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ADDITIONAL EVIDENCE FOR THE EXISTENCE AND REDUCING ABILITY OF HMgBr IN THF

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Investigation of the chemistry of HMgX systems are quite rare. There are four recorded routes to this simplest Grignard reagent: the pyrolysis of ethylmagnesium halides;[2-7] reduction of such halides by diborane [solid complexes were isolated such as $HMgX{\cdot}2(C_2H_5)_2O$ and HMgX·2THF];[8] the sintering of a mixture of MgX_2 and MgH_2;[9] and the reaction of HX in ether with magnesium.[6,10] Although Hess and Rheinboldt[10] were unable to produce HMgX via the latter method, Firestone[6] passed a solution of HBr in ether through a column of magnesium and obtained eluates that reduced an ester, a nitrile, and two amides to the corresponding alcohol and amines in low yield (< 1%).

We have found that HMgBr can be prepared in anhydrous THF (all manipulations of active solutions were done under N_2 scrubbed with H_2SO_4 and passed through 3A molecular sieve) at -55° (this temperature was obtained with 39% aq. KOH eutectic or 2-hexanol). Hydrogen bromide (Matheson 99.8%) is bubbled through a mechanically stirred suspension of Mg (2.40 g., 0.1 g.-atom--Fisher, for Grignard reagents) in anhydrous THF (50 ml--freshly distilled from $LiAlH_4$ and degassed with N_2) for 15 min. Cloudiness and a slight discoloration (lt. brown) appears around the magnesium. Stirring is stopped and the clear supernatant is decanted from residual magnesium.

$$\mathrm{HBr} + \mathrm{Mg} \xrightarrow{\mathrm{THF}} \mathrm{HMgBr}$$

Evidence for the existence of HMgBr at -55° in the solution is:

(1) The solution evolves a gas when treated with water or aq. HCl.

(2) The solution begins to evolve a gas when allowed to warm to −20°; this appears to be the result of reaction of HMgBr with dissolved HBr, as the reaction is exothermic.

(3) Reaction of the solution with phenylethanal yields a complex mixture (> 8 products), one product being identified by GLC as 1-bromo-2-phenylethane.

(4) Reaction of the solution with benzophenone also yields a complex mixture (> 7 products) of which one component was identified by GLC and mass spectrometry as diphenylmethane.

It is noteworthy that observation (4) was independent of the presence or absence of unreacted magnesium. Also, diphenylmethanol, benzene, toluene, benzyl alcohol, and biphenyl were not present in the mixture from (4). Thus, it appears that any diphenylmethanol produced is converted to diphenylmethane without cleavage of the benzylic C-C bond to give toluene.

$$HMgBr + C_6H_5-\overset{\overset{\large O}{\|}}{C}C_6H_5 \longrightarrow C_6H_5-CH_2-C_6H_5 + \text{Mixture}$$

The product mixture from (3) did not contain ethylbenzene when tested by GLC. For workup of the reaction mixtures of (3) and (4), the solutions were allowed to warm to room temperature (ca. 2 hr) and then were decomposed with 10% aq. NH_4Cl. Ether extracts of the solutions were dried and concentrated to a low volume of liquid, which was analyzed.

The view that a $MgH_2 \cdot MgBr_2$ combination is the reducing agent seems untenable in our work, although suggested as a possible composition for the solid reducing product obtained from pyrolysis of ethylmagnesium bromide, [2,4,6,11] because of the insolubility of magnesium hydride in organic solvents which would tend to preclude the existence of a Schlenk equilibrium favoring the binary complex $MgH_2 \cdot MgBr_2$. A complex, $HMgBr \cdot xTHF$, is probably soluble in THF in view of the reported solubility of $HMgCl \cdot 2THF$ in that solvent.[7] Since many products (although conversions were < 5% based on starting carbonyl compound) were obtained from (3) and (4) in our work, the reduction is obviously not specific but much more aggressive than previously implied.[6] Addition of HBr to the mixture for a period of 2 hr. before addition of phenylethanal or benzophenone did not increase the amounts of these carbonyl compounds reduced. Similarly, doubling or tripling the rate of addition of HBr (g) did not increase the conversion. However, addition of benzophenone and analysis of the mixture showed the organic products to be identical to those previously found.

Alternative intermediates capable of giving these results are made less probable by the following experiments. A blank run in which HBr (g) was passed into anhydrous THF under the usual conditions did not produce any reaction. Analysis by GLC of the reaction mixture from (4) showed the absence of 1-bromobutane or 1-butanol, conceivable products of ring cleavage of THF under reducing conditions. Since the gas evolution at -20° indicated some kind of reaction, it cannot be attributed to the presence of n-butylmagnesium bromide (conceptually) possible from ring opening of THF by HMgBr and subsequent formation of 1-bromobutane, etc.) because of the known stability of that Grignard reagent in THF.[12] Conceivably, H_2O could displace THF from a THF·HBr complex and/or from a THF·HMgBr complex and $H_3O^+Br^-$ formed could then destroy HMgBr. At -20°, the acidity of THF·HBr complex could increase and also destroy the THF·HMgBr complex.

An attempt at preparation of HMgBr in diglyme under the same conditions as used with THF failed. It is worthy to note that the relatively low solubility of HMgCl·2THF in THF may be a factor favoring the high yield of the product reported by Wiberg and Strebel.[8] Since neither rate nor duration of HBr (g) addition nor rate of stirring altered the conversions described and precipitation was not observed, it seems reasonable that the low yield of HMgBr in our system, as in that of Firestone,[6] may be due to some coating of the surface of the magnesium.

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