The Constitution of the Grignard Reagent

Sir:

It has been shown that 1:1 mixtures of diethylmagnesium (Et_2Mg) and magnesium bromide ($MgBr_2$) in ether resemble, in chemical activity, the reagent made from ethyl bromide and magnesium in ether,[1] "EtMgBr." Since both solutions have the same rate and kinetics of reaction with a substrate, hexyne-1, the conclusion was reached that they contain the same species. Employing this assumption and utilizing radioactive tracers it was shown[2] that the Schlenk equilibrium must have the form

$$2RMgX \not\rightleftharpoons R_2Mg + MgX_2 \rightleftharpoons R_2Mg \cdot MgX_2$$

and that the species RMgX does not exist (since R_2Mg and Mg^*X_2 do not exchange Mg^*).

We have now found physical evidence for the assumption that mixtures of Et_2Mg and $MgBr_2$ and the classical Grignard reagent "EtMgBr" contain the same species.

Figures 1 and 2 show values for the dielectric constant, ϵ, of mixtures of Et_2Mg and $MgBr_2$ in ether at varying $Et_2Mg/MgBr_2$ ratios, measured at 5 megacycles/sec. Also plotted are the experimental points for the reagent prepared from ethyl bromide and magnesium ("EtMgBr"). (Values of ϵ for "EtMgBr" and Et_2Mg separately at varying concentrations have been reported.[3])

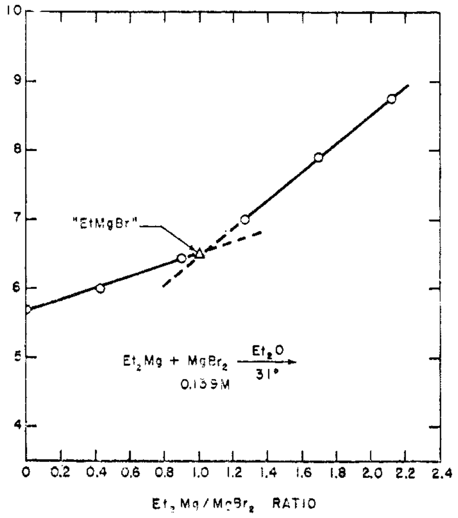

Figure 1

Figure 1 illustrates the addition of Et_2Mg to a saturated solution of $MgBr_2 \cdot 2Et_2O$ in ether. Figure 2 illustrates the addition of $MgBr_2 \cdot 2Et_2O$ to a solution of Et_2Mg.

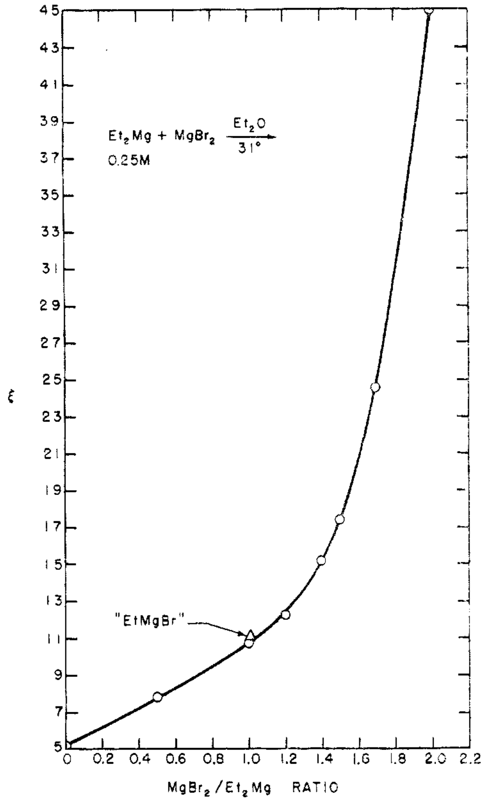

Figure 2

The following items should be noted: (1) the dielectric constant values of mixtures of Et_2Mg and $MgBr_2$ at varying $Et_2Mg/MgBr_2$ ratios show a distinct break at 1:1 ratios, indicating stable complex formation; (2) the dielectric constant values for 1:1 mixtures of Et_2Mg and $MgBr_2$ are identical with those measured for equivalent concentrations of "EtMgBr" and higher than the sum for the individual components; and (3) equilibrium is reached in 30 sec. or less.

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[1] J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Org. Chem.*, **21**, 1063 (1956).

[2] R. E. Dessy and G. S. Handler, *J. Am. Chem. Soc.*, **80**, 5824 (1958).

[3] R. E. Dessy and R. M. Jones, *J. Org. Chem.*, **24**, 1685 (1959).

