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Preliminary communication

THE REACTION OF MAGNESIUM WITH *cis*-1,3,5-TRIS(BROMOMETHYL)CYCLOHEXANE. EVIDENCE FOR A SOLUBLE TRI-GRIGNARD

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Summary

The reaction of magnesium with *cis*-1,3,5-tris(bromomethyl)cyclohexane in tetrahydrofuran gives good yields of a soluble tri-Grignard reagent. This intermediate was characterized by reactions with water, trimethylchlorosilane and methyltrichlorosilane.

Earlier we reported the synthesis and some reactions of derivatives of the novel bridgehead compound, 1-silaadamantane [1]. One of the key steps in that synthesis was the preparation of *cis*-1,3,5-tris(trimethylsilylmethyl)-cyclohexane (3) from the tribromo precursor 1, via in situ Grignard techniques in which the derivatizing trimethylchlorosilane was in solution with the tribromide 1 while the latter was reacting with magnesium [1]. Under those conditions the mechanism seemed clear: stepwise Grignard formation and silylation to give 3. The opportunity to form a di-Grignard much less a tri-Grignard was highly unlikely.

Di-Grignards of the type $XMg(CH_2)_nMgX$ ($n>2$) are widely used to prepare novel cyclic and heterocyclic compounds [2,3]. However to our knowledge, there are no reports of Grignard reagents containing more than two magnesium atoms. In this communication we describe the preparation and some reactions of the first tri-Grignard reagent, 2.

For the synthesis of 5, 3.16 g (8.7 mmol) of 1 in 15 ml of dry THF was added dropwise to rapidly stirred magnesium turnings (0.85 g, 34.9 mmol) in 10 ml of THF at 0°C under a dry nitrogen atmosphere. The contents were stirred at room temperature for 14 h, and refluxed for 1.5 h. After cooling to room temperature, the grey-black solution of 2 was transferred by means of

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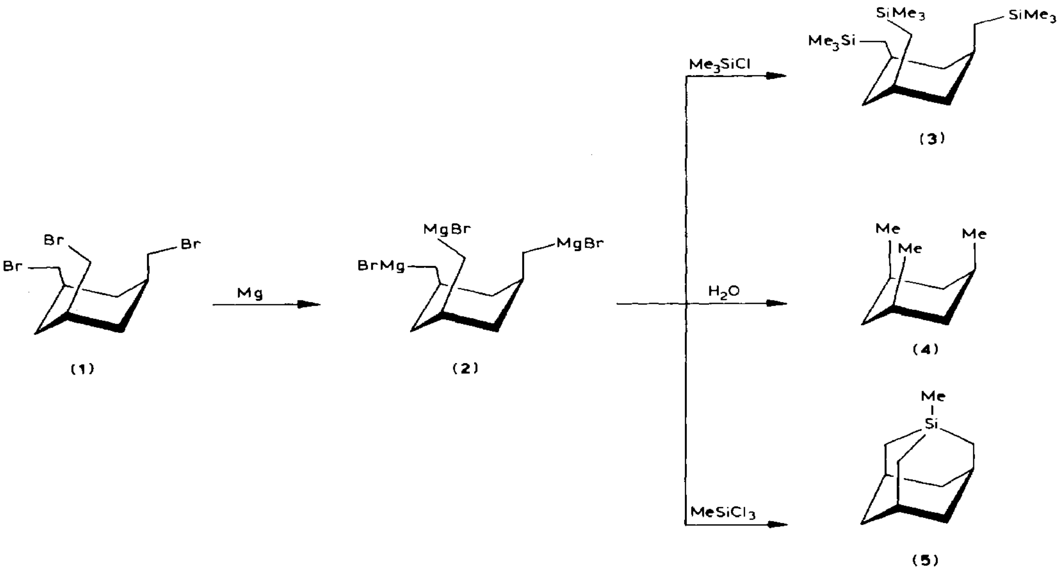
a double tipped needle into an equal pressure addition funnel under a dry nitrogen atmosphere.



Methyltrichlorosilane (1.3 g, 8.7 mmol) in 50 ml of dry THF and the solution of 2 were added simultaneously at a slow drop rate to 10 ml of refluxing THF. When a combined total of 5 ml had been added, 20 ml of dry THF was added to the reaction mixture and the reflux was maintained. The co-addition was complete in 8 h and was followed by a 15 h reflux period. Hydrolysis with ice (3 g), concentration under reduced pressure, extraction with ether (75 ml) followed by washing with saturated sodium chloride solution (2 × 40 ml) and drying over magnesium sulfate and further concentration gave a clear yellow oil. This oil (0.5 g) was mostly a polymer that could be retained on a silica gel column when eluted with pentane. A small quantity (0.05 g) of a clear colorless oil was collected and proved to be mostly 1-methyl-1-silaadamantane (5). Standard preparative GLC techniques led to isolation of a 2% yield of analytically pure 5 [1].

In spite of the low yield of 5, the successful "capping" of the tri-Grignard 2 illustrates the potential of poly-Grignards in the synthesis of novel compounds. It should be noted that the low yield is due, at least in part, to using reaction conditions which are not yet optimized and that affects the second stage of the synthesis, i.e., the reaction with methyltrichlorosilane.

With simpler electrophiles the reactions are significantly improved. For example, when the solution of 2 is prepared as described above and then treated with trimethylchlorosilane a 44% yield of analytically pure 3 [1] is obtained. If water is used to quench the tri-Grignard, *cis*-1,3,5-trimethylcyclohexane (4) [4], is recovered quantitatively. Subsequent experiments have shown that formation of 2 is complete in less than thirty minutes at room temperature. Clearly the unique structure of the tribromide permits the formation of the tri-Grignard and suggests that clever design of the organic polyhalide might allow the formation of soluble polyanions containing more than three magnesium atoms.

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