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REACTION OF MAGNESIUM HYDRIDE WITH PYRIDINE: FORMATION OF $H_3Mg_2NC_5H_6$, $HMgNC_5H_6$ AND $Mg(NC_5H_6)_2$

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Summary

The reaction of magnesium hydride with excess pyridine at room temperature results in the formation of soluble bis(*N*-dihydropyridyl)magnesium which is shown by NMR spectra, to contain 1,2- and 1,4-dihydropyridine groups bound to magnesium. A similar reaction carried out at 60°C has been shown to form bis(*N*-dihydropyridyl)magnesium containing only 1,4-dihydropyridine groups. Formation of $H_3Mg_2(NC_5H_6)$ and $HMg(NC_5H_6)$ are also reported in the controlled reactions of pyridine with magnesium hydride.

Introduction

Although simple and complex metal hydrides of boron and aluminium have been known for over two decades for their reducing properties towards organic functional groups [1], very little is known about the reducing properties of magnesium hydride. Perhaps little attention has been paid to magnesium hydride because of its insolubility in ether solvents and also because of earlier reports of a lack of reactivity towards various organic functional compounds. Wiberg and Gosele [2] in 1955 found that aluminum hydride reacts with pyridine to form (*N*-dihydropyridyl)alane. Lansbury and Peterson [3] reported the reaction of $LiAlH_4$ with pyridine and demonstrated the use of the products as a mild reducing agent towards organic substrates. Recently, we have been able to prepare an active form of MgH_2 which reacts with MgX_2, $Mg(OR)_2$, $Mg(NR_2)_2$ and R_2Mg compounds to produce THF-soluble HMgX [4], HMgOR [5], $HMgNR_2$ [6], and HMgR [7] compounds, respectively. Additionally we have shown that contrary to previous reports, MgH_2 is an effective reducing agent for several functional groups [8].

Since this manuscript was written, a report has appeared [9] describing the formation of $Mg(NC_5H_6)_2$. This complex was characterized by elemental analysis and shown to be bis(1,4-dihydro-1-pyridyl)magnesium by NMR anal-

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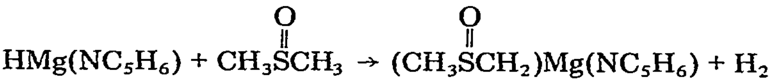
ysis. In the present study, we report the reaction of MgH_2 with pyridine which leads to the reduction of pyridine and the formation of soluble $Mg(NC_5H_6)_2$, $HMgNC_5H_6$, and $H_3Mg_2NC_5H_6$; contrary to the above report. Furthermore, the product $Mg(NC_5H_6)_2$ has been found to give either pure bis(1,4-dihydropyridyl) magnesium or a mixture of 1,4-dihydropyridyl- and 1,2-dihydropyridyl magnesium, depending upon the reaction conditions. It is important to mention here that the MgH_2 used by De Konig and coworkers, although prepared by the same method we use, was dried under vacuum before use. We have shown that MgH_2, once dried, loses its reactivity and perhaps this is the reason that the MgH_2 used by De Konig et al. shows only poor reducing ability towards cyclic ketones [9]. We have already demonstrated [8] that the active MgH_2 we use is in a slurry form and is highly reactive towards the ketones in question and gives nearly a quantitative yield of reduction product in every case in short reaction periods.

Results and discussion

Although MgH_2 is reported to be insoluble in various solvents, surprisingly, it appeared to dissolve in pyridine. When pyridine was added to a well stirred slurry of MgH_2 in diethyl ether, an exothermic reaction resulted producing a clear orange-red solution within a minute. Two different compounds have been found to form in pyridine solution depending upon the reaction conditions of time and temperature. When the above reaction was carried out at 0° C for about 15 minutes, the resulting clear solution was observed to contain magnesium and active hydrogen in 1/1 ratio and the NMR spectrum of the pyridine solution confirmed the presence of 1,4-dihydropyridyl and 1,2-dihydropyridyl groups (Table 1). The infrared spectrum of the solution showed bands due to the dihydropyridyl groups as well as bands due to the Mg—N stretching vibrations. The suggested reaction is represented by eq. 1.

$$MgH_2 + NC_5H_5 \xrightarrow[0^\circ C]{\text{pyridine}} HMgNC_5H_6 \qquad (1)$$

The reagent $HMgNC_5H_6$ was found to be very reactive and was shown to react with DMSO to give H_2 gas (eq. 2).