Polyesters from 3,9-Bis(7-carbomethoxyheptyl)-2,4,8,10-tetraoxaspiro[5.5]undecane. A New Method of Cross Linking Polyesters

Sir:

Recent reports on the synthesis of some 3,9-dicarboxylic acids of 2,4,8,10-tetraoxaspiro [5.5] undecane[1] and on the preparation of linear polycyclospiroacetals[2,3] prompt us to report work now

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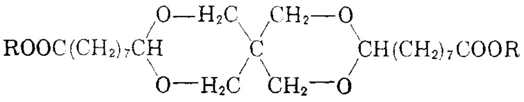
[1] J. B. Clements and L. M. Rice, *J. Org. Chem.*, **24**, 1958 (1959).

[2] D. B. Capps, U. S. Patent 2,889,290, June 2, 1959.

going on in our laboratory on a new method for cross-linking poly(ester-acetal) resins.

Condensation of 3,9-bis(7-carbomethoxyheptyl)-2,4,8,10 - tetraoxaspiro[5.5]undecane (Ib)[4] with ethylene glycol using lime as a catalyst gives a soluble polymer having a molecular weight of 5700 and melting at 78–81°. Condensation of the dibasic acid Ia with ethylene glycol with no catalyst added results in a cross-linked polymer, a rubbery gel, which swells but does not dissolve in benzene or a 50% solution of phenol in tetrachloroethane. We believe that the acidity of the free carboxyl groups is sufficient to activate the acetal bonds and thus cause cross-linking. We also prepared soluble poly(ester-acetals) from combinations of dimethyl terephthalate and the dibasic ester Ib. We discovered that these can be cross-linked by heating with such catalysts as zinc oxide, zinc acetate, litharge, boric acid, and *p*-toluenesulfonic acid.



Ia. R = H
Ib. R = CH_3

Dimethyl terephthalate (13.59 g., 0.07 mole), 3,9-bis(7-carbomethoxyheptyl) - 2,4,8,10 - tetraoxa - spiro[5.5]undecane (Ib) (14.16 g., 0.03 mole), ethylene glycol (7.45 g., 0.12 mole), and calcium oxide (0.005 g.) were placed in a 50-ml. modified distilling flask equipped with a thermometer and a fine capillary inlet for nitrogen. The flask and its contents were heated gradually, and at 180° methanol began distilling from the melt. The temperature was gradually increased to 235° over a 10-hr. period. Heating was continued at 110 mm. of mercury and 233–258° for 2 hr., and finally at 0.1 mm. and 234–280° for an additional $2^1/_4$ hr. The flask was then immersed in a silicone oil bath for 280° and fitted with a 1-ml. graduated pipet from which the tip had been removed. The time required for flow between two 0.1 ml. marks was 0.4 sec. Boric acid (0.015 g.) was added, and as heating continued, the melt viscosity increased gradually at first, then more rapidly (as shown in the Figure 1) until the polymers had set to a rubbery, insoluble gel. At a melt viscosity of 90 sec., the polymer could readily be drawn out into a fiber which showed considerable elasticity. The gel underwent a phase change at 160° but did not melt at 300°. It adhered strongly to the glass of the reaction flask and could be separated only by chilling the flask and polymer to −60°. A polymer prepared in a similar manner from dimethylterephthalate and ethylene glycol but containing no ester-acetal had a melting point of 246–248°.

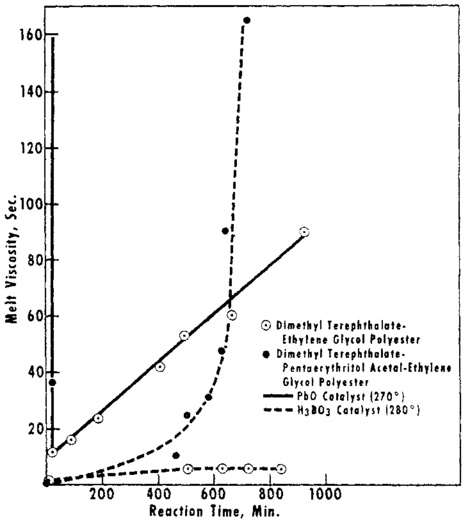


Fig. 1. Effect of Acidic Catalysts on acetal-containing polyesters

In a similar experiment, litharge was added to a soluble poly(ester-acetal) which had a melt viscosity of about 10 sec. at 270° and which had been heated 12 hr. with lime. Within 40 min., the polymer had set to an insoluble gel. Similarly, zinc oxide and zinc acetate gave gelled polymers. With 10 mole per cent of the ester-acetal Ib, polymers at the borderline of gelation were obtained which had melting points of 226° (after a reaction period of 20 min. at 280° with litharge) and of 221–225° (after 173 min. at 250–280° with boric acid). These polymers were soluble in 50% phenol in tetrachloroethane. They were light colored, hard solids which adhered strongly to the glass walls of the reaction flask.

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(3) A. Schors and O. E. van Lohuizen, abstract of talk given before the IUPAC Symposium on Macromolecules, October 12–17, 1959, Wiesbaden, as reported in *Angew. Chem.*, **72**, 117 (1960).

(4) The synthesis of this new compound will be reported in a forthcoming publication.