted the stabilization of R_3SiM compounds by tetrahydrofuran.[2,3,4] The most significant evidence in favor of the organosilylmagnesium intermediate in our reaction comes from experiments using trimethyl chlorosilane. Me_3SiCl is not coupled by *cyclo*hexylmagnesium bromide in refluxing tetrahydrofuran, and after 24 hours most of the Me_3SiCl so treated can be recovered unchanged. However when a mixture of Ph_3SiCl and Me_3SiCl was treated with the same Grignard reagent system, *$Ph_3SiSiMe_3$, m.p. 106-108°, was produced in 14 per cent yield.* It is difficult to account for the formation of this unsymmetrical coupling product except by the reaction of the intermediate Ph_3SiMgX with Me_3SiCl. Apparently aromatic groups on silicon are necessary for the stabilization of the silyl Grignard reagent, just as they appear necessary for the formation of organosilylalkali compounds.[4]

We suggest the following tentative mechanism for the coupling reaction with *cyclo*hexyl Grignard reagent. Ph_3SiCl and *cyclo*hexylmagnesium bromide may undergo a four-center reaction, with the formation of $Ph_3SiMgBr$, *cyclo*hexene, and HCl:

The $Ph_3SiMgBr$, which need not be present in large concentration at any time, would couple with an additional molecule of chlorosilane. The HCl formed as a by-product would attack another molecule

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[1] R. A. Benkeser and R. G. Severson, *J. Amer. Chem. Soc.* 73, 1424 (1951).

[2] A. G. Brook and H. Gilman, *J. Amer. Chem. Soc.* 76, 278 (1954).

[3] H. Gilman and G. D. Lichtenwalter, *J. Amer. Chem. Soc.* **80**, 608 (1958).

[4] H. Gilman and T. C. Wu, *J. Amer. Chem. Soc.* 73, 4031 (1951).