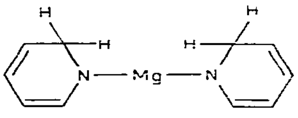


$$HMg(NC_5H_6) + CH_3\overset{\overset{\displaystyle O}{\|}}{S}CH_3 \rightarrow (CH_3\overset{\overset{\displaystyle O}{\|}}{S}CH_2)Mg(NC_5H_6) + H_2 \qquad (2)$$

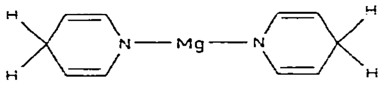
When the solution containing $HMgNC_5H_6$ was kept at 0° C for some time (3 h) further reduction of pyridine by active Mg—H took place. And when the same solution was allowed to warm to room temperature, complete reaction of the Mg—H bond with additional pyridine took place over a 4 h period producing an orange-red solution of bis(dihydropyridyl)magnesium. Gas analysis of this sample showed the absence of any active hydrogen. The same product could also be prepared directly by the reaction of excess pyridine with MgH_2 at room temperature over 4 h reaction period (eq. 3). In order to determine whether the product of the reaction of MgH_2 with pyridine at room temperature is bis(1,2-dihydropyridyl)magnesium (I) or bis(1,4-dihydropyridyl)magne-

$$MgH_2 + 2\ C_5H_5N \xrightarrow[\text{room temperature}]{\text{pyridine}} C_5H_6N{-}Mg{-}NC_5H_6 \qquad (3)$$

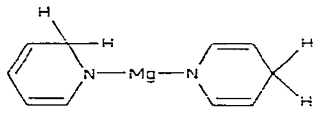
sium (II) or an intermediate form of I and II, i.e. III, NMR spectroscopy was employed.



(I)

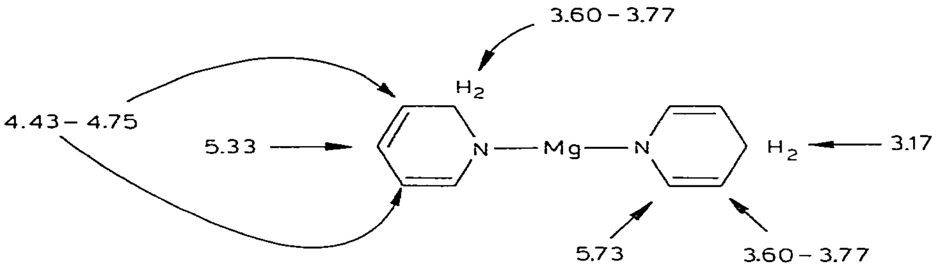


(II)



(III)

The NMR spectrum of the product obtained from the reaction of MgH_2 with pyridine at room temperature showed a number of peaks (Fig. 1) which have been assigned [3] (Table 1) and summarized in the structural formula shown below:



(IV)

When the reaction of MgH_2 with pyridine was carried out at 60°C for 4 h, the NMR spectrum of the solution showed the absence of peaks in the region 4.43—4.75 and 5.33 cps, suggesting the formation of pure bis(1,4-dihydropyridyl)magnesium (II). This result was further confirmed by treating MgD_2 with pyridine under the same conditions and recording the NMR spectrum. The spectrum showed a reduction of intensity of the peak at 3.17 cps (present in the earlier reaction due to the 4-methylene hydrogens) indicating deuterium at the 4-position.

MgH_2 and MgD_2 used in the above reactions were prepared by the reaction of Et_2Mg with $LiAlH_4$ and $LiAlD_4$, respectively, in diethyl ether (eq. 4).

$$Et_2Mg + LiAlH_4\ (\text{or } LiAlD_4) \xrightarrow{Et_2O} MgH_2\ (\text{or } MgD_2 + LiAlH_2Et_2 \qquad (4)$$
$$(\text{or } LiAlD_2Et_2)$$

Interestingly, when about 5-fold excess of pyridine was added to a slurry of MgH_2 in diethyl ether, a yellow crystalline solid resulted. When this solid was filtered and washed with diethyl ether, it corresponded in analysis to $H_3Mg_2(NC_5H_6) \cdot 1.5\ (C_5H_5N)$. The solid was stable at room temperature and reacted exothermically with DMSO to give a clear yellow solution and three mol of hydrogen gas evolution for each mol of compound.

