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The Reaction of 1-Alkynes with Organometallic Compounds. V.[1] The Reaction of Diethylmagnesium with Hexyne-1 in the Presence of Magnesium Bromide

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The formulation of a Grignard reagent by the Schlenk equilibrium $R_2Mg + MgBr_2 \rightleftharpoons 2\ RMgBr$ was successfully tested by the addition of varying amounts of $MgBr_2$ to $(C_2H_5)_2Mg$. Equilibration was attained rapidly. Such solutions were reacted with hexyne-1 and the rate of evolution of ethane decreased with increasing quantities of added $MgBr_2$. In the reactivity toward hexyne-1, a mixture of $(C_2H_5)_2Mg$ and $MgBr_2$ behaved identically with C_2H_5MgBr prepared by the reaction of C_2H_5Br and Mg, provided the same ratio of Mg to Br is present.

The constitution of Grignard reagents is frequently conveniently formulated by the Schlenk equilibrium reactions.[3,4]

$$2\ RMgBr \rightleftharpoons R_2Mg + MgBr_2$$

Since it was recently[1] shown that halogen-free diethylmagnesium reacts three times faster with hexyne-1 than does ethylmagnesium bromide, the equilibration was tested by adding varying amounts of magnesium bromide to diethylmagnesium and reacting such mixtures with hexyne-1.

The rates of reaction were determined using 1.0 N solutions of reactants in ether solutions of magnesium bromide at the boiling point of the mixture. Relative reactivities were determined from half-lives by assigning a value of 100 to the reaction of hexyne and ethylmagnesium bromide.[5]

EXPERIMENTAL

Ethylmagnesium bromide. The same reagent was used in reference 5b. The Br/basic Mg ratio was determined to be 1.15, using a potentiometric titration with silver nitrate to determine halogen and titration with standard acid to determine the amount of basic magnesium.

Hexyne-1 was prepared in the same manner described in reference 5a.

Diethylmagnesium was the same reagent described in reference 1.

Magnesium bromide. Magnesium turnings (B. & A. Code 1904), 1.1 g.-atoms (26 g.), were placed in a three-necked flask equipped with a cold finger condenser, addition funnel, and glass blade stirrer, and 300 cc. of ether (Mallinckrodt Anhydrous Ether) was added. One mole (160 g.) of bromine was added slowly. The system separated into two layers, a dark heavy lower layer (70% magnesium bromide dietherate[6]) and a straw-colored upper one (7% magnesium bromide dietherate.) The solvent was evaporated under reduced pressure and the resulting white solid was dissolved in 250 cc. of ether. Two layers were again formed, and the lower layer was separated and stored in the same manner as the ethylmagnesium bromide. Analysis for total halide present by means of a potentiometric titration with silver nitrate indicated a magnesium bromide concentration of 485 mg. per cc. Slough and Ubbelohde have shown[7] that such a procedure does not lead to reaction of the bromine with the ether.

Determination of rates. All determinations were made using 0.0235 equivalent of organometal[8] and varying amounts of magnesium bromide in 1.0 N[9] ether solutions in the gasometric apparatus previously described.[5b] The organometal and ether solvent were added to the reaction vessel and the whole was brought to reflux. The magnesium bromide solution then was added. After the specified time period an equivalent amount of hexyne-1 was added and the rate of evolution of ethane was measured.

When the contact time was extended beyond 24 hours, the organometal and the magnesium bromide were dissolved in enough ether to yield 1.0 N solutions of organometal, and an amount equivalent to 0.025 equivalent was sealed in glass ampoules under nitrogen, after cooling them in Dry-Ice. They were stored the specified time period at room temperature with intermittent agitation. The ampoules then were opened at room temperature and a volume equivalent to 0.02 equivalent was withdrawn and placed in the reaction flask. The material was brought to reflux, and after 15 minutes an equivalent amount of hexyne-1 was added and the rate of evolution of ethane was measured.

All reactions and transfers were made in an inert atmosphere of nitrogen, and all transfers were made by hypodermic techniques.

DISCUSSION OF RESULTS

The relative reactivity of diethylmagnesium with hexyne in refluxing ether at 1.0 N concentrations was found to be 300. The addition of magnesium bromide to the diethylmagnesium solution resulted in a decrease in relative reactivity which was dependent upon both the amount of magnesium bromide added, and the time interval (contact time) between the addition of the magnesium bromide to the diethylmagnesium, and the addition of the hexyne.

The observed relative reactivities of an equi-

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[1] Part IV, *J. Am. Chem. Soc.*, **78**, 1221 (1956).

[2] National Science Foundation Predoctoral Fellow.

