Tetrahedron Letters No.5, pp. 599-601, 1968. Pergamon Press. Printed in Great Britain.

FRAGMENTATION OF A GRIGNARD REAGENT

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(Received in USA 25 August 1967)

Fragmentation reactions of organometallic compounds generally involve 1,2-eliminations to form olefins. The elimination of bromine from 1,2-dibromoalkanes with zinc or magnesium is

$$\underset{1}{ACH_2CH_2M-} \longrightarrow A^- + CH_2{=}CH_2 + M^+-$$

believed to follow this path (1).

Recently Sommer et. al. reported that treatment of 1-chloro-2-trialkylsilylethanes with alkoxide results in the formation of ethylene and alkoxytrialkylsilanes (2). Amstutz (3) has reported that treatment of 1-bromo-2-alkoxyethanes with magnesium produces ethylene and magnesium alkoxide.

So far eliminations involving carbon-carbon bond scission have been reported only when very reactive alkali metals were used. Wooster and Morse (4) found that sodium in liquid ammonia cleaved 3,3,3-triphenyl-1-iodopropane to ethylene and tritylsodium. Pines and Schaap (5) reported that 3-phenyl-3-methyl-butylpotassium cleaved to 2-phenyl-2-propylpotassium and ethylene in refluxing cyclohexane.

We wish to report that a Grignard reagent undergoes an elimination similar to those described above. While studying pyridylalkyl carbanions we observed that treatment of 3-(4-pyridyl)-3-methyl-1-chlorobutane, 1, with triply sublimed magnesium in tetrahydrofuran at 0^o- 40^o produced a deep red solution. The nuclear magnetic resonance spectrum, Figure 1, shows two doublets at 3.66 and 4.78τ, a singlet at 4.64τ, a triplet at 9.27τ, J=6Hz together with A_2B_2 absorption indicative of a 4-substituted pyridine at 1.11τ and 2.46τ. The upfield triplet was assigned to the CH_2Mg hydrogens in the Grignard reagent of 1; the doublets at 3.66 and 4.78τ to the A_2B_2 region of the magnesium salt of isopropylpyridine while the single line corresponded to ethylene.*

These assignments were confirmed by analysis of the hydrolysis products of the above

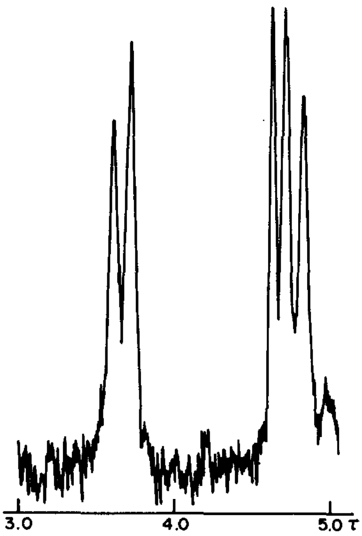
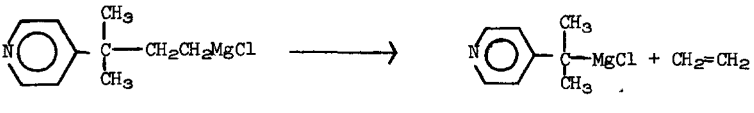


Figure 1. Olefinic NMR absorption for cleavage product from 3-(4-pyridyl)-3-methylbutylmagnesium chloride.

solution by nmr spectroscopy and vapor phase chromatography. They consisted of 35% isopropylpyridine, 55% 3-(4-pyridyl)-3,3-dimethyl-butane, ethylene, and 10% starting material. These ratios were independent of the reaction temperature. Clearly, the reaction taking place involves elimination of 2-(4-pyridyl)-2-propylmagnesium chloride from the original Grignard reagent,, **2**. We believe this is the first elimination of this type observed for a Grignard reagent. The ease with which **2** fragments must be ascribed to the stability of the departing 2-(4-pyridyl)-2-propyl anion, **4**. It is evident from the ring shifts that there is consider-



2 **3**

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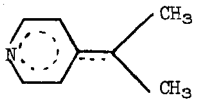
* Note that the ring shifts of the lithium salt of 4-picoline in ether are 3.10 and 4.28τ, $J_{\underline{o}} + J_{\underline{p}} = 6.8$ Hz.

able delocalization of charge in **3**.



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The lithium compound was prepared from **1** in tetrahydrofuran. However, this reagent did not undergo the elimination reaction. All attempts to prepare either the Grignard reagent or lithium compound in diethyl ether were unsuccessful.

Acknowledgment. This research was supported in part by the National Institutes of Health, Grant No. GM-08686-03.

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