[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

Reactions of Monochloroamine with Dialkylmagnesium Compounds and Grignard Reagents[*]

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Reactions of monochloroamine and other halogen amines[1] with Grignard reagents have been studied previously in this Laboratory. In these reactions the yields of amines formed with Grignard reagents prepared from chlorides are greater than those from bromides or iodides.

The present paper deals with a comparison of the reactions of monochloroamine with Grignard reagents and with dialkylmagnesium compounds and the possible relation to the following equilibrium present in solutions of Grignard reagents[2,3,4]

$$2\,RMgX \rightleftarrows R_2Mg + MgX_2 \qquad (1)$$

The *n*-butyl series was selected as typical of the alkyl halides. Some of the previous work with monochloroamine and Grignard reagents was repeated in order to check the uniformity of results and to standardize the procedure for the present comparison. The average yields of *n*-butylamine from the reaction of monochloroamine with Grignard reagents prepared from *n*-butyl chloride, bromide and iodide were approximately 57, 29 and 12%, respectively. These results agree with earlier work.

Di-*n*-butylmagnesium was prepared from *n*-butyl chloride, *n*-butyl bromide and *n*-butyl iodide by the addition of dioxane to the Grignard reagents.[5,6] The reaction of monochloroamine with di-*n*-butylmagnesium was carried out under a variety of conditions. The average yield of *n*-butylamine from di-*n*-butylmagnesium in diethyl ether solution was about 82%, in ether–dioxane solution 86%, and in dioxane solution 90%. The preparation of solid di-*n*-butylmagnesium and its solutions in diethyl ether and in dioxane are described in the experimental part.

The effect on the yields of amine and ammonia of adding various amounts of anhydrous magnesium iodide to solutions of di-*n*-butylmagnesium in diethyl ether before reaction with monochloroamine was studied. The results are given in Table I.

The reactions of both the Grignard reagents and di-*n*-butylmagnesium solutions with monochloroamine were usually carried out at 0°, but in several experiments temperatures of −60° were used. In these the yields of *n*-butylamine were somewhat higher than in the reactions carried out at 0°. The highest yield of amine was 97%, using a rather large excess of di-*n*-butylmagnesium. In order to obtain good yields in ether–dioxane solution it proved to be unnecessary to remove the precipitated halogen compounds before adding monochloroamine.

Without considering the possible mechanism in detail the reactions of monochloroamine with R_2Mg and RMgX may be represented as

$$R_2Mg + NH_2Cl \longrightarrow RNHMgCl + RH \qquad (2)$$

$$RMgX + NH_2Cl \longrightarrow RCl + MgXNH_2 \qquad (3)$$

If any primary amine is formed from RMgX the following equation should be included

$$2\,RMgX + NH_2Cl \longrightarrow RNHMgX + MgXCl + RH \qquad (4)$$

Subsequent reactions of any of the products are not indicated.

Determinations of the percentages of di-*n*-butylmagnesium in the Grignard reagents were made by the dioxane method. These were found to be 75, 74 and 67% for the chloride, bromide and iodide reagents, respectively. These results were duplicated repeatedly under specified experimental conditions but showed considerable variation with relatively slight variation in the procedure. The reliability of the dioxane method has been the subject of several studies.[6,7] Noller and Raney[8] have shown that on the basis of the equilibrium constant for equation (1) determined by their method in a solution of *n*-butylmagnesium chloride the percentage of di-*n*-butylmagnesium at equilibrium is very small. The determination of equilibrium constants by this method involves the assumption that the concentration of magnesium chloride in the solution of the Grignard re-

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[1] Coleman and co-workers, THIS JOURNAL, **50**, 1193 (1928); **51**, 567 (1929); **55**, 2075 (1933); **55**, 3001 (1933); **55**, 3669 (1933); **56**, 965 (1934); **58**, 27 (1936).

[2] Gilman and Fothergill, *ibid.*, **51**, 3149 (1929).

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

[4] Gilman and Brown, THIS JOURNAL, **52**, 1181 (1930).

[5] Noller, *ibid.*, **53**, 635 (1931).