[3] Schlenk and Schlenk, *Ber.*, **62**, 920 (1929).

[4] For a recent review see Kharasch and Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, Inc., New York, N. Y., 1954, pp. 104–109.

[5a] Wotiz, Hollingsworth, and Dessy, *J. Am. Chem. Soc.*, **77**, 103 (1955); (b) *J. Org. Chem.*, **20**, 1545 (1955).

[6] Doering and Noller, *J. Am. Chem. Soc.*, **61**, 3436 (1939).

[7] Slough and Ubbelohde, *J. Chem. Soc.*, 108 (1955).

[8] The word organometal is used to embrace both diethylmagnesium and "ethylmagnesium bromide."

[9] A solution 1.0 N in organometal is defined as one containing one mole of available alkyl radical or one equivalent of basic magnesium per liter of solution.

molar mixture of diethylmagnesium and magnesium bromide (Br/Mg = 1) with an equivalent amount of hexyne after various contact times are as follows: 300 (zero time), 123 (ten minutes), 115 (7 days), and 112 (14 days). Concentrations were 1.0 *N* in hexyne and organometal.[8,9] If an equilibrium such as the Schlenk equilibrium did exist, such a solution should eventually lead to what we call "ethylmagnesium bromide," which has a relative reactivity of 100. However, because of the "Wurtz type" of side reaction which occurs in the formation of the Grignard reagent from ethyl bromide and magnesium, the Br/basic Mg ratio of the standard ethylmagnesium bromide used was 1.15. In view of this the relative reactivity of ethylmagnesium bromide with hexyne is in good agreement with the value found for the reactivity of an equilibrium mixture of diethylmagnesium and magnesium bromide with hexyne. This would seem to indicate that the same species exists in each solution. Complete equilibrium was apparently reached after several days, and was, for all practical purposes (95% complete) obtained after ten minutes.

$$2\ C_2H_5Br + Mg \longrightarrow MgBr_2 + C_4H_{10}$$

Figure 1 shows the relative reactivities of mixtures of diethylmagnesium and magnesium bromide, with various Br/Mg ratios, with hexyne after a contact time of ten minutes. Concentrations were 1.0 *N* in hexyne and organometal.[8,9] The decrease in reactivity, which is interpreted as the result of a decrease in the amount of diethylmagnesium present, is a function of the amount of magnesium bromide added, up to two moles of magnesium bromide per mole of diethylmagnesium. After this point no further decrease in reactivity was noted. Since the reaction mixtures were homogeneous, and the solubility of magnesium bromide dietherate in ether is only 7% by weight at 30°[6] some coordination of the Grignard reagent with the magnesium bromide must have taken place. Such coordination apparently does not effect the rate of the reaction of the complex with hexyne to any great extent.

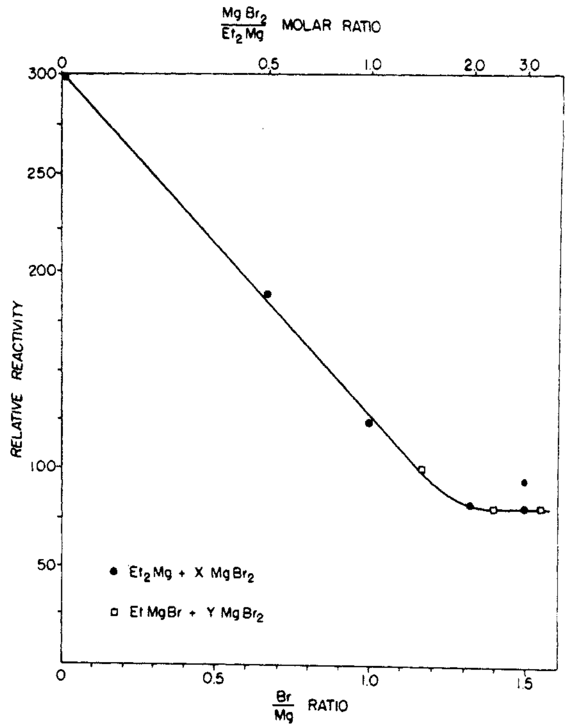

FIG. 1.—PLOT OF RELATIVE REACTIVITY AGAINST Br/Mg RATIO

Also shown in Figure 1 are the relative rates of reaction of hexyne with solutions of magnesium bromide and ethylmagnesium bromide under the same conditions as those for the diethylmagnesium, magnesium bromide determinations. After correcting for the $MgBr_2$ already present in the Grignard reagent as a result of Wurtz reactions the points fall on the curve.

These results are in agreement with a formulation of the Grignard reagent as expressed by the Schlenk equilibrium.

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