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THE PREPARATION OF DI-n-BUTYLMAGNESIUM-*N,N,N',N'*-TETRAMETHYLETHYLENEDIAMINE COMPLEX FROM A NON-ETHEREAL GRIGNARD

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SUMMARY

A 1/1 complex of di-n-butylmagnesium with *N,N,N',N'*-tetramethylethylenediamine has been isolated from the product of the reaction of n-butyl chloride, magnesium and the diamine in hexane solution.

It has been known for some time that Grignard-type reagents can be formed in the presence of coordinating molecules other than diethyl ether or tetrahydrofuran. Ashby and Reed[1,2] have shown that Grignard-type reagents can be prepared in hydrocarbon solvents such as benzene or toluene using tertiary amines, *e.g.* triethylamine, as complexing agents. We have found that *N,N,N',N'*-tetramethylethylenediamine (TMED) can also be used to form Grignard-type reagents in hydrocarbon solvents.

Ashby and Walker[3] have reported that the composition of a number of Grignards in triethylamine solvent is best represented by a Schlenk equilibrium $R_2Mg + MgX_2 \rightleftharpoons 2RMgX$ with the equilibrium lying almost completely to the right when $X = Cl$ and Br. They also noted the redistribution of dimethylmagnesium TMED and magnesium bromide·TMED complexes in diethyl ether and benzene to form a methylmagnesium bromide·TMED complex.

Zakharkin[4], in 1964, described the preparation of 1/1 TMED complexes of dialkylmagnesium compounds by the reaction of the diamine with the dialkylmagnesium in ethereal solution. The complexes are thermally stable and can be distilled *in vacuo*. If a Schlenk-type equilibrium exists in the case of a Grignard compound formed using TMED in a hydrocarbon solvent,

$$2RMgX \cdot TMED \rightleftharpoons R_2Mg \cdot TMED + MgX_2 \cdot TMED$$

it should be possible to distill the volatile dialkylmagnesium·TMED complex out of the mixture. We have indeed found this to be the case and have isolated a 1/1 dialkylmagnesium/diamine complex from the non-ethereal Grignard.

This method eliminates the tedious multi-step procedures previously used to prepare $R_2Mg \cdot TMED$ complexes[3,5] which involved the prior preparation of R_2Mg via a dialkylmercury or the dioxane precipitation method[6].

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Our results also confirm the presence of a Schlenk-type equilibrium and indicate that under appropriate conditions the equilibrium can be driven to one direction sufficiently to permit isolation of a dialkylmagnesium·TMED complex.

The reaction between n-butyl chloride, magnesium (chip), and the diamine in hexane solution occurs upon refluxing for a short time, most of the magnesium being consumed. During the course of the reaction, precipitation of a white solid occurs. This material has been identified as the 1/1 magnesium chloride/TMED complex by comparison of its X-ray powder pattern with that of an authentic sample. After removal of the magnesium chloride complex and solvent from the solution, the pasty semi-solid residue can be distilled *in vacuo* to give the 1/1 di-n-butylmagnesium/TMED complex in 21% yield. The dialkylmagnesium complex is an air and moisture-sensitive liquid.

EXPERIMENTAL

N,*N*,*N'*,*N'*-Tetramethylethylenediamine and n-hexane were dried over calcium hydride. All reactions were conducted under an atmosphere of dry nitrogen.

To 12.2 g (0.5 g-atom) magnesium chip and 58.1 g (0.5 mole) tetramethylethylenediamine was added about 25 ml of a solution of 46.3 g (0.5 mole) n-butyl chloride dissolved in 200 ml hexane contained in a dropping funnel. The mixture required 1–2 h of refluxing with stirring and the addition of ca. 1 ml n-butyl bromide for initiation. After reaction had commenced, the halide/hexane solution was added slowly at a rate sufficient to maintain exothermicity. The mixture was refluxed for 2 h after all the halide had been added in order to ensure complete reaction. To the reaction mixture then was added 250 ml hexane and the supernatant liquid was separated from the precipitate of $MgCl_2$·TMED using a filter stick. The solvent was removed from the filtrate under vacuum and the pasty residue distilled *in vacuo* to give 12.9 g (21%) of di-n-butylmagnesium·TMED complex, b.p. 175–180° (0.8 mm) [lit.[4] b.p. 190–192° (2 mm)] (Found: Mg, 9.70; N, 11.03. $C_{14}H_{34}MgN_2$ calcd.: Mg, 9.55; N, 11.00%.) The intermediate non-ethereal Grignard solution could be carbonated and subsequently hydrolyzed in the usual manner to give valeric acid in ca. 50% yield.

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