

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

CYCLOHEXYLMAGNESIUM CHLORIDE AND BROMIDE

BY HENRY GILMAN AND E. A. ZOELLNER

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Introduction

Grignard reagents are alike in the sense that they can be represented by the general formula RMgX . Strictly speaking, the resemblance ends here because of differences in rate of formation,¹ differences in yields,² differences in conditions for obtaining optimal yields,³ differences in rates of reaction⁴ and yields and kind of products with other reactants,⁵ and differences in the degree of dissociation⁶ and the extent of the equilibrium with $\text{R}_2\text{Mg} + \text{MgX}_2$ compounds.^{6,7}

There are essential differences in the optimal conditions for the preparation of various RMgX compounds. Fortunately, these are not of a kind to warrant special procedures for every possible Grignard reagent. Actually it is possible to arrange roughly the methods for the preparation of RMgX compounds after the relative reactivities of the halogen in definite groups of RX compounds like R_3CX , $\text{RCH}=\text{CHX}$, $\text{RCH}=\text{CH}-\text{CH}_2\text{X}$, etc.

Cyclohexyl halides have properties which serve to set them apart from other RX compounds. This is reflected in some of the results reported in the present study. The relatively low and erratic yields and the troublesome by-products of cyclohexylmagnesium chloride and bromide, as reported very recently by different investigators,⁸ can be avoided. It is possible to prepare cyclohexylmagnesium bromide in yields of about 92%, and cyclohexylmagnesium chloride in yields of about 96.5%.

The decrease in yield when cyclohexyl bromide is added very rapidly to magnesium in ether is one of the largest so far observed for RMgX

¹ Gilman and Zoellner, *THIS JOURNAL*, **50**, 2520 (1928).

² Gilman and McCracken, *ibid.*, **45**, 2462 (1923), and *Rec. trav. chim.*, **46**, 463 (1927); Marvel, Blomquist and Vaughn, *THIS JOURNAL*, **50**, 2810 (1928); Gilman, Zoellner and Dickey, *ibid.*, **51**, 1576 (1929).

³ Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928); Gilman and Zoellner, *THIS JOURNAL*, **50**, 425 (1928); **51**, 3493 (1929); **52**, 3984 (1930).

⁴ Gilman, Heck and St. John, *Rec. trav. chim.*, **49**, 212 (1930); Gilman and St. John, *ibid.*, **49**, 222 (1930).

⁵ A leading recent reference is that of Conant and Blatt, *THIS JOURNAL*, **51**, 1227 (1929).

⁶ Gilman and Fothergill, *ibid.*, **51**, 3149 (1929).

⁷ Schlenk and Schlenk, *Ber.*, **62**, 920 (1929); Gomberg and Bachmann, *THIS JOURNAL*, **52**, 2455 (1930); Bachmann, *ibid.*, **52**, 4412 (1930); Noller, *ibid.*, **53**, 635 (1931).

⁸ Palmer and Kipping, *J. Chem. Soc.*, 1020 (1930); Zelinsky and Titz, *Ber.*, **64**, 183 (1931).

compounds, and is the largest decrease now known for a secondary bromide. On the other hand, the corresponding chloride shows but a small decrease in yield when the RCl compound is added rapidly. Very generally, a significant drop in yield of RMgX compound with a rapid addition of halide can be correlated with low and erratic results unless special conditions are observed. Partly for this reason it is recommended that cyclohexylmagnesium chloride instead of the bromide be used whenever possible. Not only does the chloride give higher yields of RMgX compound, but it gives higher yields with an astonishing abuse or lack of care in addition. Furthermore, RMgCl compounds enjoy other advantages over RMgBr and RMgI compounds: (1) they frequently undergo more ready reaction with another compound; (2) they generally give higher yields of products with a given reactant, and on the basis of an equal content of RMgX compound; and (3) there is probably a general lesser opportunity for side reactions because the binary system ($\text{MgCl}_2 + \text{Mg}$) is less active⁹ than the corresponding systems with magnesium bromide and magnesium iodide. Over and against these general advantages, they are formed with slightly greater difficulty than the corresponding bromides or iodides; but the difference in time of starting, when a catalyst like iodine or the activated magnesium-copper alloy is used, is very small.

Experimental Part

The apparatus and general procedure were those used in related studies.¹⁰ The quantity of RX compound was 0.05 mole, and the yields so obtained were duplicated in larger runs (0.2 and 0.5 mole). Additional confirmation of the essential correctness of the results obtained by titration was had in the very high yield of cyclohexanecarboxylic acid isolated subsequent to carbonation.

TABLE I
YIELDS OF CYCLOHEXYLMAGNESIUM CHLORIDE AND BROMIDE IN 0.05 MOLE EXPERIMENTS

RMgX (0.05 mole)	Magnesium (atom)		Av. % yield of RMgX
	Turnings	30-80 mesh	
$\text{C}_6\text{H}_{11}\text{MgCl}$	0.055	..	91.1 ^a
$\text{C}_6\text{H}_{11}\text{MgCl}$...	0.055	94.4 ^b
$\text{C}_6\text{H}_{11}\text{MgCl}$15	96.6 ^c
$\text{C}_6\text{H}_{11}\text{MgBr}$.055	..	80.1 ^d
$\text{C}_6\text{H}_{11}\text{MgBr}$055	84.0 ^b
$\text{C}_6\text{H}_{11}\text{MgBr}$15	92.0 ^c

^a About a 10% solution of chlorocyclohexane in ether was used to start the reaction with magnesium. In all experiments a small crystal of iodine was used. When all of the chloride had been added, the apparent reaction (as indicated by gentle refluxing, with no application of external heat) was five to ten minutes. When this spontaneous reaction had ceased, the mixture was stirred and refluxed for ten to fifteen minutes be-

⁹ Gomberg and Bachmann, *THIS JOURNAL*, **49**, 2584 (1927); Gilman and Brown, *ibid.*, **52**, 1128 (1930).