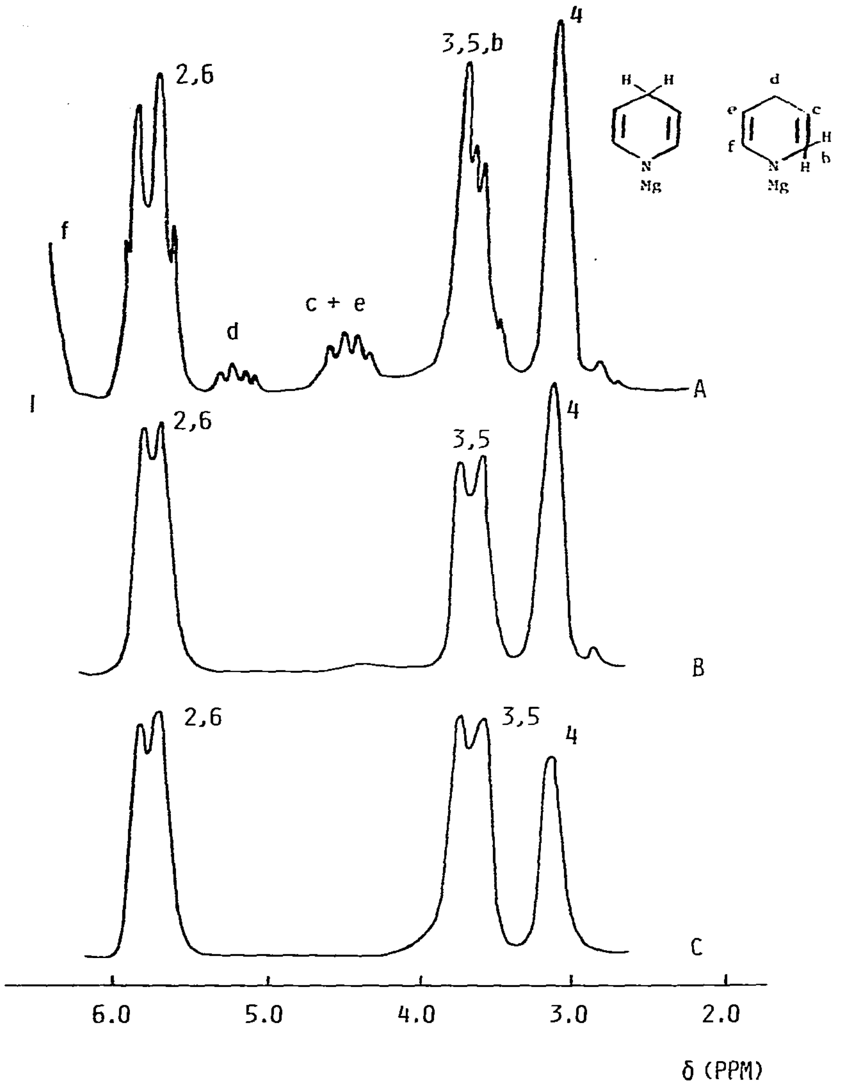


Fig. I. NMR spectra of bis(*N*-dihydropyridyl)magnesium prepared from: A, pyridine and MgH_2 at room temperature; B, pyridine and MgH_2 at 60°C; C, pyridine and MgD_2 at 60°C.

TABLE 1

CHEMICAL SHIFTS (ppm) OF PROTONS IN BIS(*N*-DIHYDROPYRIDYL)MAGNESIUM AND (DIHYDROPYRIDYL)MAGNESIUM HYDRIDE IN PYRIDINE

Peak	Assignment
3.17	4-methylene
3.60—3.77	2-methylene plus 3- and 5-vinyl protons in 1,4-dihydropyridyl
4.43—4.75	3- and 5-vinyl protons in 1,2-dihydropyridyl
5.33	4-vinyl protons
5.93	2- and 6-vinyl protons in 1,4-dihydropyridyl

$$H_3Mg_2(NC_5H_6) + 3\,CH_3\overset{\overset{O}{\|}}{S}CH_3 \xrightarrow{DMSO} (CH_3\overset{\overset{O}{\|}}{S}CH_2)_3Mg_2NC_5H_6 + 3\,H_2 \qquad (5)$$

The infrared spectrum of $H_3Mg_2NC_5H_6$ was taken in a Nujol mull. It showed the presence of pyridyl groups and broad bands due to Mg –H stretching vibrations. Vacuum DTA/TG studies showed that $H_3Mg_2NC_5H_6$ decomposes over the range 230—410°C (max. 330°C) evolving H_2 gas.

