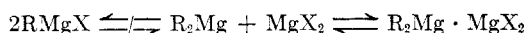


## The Constitution of the Grignard Reagent

Sir:

It has been shown that 1:1 mixtures of diethylmagnesium ( $\text{Et}_2\text{Mg}$ ) and magnesium bromide ( $\text{MgBr}_2$ ) in ether resemble, in chemical activity, the reagent made from ethyl bromide and magnesium in ether,<sup>1</sup> "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<sup>2</sup> that the Schlenk equilibrium must have the form



and that the species  $\text{RMgX}$  does not exist (since  $\text{R}_2\text{Mg}$  and  $\text{Mg}^*\text{X}_2$  do not exchange  $\text{Mg}^*$ ).

We have now found physical evidence for the assumption that mixtures of  $\text{Et}_2\text{Mg}$  and  $\text{MgBr}_2$  and the classical Grignard reagent "EtMgBr" contain the same species.

Figures 1 and 2 show values for the dielectric constant,  $\epsilon$ , of mixtures of  $\text{Et}_2\text{Mg}$  and  $\text{MgBr}_2$  in ether at varying  $\text{Et}_2\text{Mg}/\text{MgBr}_2$  ratios, measured at 5 megacycles/sec. Also plotted are the experi-

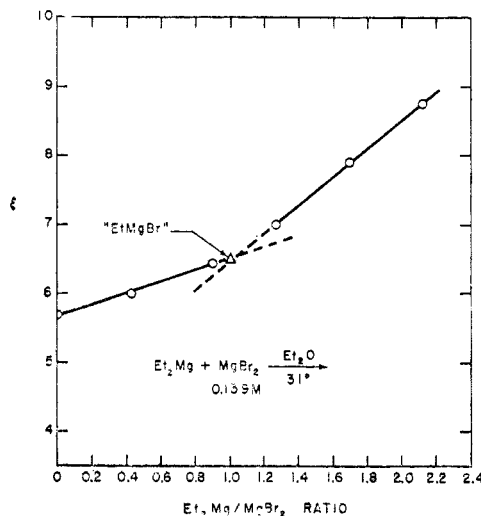


Figure 1

mental points for the reagent prepared from ethyl bromide and magnesium ("EtMgBr"). (Values of  $\epsilon$  for "EtMgBr" and  $\text{Et}_2\text{Mg}$  separately at varying concentrations have been reported.<sup>3</sup>)

Figure 1 illustrates the addition of  $\text{Et}_2\text{Mg}$  to a saturated solution of  $\text{MgBr}_2 \cdot 2\text{Et}_2\text{O}$  in ether. Figure 2 illustrates the addition of  $\text{MgBr}_2 \cdot 2\text{Et}_2\text{O}$  to a solution of  $\text{Et}_2\text{Mg}$ .

(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).

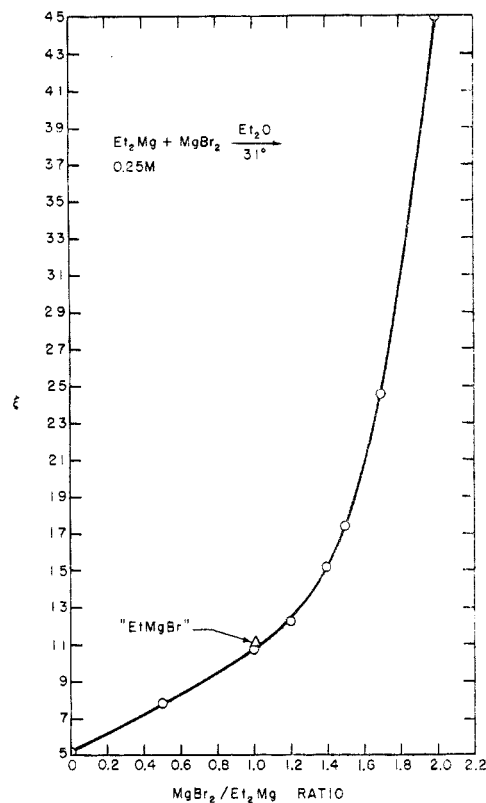


Figure 2

The following items should be noted: (1) the dielectric constant values of mixtures of  $\text{Et}_2\text{Mg}$  and  $\text{MgBr}_2$  at varying  $\text{Et}_2\text{Mg}/\text{MgBr}_2$  ratios show a distinct break at 1:1 ratios, indicating stable complex formation; (2) the dielectric constant values for 1:1 mixtures of  $\text{Et}_2\text{Mg}$  and  $\text{MgBr}_2$  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.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF CINCINNATI  
CINCINNATI, OHIO

RAYMOND E. DESSY

Received September 1, 1960

### 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<sup>1</sup> and on the preparation of linear polycyclospiroacetals<sup>2,3</sup> prompt us to report work now

(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.