¹⁰ Gilman, Zoellner and Dickey, *ibid.*, **51**, 1576, 1583 (1929).

fore removing aliquots for analysis. In an experiment where the chloride in ether was added at one time (instead of dropwise over a period of thirty minutes), the yield was 90%, and the spontaneous reaction continued for thirty-five minutes after all the halide had been added. This yield was decreased 5% when undistilled chloride was used.

^b Reaction sets in immediately with the fine magnesium (30–80 mesh). These runs were made under the same conditions as those with commercial turnings, with the exception that 8 equivalents of ether were used. The time of addition of the halide in ether was thirty minutes.

^c The time of addition in these experiments was one hour, and 0.425 mole of ether was used. A larger ratio of ether is used with fine magnesium in order to reduce the spattering of magnesium on the walls of the flask.

^d The bromide reacts more readily than the chloride, and an initial concentration of 6–7% in ether is sufficient to start the reaction. Spontaneous reaction continued for five minutes after adding all of the bromide over a period of thirty minutes, and the mixture was then stirred and refluxed for ten minutes before removing samples for analysis. When all of the bromide in ether is added at once (after starting the reaction with a part of the bromide), the spontaneous reaction continues for twelve minutes and the yield drops to 54%. The time during which the spontaneous reaction occurs subsequent to addition of all of the halide is apparently a qualitative measure of the relative reactivity of the halide toward magnesium. Undistilled bromide decreases the yield 3%.

The halides were freshly distilled, and as such gave higher yields and started to react with magnesium more readily than undistilled material. The time, and with some RX compounds the yield, is influenced by the nature of commercially available magnesium turnings. It is not an easy matter to describe the physical condition of the turnings, but those which gave the best results in the present study were about 0.48 mm. in thickness, 4 mm. in breadth and 10–50 mm. in length, when the coils were unwound.

Recommended Procedure for Laboratory Preparation.—The magnesium turnings (1.1 atom equivalents) are barely covered with ether and sufficient pure halide is added to give an optimal initial concentration (6–7% with bromide and 15% or greater with the chloride). After adding a crystal of iodine heat is applied, without stirring, and these conditions are maintained for five to ten minutes after the iodine color has disappeared. Reaction having set in, sufficient ether is added to cover the magnesium while it is stirred, and then the remainder of the halide in ether¹¹ is added. The rate of addition varies with the halide. With the chloride, there is no appreciable harm in rapid addition. However, the bromide must be added more slowly, and generally at a rate that causes gentle refluxing.

When all of the halide has been added, stirring and refluxing are continued for fifteen to twenty minutes with the chloride, and for ten minutes with the bromide.

The yield of cyclohexylmagnesium chloride in 0.2 and 0.5 mole runs under the above conditions is 92–95%.

In carbonating the Grignard reagent prepared as above, it is recommended that provision be made to admit an inert gas like nitrogen during

¹¹ In all about 6 mole equivalents of ether are used. One-half of this ether can be added to the mixture after the reaction has started, and the remainder is used to dilute the halide.

the cooling which is preliminary to carbonation. By so doing, the yield is improved because otherwise oxygen from the atmosphere would be pulled in and react with the Grignard reagent. In a 0.2 mole run the yield of cyclohexanecarboxylic acid based on an 80% yield of cyclohexylmagnesium bromide was 83%; and the yield of acid based on a 92% yield of cyclohexylmagnesium chloride was 93%. It is recommended that the solution be diluted with ether (300-500 cc. in a 0.2 mole run) prior to carbonation, because of the sparingly soluble salt (RCOOMgBr) which is formed.

Summary

Cyclohexylmagnesium chloride and bromide can be prepared in excellent yields. In its reaction with magnesium, bromocyclohexane differs significantly from other secondary bromides. General recommendations are given for the use of RCl in preference to RBr and RI compounds for the preparation of Grignard reagents.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

PHYSICAL PROPERTIES OF THE NORMAL PARAFFIN HYDROCARBONS, PENTANE TO DODECANE

BY A. F. SHEPARD, A. L. HENNE AND T. MIDGLEY, JR.

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This paper presents some physical constants of the normal paraffin hydrocarbons, from pentane to dodecane, inclusive. These compounds have been prepared from a common source, and have all been purified by the same method and to the same extent. Consequently, physical measurements obtained with such samples are more comparable among themselves than are the isolated results obtained by various workers who have used different methods of synthesis, purification and measurement.

Preparation of the Samples.—The starting material was a special gasoline with a normal paraffin hydrocarbon content of about 70%. It was obtained from The Standard Oil Company of Indiana through the courtesy of R. E. Wilson. It was roughly separated into its constituents by distillation. Each cut was then treated with chlorosulfonic acid until a one-week treatment no longer altered the density. The details of this treatment have been reported previously.¹ Further purification was accomplished by careful fractionation through a flat spiral fractionating column, equipped with an efficient dephlegmator. The progress of the purification was measured by the density variations of the distillates. The purification was regarded as having reached its practical limit when the over-all density differences of several successive distillate fractions did

¹ Shepard and Henne, *Ind. Eng. Chem.*, **22**, 356 (1930).