When the product $H_3Mg_2(NC_5H_6)$ was placed in pyridine, it reacted immediately to give an orange-red solution which contained a product of composition $HMg(NC_5H_6)$. $H_3Mg_2(NC_5H_6)$ was found to have some solubility in THF suggesting that it is not a mixture of MgH_2 (insoluble in THF) and $HMg(NC_5H_6)$.

Reactions of zinc hydride with pyridine were also studied [9] *. When about 5-fold excess of pyridine was added to a slurry of zinc hydride in diethyl ether, a yellow crystalline solid resulted which analyzed for $H_5Zn_3(NC_5H_6) \cdot 2$ Py (eq. 6). The infrared spectrum of this solid as a Nujol mull gave a broad band in the region 1720—1570 cm^{-1} probably due to the terminal Zn—H stretching vibration [11]. This band was found to be shifted to 1200—1190 cm^{-1} in the deuterated analog $D_5Zn_3(NC_5H_5D)$. ZnH_2 or ZnD_2 was prepared by the reaction

$$ZnH_2 + 5(NC_5H_5) \xrightarrow{Et_2O} H_5Zn_3NC_5H_6 \cdot 2\,NC_5H_5 \qquad (6)$$

of diphenylzinc with $LiAlH_4$ and $LiAlD_4$, respectively, in diethyl ether. $H_5Zn_3NC_5H_6$ has been found to be soluble in pyridine. It has also been found to be soluble in DMSO without reaction. Proton NMR spectra gave signals due to the 1,4-dihydropyridyl group.

Reactions of (dihydropyridyl)magnesium hydride and bis(*N*-dihydropyridyl)magnesium with cyclic ketones and other organic substrates are in progress. Podall and Foster [12] had attempted to reduce olefins with magnesium hydride in pyridine solvent and found about 5% reduction. In fact, the above studies showed that no active MgH_2 was left in pyridine after 4 h reaction time and bis(*N*-dihydropyridyl)magnesium was formed which perhaps reacted with olefins to give about 5% reduced product.

Experimental

Reactions were performed under nitrogen using Schlenk tube techniques [13]. Infrared spectra were obtained using a Perkin—Elmer 621 spectrophotometer. Solutions were studied in matched 0.1 mm pathlength KBr cells. Proton NMR spectra were obtained on a Varian A-60 spectrometer.

Gas analysis were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump [13]. Magnesium and zinc were determined by EDTA titration at pH 10. Pyridine and dihydropyridine were analyzed by GLC.

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* Reaction of ZnH_2 with pyridine forming ($C_5H_6NZnH \cdot 2\,ZnH_2 \cdot 2$ pyridine) has recently been reported by De Koning et al. [10]. The product has been characterized by elemental analysis and NMR spectroscopy.

Diethylmagnesium [14] was prepared by the reaction of diethylmercury with magnesium metal at 60—80° C and a standard solution in diethyl either was calibrated by magnesium analysis. Lithium aluminium hydride solution in diethyl ether was prepared by the standard method and standardized by aluminium analysis.

Preparation of MgH_2 or MgD_2 slurry in ether. $LiAlH_4$ or $LiAlD_4$ (20.0 mmol) in diethyl ether (45 ml) was allowed to react with a diethyl ether (40 ml) solution of Et_2Mg (20.0 mmol) at room temperature with constant stirring. The reaction mixture was stirred for 1 h and the insoluble solid was separated by removing the supernatant solution by syringe after contrifugation. This solid was washed with ether 3—4 times and analyzed. Anal. Calcd. for MgH_2: Mg/H = 1.00/2.00. Found: 1.00/2.02.

