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The reaction of trimethyl phosphate with magnesium

The existence of silyl Grignard reagents has been postulated by several workers[1], however, at the present time the isolation of such a reagent has not been reported. Compelling evidence for the existence of triphenylsilylmagnesium bromide has been presented by Selin and West[2]. In addition, numerous couplings of chlorosilanes have been observed[3] which may involve silyl Grignard reagents as intermediates.

Recent reports[4] on the use of trialkyl phosphates as alkylating agents for silyllithium compounds, prompted us to attempt the trapping of silyl Grignard reagents (formed "*in situ*") using phosphates of this type. When chlorotriphenylsilane was reacted with magnesium in tetrahydrofuran (THF) solvent in the presence of trimethyl phosphate, a 63.5% yield of methyltriphenylsilane was obtained. While it is possible that this latter material resulted from the reaction of triphenylsilylmagnesium chloride with trimethyl phosphate, further investigation revealed that trimethyl phosphate reacts with magnesium to give a soluble Grignard-type reagent. Derivatization of this reagent with chlorotriphenylsilane gave methyltriphenylsilane (55.5%).

Similar reactions of dialkyl sulfates have been reported to give Grignard-type reagents. Diethyl sulfate reacts with magnesium in ether to give a slightly soluble Grignard-type reagent which, upon reaction with benzaldehyde, gives "good" yields of ethylphenylcarbinol.[5] In addition, di-n-butyl sulfate reacts similarly with magnesium and upon hydrolysis affords butane[6]*. More recently, dimethyl sulfate has been reported[7] to give good yields of the Grignard-type reagent "methylmagnesium methyl sulphate" when the reaction is carried out in THF.

In view of the above, it appears that the formation of methyltriphenylsilane involved alkylation of chlorotriphenylsilane by a Grignard-type reagent rather than the prior formation of triphenylsilylmagnesium chloride. Although the exact nature of this reagent is not known at the present time, two possible active species are methylmagnesium dimethyl phosphate and dimethylmagnesium. This latter compound could be formed by disproportionation of any initially formed methylmagnesium dimethyl phosphate in a manner analogous to that previously postulated for n-butylmagnesium n-butyl sulfate[6].

Experimental

The trimethyl phosphate was obtained from Columbia Chemical Company and was redistilled before use. All melting points are uncorrected. Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. The tetrahydrofuran (THF) was freed from peroxides and moisture before use by refluxing over sodium, followed by distillation from lithium aluminum hydride immediately before use. Chlorotriphenylsilane was purchased from Dow Corning Corporation, and used without further purification.

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* The authors in ref. 6 report that the products of the reaction of di-n-butyl sulfate with magnesium are di-n-butylmagnesium and bis(n-butylmagnesium) sulfate.

Reaction of chlorotriphenylsilane with magnesium in the presence of trimethyl phosphate. A mixture of 14.7 g (0.046 mole) of chlorotriphenylsilane, 6.44 g (0.046 mole) of trimethyl phosphate, 2.46 g (0.1 g-atom) of magnesium and three drops of ethyl iodide was heated with 50 ml of THF for *ca.* 10 min. At this time Color Test I[8] was positive. After refluxing for 48 h the reaction mixture was hydrolyzed by pouring upon crushed ice acidified with 5 *N* hydrochloric acid. Subsequent to the usual work-up, evaporation of the solvents gave 10.3 g of semi-solid residue. This residue was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on an alumina column. Elution with the same solvent gave 8.05 g (63.5%) of white solid, m.p. 69–70°. A mixture melting point with a known sample of methyltriphenylsilane was not depressed and the infrared spectra were superimposable.

Reaction of trimethyl phosphate with magnesium in THF. A solution of 6.44 g (0.046 mole) of trimethyl phosphate in 50 ml of THF was slowly added to 2.43 g (0.1 g-atom) of magnesium in 5 ml of THF containing three drops of ethyl iodide. After a short induction period (*ca.* 10 min), the reaction became exothermic and a brown color developed. When the heat of reaction had dissipated, the mixture was decanted from excess magnesium and added to 14.7 g (0.046 mole) of chlorotriphenylsilane in 30 ml of THF. Color Test I was negative immediately after addition. Work-up of the reaction as described above gave 7.0 g (55.5%) of methyltriphenylsilane, m.p. and mixed m.p. 69–70°.

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