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Preliminary communication

REACTION OF MAGNESIUM HYDRIDE WITH PYRIDINE

A.J. DE KONING, P.H.M. BUDZELAAR, B.G.K. VAN AARSSSEN, J. BOERSMA, and G.J.M. VAN DER KERK

Laboratory for Organic Chemistry, State University, Croesestraat 79, 3522 AD Utrecht (The Netherlands)

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Summary

A reinvestigation of the reduction of pyridine by magnesium hydride has proven unambiguously that the final product is the bis-pyridine complex of bis(1,4-dihydro-1-pyridyl)magnesium. The claim of Ashby and Goel [5], that the product of the room temperature reaction also contains 1,2-dihydro-1-pyridyl moieties after extended reaction periods has been traced back to the presence of aluminium-bound hydrogen in the magnesium hydride used by these workers.

In a series of articles [1-4], we have described the reactions of ZnH_2 and MgH_2 with pyridine, which yield the pyridine complexes of bis(dihydro-pyridyl)-zinc and -magnesium. These complexes are suitable reducing agents for ketones, nitriles, heterocyclic compounds and other substrates [3,4]. The complexes were spectroscopically pure 1,4-dihydro-1-pyridyl derivatives, no 1,2-dihydro-1-pyridyl moieties being present. Ashby and Goel repeated this work and in a recent communication [5] they confirmed most of our earlier results. There is, however, one notable deviation. These authors claimed that the room temperature reaction of pyridine and MgH_2 yielded a product containing both 1,2- and 1,4-dihydropyridyl groups bound to magnesium. In order to resolve this discrepancy, we decided to reinvestigate the reduction reaction.

There is one distinct difference between the reaction sequences employed, viz. the ratio $Et_2Mg/LiAlH_4$ used in the preparation of the magnesium hydride. Ashby and Goel consistently used a 1/1 ratio for this preparation [5-8]. However, as early as 1951 Schlesinger et al. noted that it was necessary to use a ratio in excess of 2/1 to obtain a product substantially free of aluminium hydride [9]. Therefore, in our work ratios in excess of 2½/1 were used

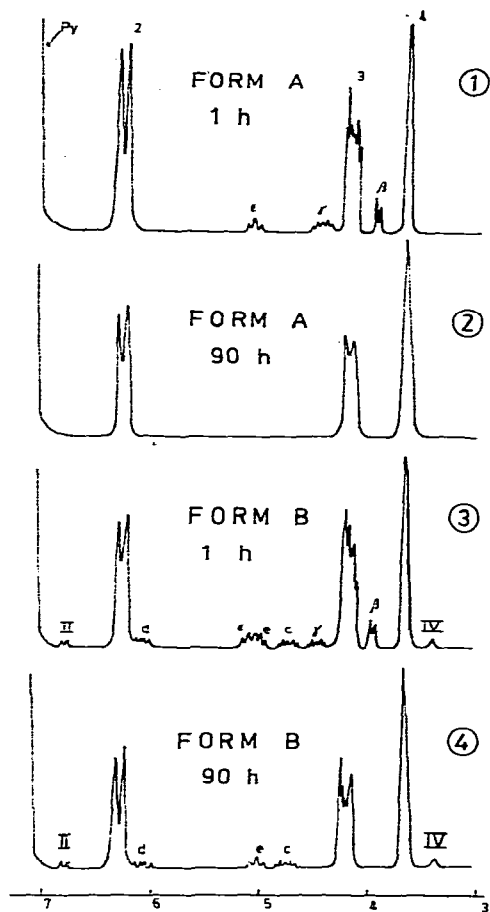


Fig. 1. ^1H NMR spectra of reaction mixtures of form A and B of MgH_2 with pyridine.

throughout [2]. To check the significance of this factor, we prepared magnesium hydride from Et_2Mg and LiAlH_4 in the ratios 3/1 (form A, as used by us) and 1/1 (form B, prepared according to Ashby and Goel). Both products were washed 4 times with ether, and treated, as a slurry in ether, with a large excess of pyridine at room temperature. The reactions were followed by ^1H NMR spectroscopy, using a Varian EM-390 90 MHz spectrometer.

Form B of MgH_2 dissolved rapidly in the excess of pyridine to form a dark-red solution. Its NMR spectra 3 and 4 (Fig. 1) were recorded after 1 h and 90 h, respectively. The 3 prominent signals in the spectra are due to the 1,4-dihydro-1-pyridyl group bound to Mg [2]. The peaks labeled c, d and e were assigned by Ashby and Goel to the 1,2-dihydro-1-pyridyl group bound to magnesium. In addition to these peaks, spectrum 3 shows some absorptions (labeled β , γ and ϵ) which are notably absent after 90 h reaction time.

Form A of MgH_2 dissolved more slowly in pyridine. Again, spectra were recorded after 1 h and 90 h (spectra 1 and 2, respectively). The only absorptions in these spectra are those of the 1,4-dihydropyridyl group bound to Mg, and also the transient absorptions β , γ and ϵ . These transient absorptions were

not visible in the spectra presented by Ashby and Goel, presumably because their spectra were recorded only after an extended reaction period. Since these absorptions disappear, leaving in the case of form A MgH_2 the spectrum of pure 1,4-dihydro-1-pyridylmagnesium, the conclusion must be that the transient species causing the absorptions β , γ and ϵ is a 1,2-dihydro-1-pyridyl group bound to Mg. A preliminary study using MgH_2 and fully deuterated pyridine indicates that 1,4-dihydropyridine is formed both directly and via 1,2-dihydropyridine, the latter producing the former by transfer of hydrogen to an unreduced pyridine molecule*. The question then remains: what is the species causing the absorptions c, d and e attributed by Ashby and Goel to the 1,2-dihydropyridyl group bound to Mg?

