A Grignard Reagent from Chloromethyl Methyl Sulphide and Its Use in the Preparation of Methylthiomethyl-substituted Polysilanes

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RECENTLY, a number of Grignard reagents with a negative group in the α-position, such as α-halogenoalkyl Grignard reagents[1] and α-alkoxyalkyl Grignard reagents,[2] have been prepared and utilized in syntheses. For the sulphur analogue, however, only one example, benzylthiomethylmagnesium chloride has been reported by Normant and Castro.[3] But they reported that ethyl chloromethyl sulphide did not afford a magnesium compound even in tetrahydrofuran. Chloromethyl methyl sulphide (I) has also been shown not to react with magnesium in diethyl ether, whereas chloromethyl phenyl sulphide only gave a coupling compound under the same conditions.[4]

Incidental to studies on carbon-functional organopolysilanes, we have found that the sulphide (I) does give the Grignard reagent at room temperature in tetrahydrofuran.

In a typical run, 29·0 g. (0·30 mole) of (I) in 150 ml. of tetrahydrofuran was added to 7·5 g. (0·31 g. atom) of magnesium activated with a small amount of iodine and ethylene bromide in 100 ml. of tetrahydrofuran. An exothermic reaction took place and the colour of the solution changed to black. After the addition of (I) was complete, trimethylchlorosilane (31·0 g., 0·29 mole) was added to this solution. The mixture was heated under reflux for 6 hr. The solvent was then distilled off to ensure a complete reaction and the residual mass was hydrolysed. After the usual work-up, 12·5 g. (32·6%) of methylthiomethyltrimethylsilane,[5] $CH_3{\cdot}SCH_2{\cdot}Si(CH_3)_3$, were obtained as a pure (homogeneous on v.p.c.) colourless liquid.

Although the fact that the Grignard reagent from (I) can be prepared separately should be important for its potential applicability in organic synthesis, some methylthiomethyl-substituted polysilanes were prepared in better yield by *in situ* Grignard and concurrent coupling reactions[6] of (I) with corresponding chlorosilanes. The yields, physical constants, and results of analyses of these new carbon-functional polysilanes will be reported later.

Recently Corey and Seebach[7] have described the procedures to generate phenylthiomethyl-lithium and bis(phenylthio)methyl-lithium by metalation together with some of their synthetic application. Since (I) and related chloroalkyl sulphides are readily available from dimethyl sulphoxide and the corresponding sulphoxides, respectively,[4] the present procedure may afford a useful method in organic synthesis.

(*Received, July* 10*th*, 1967; *Com.* 716.)

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