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THE EFFECT OF MAGNESIUM BROMIDE ON THE RATE OF ADDITION OF METHYLMAGNESIUM BROMIDE TO KETONES[1]

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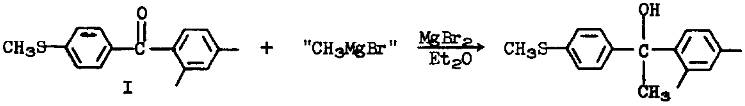
An understanding of the effect of magnesium bromide on the rate and course of the reaction of Grignard reagents with ketones is important to the elucidation of the mechanism of the reaction. Previous studies (3,4) indicate that the presence of magnesium bromide affects the kinetics (5) and product distribution when enolization, addition and reduction compete. In tetrahydrofuran as solvent, it has been reported (6) that the addition of an equivalent amount of magnesium bromide to methylmagnesium bromide decreases the rate of addition to benzophenone by a factor of about four.

We have studied (7) the effect of various concentrations of magnesium bromide on the rate of addition of methylmagnesium bromide to ketone I in diethyl ether solvent at 25.0° under conditions where the nature of the Grignard reagent is reasonably constant during the reaction. This was accomplished by using a relatively low ketone concentration (ca. 10^{-4} M). The results, summarized in graphical form in figure 1, indicate that the rate of the addition reaction is



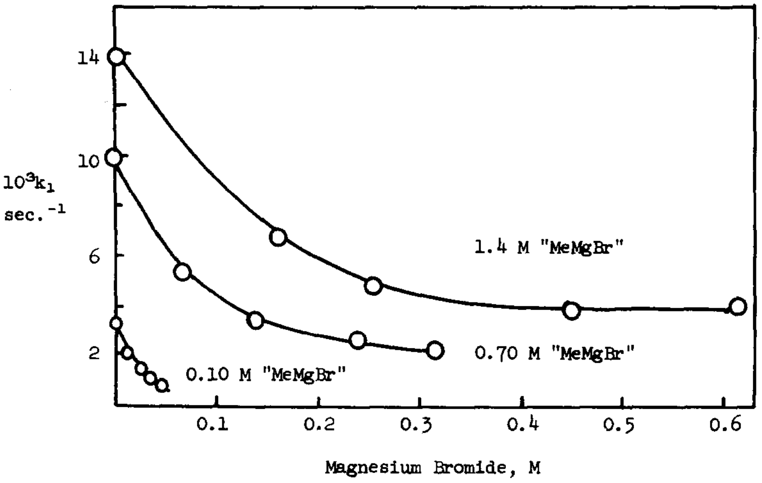


FIG. 1. Plot of the pseudo-first order rate constant for the addition of methylmagnesium bromide to ketone I vs. concentration of magnesium bromide for various concentrations of the Grignard reagent in diethyl ether solvent at 25.0°.

greatly depressed by small amounts of magnesium bromide, with 1.4 M Grignard reagent, 0.15 M salt decreases the rate by a factor of ca. two. The rate depressing effect of magnesium bromide becomes saturated in the region of 0.4 M to 0.6 M magnesium bromide in the presence of 1.4 M methylmagnesium bromide.

The influence of magnesium bromide on the reaction may be qualitatively accounted for in terms of two independent effects. Any free magnesium bromide in solution would compete with Grignard reagent for ketone (7,8). This would decrease the fraction of the ketone complexed with the Grignard reagent and produce a new species with a different reactivity toward methylmagnesium bromide. Secondly, the presence of the salt may also alter the nature of the reagent. For example, the effect of a Grignard reagent on the solubility of magnesium bromide (9,10) makes it clear that there is a marked tendency for these two species to associate. A complex between magnesium bromide and methylmagnesium bromide could have a lower reactivity than the Grignard reagent itself. Furthermore, to the extent that it is important, magnesium bromide would be expected to alter the position of the Schlenk equilibrium (11) by altering the balance of species present and the gross reactivity of the system (4). A quantitative discussion of these possibilities will be presented in subsequent publications.

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