The reduction of pyridine by $LiAlH_4$, described in 1963 by Peterson and Lansbury [10], produces a compound $LiAl(C_5H_6N)_4$ which contains both 1,2- and 1,4-dihydropyridyl groups bound to Al (in the ratio 2/1 if the reduction is carried out at room temperature). The chemical shifts reported by these authors for the 1,2-dihydropyridyl group bound to Al agree nicely with those given by Ashby and Goel for the peaks c, d and e (after correction for the difference in reference signal). It is clear that the assignments given by Ashby and Goel for these peaks are incorrect. The small humps labeled II and IV in spectra 3 and 4 must be attributed to the 1,4-dihydropyridyl group bound to Al. Even the observed ratio 1,2(Al)/1,4(Al) of 2/1 agrees with that found by Peterson and Lansbury [10]. Fig. 2 and Table 1 summarize the complete inter-

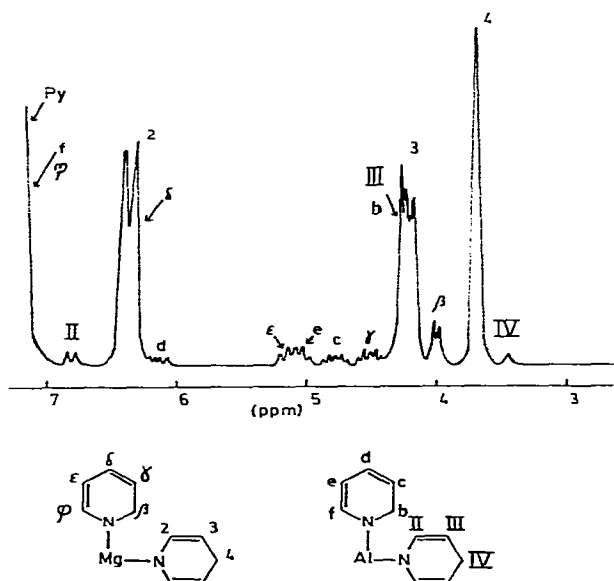


Fig. 2. Interpretation of spectrum of form B of MgH_2 /pyridine after 1 h reaction time.

pretation of the spectrum of the form B MgH_2 /pyridine reaction mixture after 1 h reaction time. Both 1,2- and 1,4-dihydropyridyl groups bound to both Mg and Al are present.

*Details will be given in a subsequent paper.

TABLE 1

CHEMICAL SHIFTS OF PROTONS OF DIHYDROPYRIDYL GROUPS BOUND TO MAGNESIUM AND ALUMINIUM (in pyridine, relative to internal TMS)

(Mg)	2	3	4	β	γ	δ	ϵ	ϕ	
δ (ppm)	6.40	4.25	3.73	4.03	4.53	$\sim 6.4^b$	5.20	$> 7^d$	
ref. 2	6.30	4.23	3.70						
ref. 5 ^a	6.29	4.16-4.33	3.73						
(Al)	II	III	IV	b	c	d	e	f	
δ (ppm)	6.87	$\sim 4.25^c$	3.48	$\sim 4.25^c$	4.82		6.17	5.06	$> 7^d$
ref. 10	6.7	4.3	3.3	4.2	4.7-5.3	6.2	4.7-5.3	7.2	
ref. 5 ^a				4.16-4.33	4.99-5.31	5.89	4.99-5.31	$> 7^d$	

^a After correction for difference in reference signal. ^b Obscured by absorptions of protons 2.
^c Obscured by absorptions of protons 3. ^d Obscured by absorptions of 3-protons of pyridine.

In short, the peaks attributed by Ashby and Goel to 1,2-dihydropyridyl groups bound to Mg actually belong to 1,2-dihydropyridyl groups bound to Al. This contamination must be due to the presence of aluminium-hydrogen species in the magnesium hydride used by these workers*. This, in turn, is caused by the use of a 1/1 Et₂Mg/LiAlH₄ ratio in their preparation of MgH₂. A visual estimate from the spectra presented by Ashby and Goel indicates that the amount of aluminium-bound hydride is slightly in excess of 10%. This figure does not seem unlikely, considering the data given by Schlesinger. In order to obtain direct evidence for the presence of aluminium compounds in form B MgH₂, we analyzed both forms of MgH₂ for Al by atomic absorption spectroscopy (after drying in vacuo). Form B was found to contain 6.6 wt.% of Al, whereas form A contained only 0.2 wt.% of Al.

In view of the well-known reactivity of these aluminium compounds towards ketones and other substrates, results obtained using such a contaminated form of magnesium hydride must be interpreted with caution.

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*Presumably, these species are hydride-containing aluminate ions, AlEt_xH_{3-x}⁻, bound to Mg, since they cannot be removed by washing; Upon treatment with pyridine, they could produce anions AlEt_x(C₅H₆N)_{3-x}⁻, closely related to the anion Al(C₅H₆N)₃⁻ described by Lansbury and Peterson [10].