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A Convenient Preparation of Pure Dialkylmagnesium from a Grignard Reagent

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Dimethyl ether of acyclic polyethers, $Me(OCH_2CH_2)_nOMe$, predominantly coordinated to MgX_2 in an ether solution of Grignard reagent and the MgX_2 adduct was removed as a precipitate. Consequently, an ethereal solution of pure R_2Mg was obtained in reasonable yield. This method is more convenient than those known general.

Numbers of synthetic methods for dialkylmagnesium (R_2Mg) have been reported.[1-11] Dioxane[3,4] or pyridine[5] is generally used as a complexing agent for the removal of MgX_2 as insoluble complex from an ethereal solution of Grignard reagent. There are some limitation to the use of this method, since it frequently happens that the $RMgX_2$•dioxane (pyridine) or R_2Mg-MgX_2•dioxane (pyridine) complex are contained in the precipitates. Therefore, the unreasonable yields of intended pure R_2Mg were obtained in many cases. To overcome this problem, specific reactions or more complicated path ways for the preparation of R_2Mg were peculiarly designed for each.[6-11]

Recently, we discovered that the acyclic polyethers were effective for the removal of MgX_2 from an ethereal Grignard solution by the formation of insoluble complex. In the present paper, we wish to report a convenient method for preparation of pure R_2Mg. An example of typical procedure will hereinafter be described.

A Grignard reagent was prepared in the usual way by the reaction of n-BuBr with Mg in diethyl ether. To the clear solution of the Grignard reagen, 1/2 mol equivalent of $Me(OCH_2CH_2)_2OMe$ as diethyl ether solution was added dropwise at about 0 to -10 °C during 30 min, and the mixture was stirred for 2 h. Immediately after the addition of this complexing agent, a grayish-white precipitate appeared. The precipitate was filtered with glass filter and washed with diethyl ether under an inert atmosphere. This hygroscopic precipitate had no longer reactivity to water, acetone, alcohols and other electrophiles, and hence we inferred that the precipitate did not include any R-Mg moiety, whereas the filtrate was vigorously reacted with them. From these tests, the precipitate was supposed to be $MgBr_2$•$Me(OCH_2CH_2)_2OMe$ complex and the species in the filtrate must be $(Bu)_2Mg$. Certainly, the ^1H-NMR spectra(in C_6D_6/TMS) of the solid obtained by the removal of diethyl ether of the filtrate under reduced pressure(100 °C/1 mmHg over a period of 5 h), showed no resonance in the region of δ -0.5, which characteristically observed in the case of Grignard reagent.[12]

To make sure the above results, the gas analysis(modified Gilman method)(evoled by the reaction with water)[6,7] and elemental analysis of the solid expected to be R_2Mg were performed,[13] and the results, including the case of $Me(OCH_2CH_2)_5OMe$, were summarized in Tables 1 and 2 respectively.

Table 1. Yields of R_2Mg based on the gas analysis

	Yield/%	Preparation conditions
This method (n-Bu)	96 (98)[a]	-10 °C, 2 h
" " (Et)	95 (96)[a]	-10 °C, 2 h
Dioxane method(n-Bu)	90	r.t., 3 d[b]
" "	70-74	20 °C, 15 min[c]
Pyridine method(phenyl)	78-79	20 °C, 15 min[c]

a) Data obtained by using $Me(OCH_2CH_2)_5OMe$ is shown in parentheses.
b) Data from Ref. 4. c) Data from Ref. 5.

Table 2. Elemental analysis

	C (%)	H (%)
Solid A	68.82, 69.09 (69.36)	13.05, 13.04 (13.10)
Solid B	57.76, 57.89 (58.28)	12.17, 12.19 (12.23)
Solid C	22.56, 22.97 (22.64)	4.45, 4.40 (4.43)
Solid D	21.79, 22.09 (22.71)	4.09, 4.10 (4.13)

Solid A; obtained from filtrate $(Bu)_2Mg$. Solid B; obtained from filtrate $(Et)_2Mg$. Solid C; obtained from precipitate $MgBr_2.Me(OCH_2CH_2)_2OMe$. Solid D; obtained from precipitate $MgBr_2.1/2\ Me(OCH_2CH_2)_5OMe$. Value in the parentheses is the theoretical one.

As can be seen in Tables 1 and 2, each experimental result indicates that acyclic polyethers predominantly coordinate to MgX_2 in a diethyl ether solution of Grignard reagent to give pure R_2Mg.

Above procedure serves as a convenient method to afford pure dialkylmagnesium free from RMgX in reasonable yield.

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