Preparation of ZnH_2 or ZnD_2 slurry in ether. $LiAlH_4$ or $LiAlD_4$ (15.0 mmol) in diethyl ether (35 ml) was added to a magnetically stirred solution of Ph_2Zn (15.0 mmol) in diethyl ether (40 ml) at room temperature. An insoluble white solid appeared immediately. The reaction mixture was stirred further for ~1 h and the insoluble solid separated by centrifugation and removal of the supernatant solution by syringe. This solid was washed with dry ether 3—4 times and analyzed as a slurry. Anal. Calcd. for ZnH_2: Zn/H 1.00/2.00. Found: 1.00/1.96.

Reaction of MgH_2 or MgD_2 with excess pyridine at room temperature. 10 ml of pyridine was added dropwise to a well stirred slurry of MgH_2 (5.0 mmol) in diethyl ether (5 ml). The reaction was exothermic and resulted in a clear orange-red solution within a few hours. The reaction solution was then stirred at room temperature for 3 h. Diethyl ether from the solution was removed under reduced pressure and the analysis of the solution showed that it contained no hydrolysable hydrogen. The solution was analyzed by infrared and NMR spectroscopy. The solvent was removed under vacuum and the resulting pasty mass analyzed. Anal. Found: Mg/H/dihydropyridine/pyridine: 1.00/0.05/1.98/2.04. Calcd. for $Mg(NC_5H_6)_2 \cdot 2$ Py 1.00/0.00/2.00/2.00. IR (in pyridine): 2920m, 2843m, 2760m(br), 2688m, 2661m, 2628w, 1660m, 1560m, 1489vs, 1420m, 1360m, 1320w, 1280vs, 1262s, 1235vs, 1220(sh), 1150w, 1100s, 1034m, 995s, 972s, 935s, 875w, 757m, 720w, 648m, 627s, 612vs, 570s, 520s, 504vs, 415s and 374m cm^{-1}.

Reaction of excess pyridine with MgH_2 slurry in diethyl ether at 0° C. When 10 ml of pyridine was added to a well stirred slurry of MgH_2 (5.0 mmol) in diethyl ether (5 ml) at 0° C, a clear solution resulted within a minute. The reaction mixture was stirred at 0° C for 15 min and the diethyl ether removed under vacuum. The pyridine solvent was removed under reduced pressure at 0° C and the resulting foamy solid was washed with n-hexane and analyzed. Found: Mg/H/dihydropyridine/pyridine: 1.00/0.94/1.09/1.98. Calcd. for $HMg(NC_5H_6) \cdot 2$ Py 1.00/1.00/1.00/2.00. IR (in pyridine): 2920m, 2840m, 2758m(br), 2685m, 1652m, 1598m, 1520m, 1475s, 1440s(br), 1370m, 1285s, 1265m, 1228m, 1154w, 1100m, 1038m, 998s, 940s, 752m, 724m, 700m, 635m, 620m, 560s(br), 520s, 412m cm^{-1}.

Reaction of pyridine with MgH_2 in 5/1 molar ratio in diethyl ether. To a magnetically stirred slurry of MgH_2 (6.34 mmol) in diethyl ether (20 ml), pyridine (2.5 g; 31.7 mmol) was added dropwise. The reaction mixture was stirred for ~1/2 hour to give a yellow crystalline solid. It was filtered and washed with ether and dried in vacuum. The solid was analyzed. Found: Mg/H/dihydropyridine/pyridine: 1.00/1.49/0.50/0.75. IR (in Nujol): 1850w, 1640m, 1597s, 1570(sh), 1510m, 1465s, 1446s(br), 1378s, 1320s, 1320w, 1285m, 1262m, 1220m, 1152m, 1090m, 990m, 725m, 700s, 625—10m(br), 550m(br), 520m(br), 412m cm^{-1}.

Reaction of $HMg(NC_5H_6)$ and $H_3Mg_2(NC_5H_6)$ with excess DMSO. About 2 ml of DMSO was transferred to samples of $HMg(NC_5H_6)$ (2.2 mmol) and $H_3Mg_2(NC_5H_6)$ (1.0 mmol) on a vacuum line kept at liquid nitrogen temperature. The samples were warmed to room temperature and the evolved gas analyzed. In case of $HMg(NC_5H_6)$ (2.2 mmol) about 2.1 mmol of H_2 was measured and in case of $H_3Mg_2(NC_5H_6)$ (1.0 mmol) about 2.85 mmol of H_2 was observed.

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