[6] Noller and White, *ibid.*, **59**, 1354 (1937).

[7] Cope, *ibid.*, **60**, 2215 (1938).

[8] Noller and Raney, *ibid.*, **62**, 1749 (1940).

TABLE I

YIELDS OF AMINES AND AMMONIA FROM ORGANOMAGNESIUM COMPOUNDS AND MONOCHLOROAMINE

Reagent	Solvent	Temp., °C.	Modification of Organomagnesium solutions	Av. yield of ammonia, %	Av. yield of amine, %
n-$C_4H_9MgCl^a$	Ether	0		43	57
n-C_4H_9MgBr	Ether	0		70	29
n-C_4H_9MgI	Ether	0		70	12
$(n$-$C_4H_9)_2Mg$	Ether	0		14	82
$(n$-$C_4H_9)_2Mg$	Ether–dioxane	0	Halide ppt. sepd. by centrif.	8	86
$(n$-$C_4H_9)_2Mg$	Dioxane	0		0	90
$(n$-$C_4H_9)_2Mg$	Ether–dioxane	0	Halide ppt. not removed	7	87
$(n$-$C_4H_9)_2Mg$	Ether–dioxane	−60	Halide ppt. sepd. by centrif.	0^b	97
n-C_4H_9MgCl	Ether	−60		37^b	63
$(n$-$C_4H_9)_2Mg$	Ether	0	1.0 mole MgI_2 added	82^b	18
$(n$-$C_4H_9)_2Mg$	Ether	0	0.5 mole MgI_2 added	66^b	34
$(n$-$C_4H_9)_2Mg$	Ether	0	0.1 mole MgI_2 added	14^b	82
n-C_4H_9MgI	Ether	0	1.0 mole MgI_2 added	87^b	10

[a] RMgX represents a Grignard reagent. [b] Result of a single run.

agent at equilibrium is the same as that in a saturated solution of magnesium chloride in the pure solvent diethyl ether. As these authors indicate this assumption is open to question.

A part of the work of Noller and Raney[8] on the equilibrium constant was repeated in this Laboratory with some modifications. Di-*n*-butyl ether was used in place of diethyl ether. The value of the equilibrium constant in a solution of *n*-butylmagnesium chloride was of the same general order as that reported by them for the solution in diethyl ether.

If the percentages of R_2Mg present in solutions of Grignard reagents as determined by the dioxane method were accepted as correct, certain conclusions might be drawn from the experiments with monochloroamine and the *n*-butyl series. The yields of primary amines and ammonia could be approximately accounted for by assuming that the $(n$-$C_4H_9)_2Mg$ forms only primary amine (100% synthetic reaction) and that the n-C_4H_9MgX forms only ammonia (100% reducing reaction). This would also require consideration of the relative rates of reaction of the various forms present in the solutions of the Grignard reagents.

Since there is doubt of the reliability of the dioxane method of determining the percentage of R_2Mg in Grignard reagents and the results of reactions with only the butyl series are considered in this work these assumptions are only presented as possibilities. If the percentage of R_2Mg is very small as indicated for a solution of *n*-butylmagnesium chloride by the work of Noller and Raney these assumptions would not be readily tenable.

Experimental

Monochloroamine.—This compound was prepared in ether solution from sodium hypochlorite and ammonia as described previously.[9]

Preparation of Dialkyl Magnesium.—A slight modification of Noller's method was used. After filtering and analyzing the Grignard reagent the dioxane solution was added at a uniform rate through a dropping funnel. The mixture was stirred continuously and the temperature maintained at about 0°. All operations including transfer of solutions to and from centrifuge tubes were carried out in an atmosphere of nitrogen.

For the preparation of dialkyl magnesium in a single solvent, the solution in the mixed ether–dioxane solvent was first prepared. From this the solvent was removed by distillation under reduced pressure. A white solid residue remained.[10] This residue would ignite spontaneously if exposed to air. The white solid was then dissolved in pure ether or dioxane as desired. Clear solutions were formed.

Reaction of Organomagnesium Compounds with Monochloroamine.—The solution of Grignard reagent or of dialkyl magnesium in either ether or dioxane or the mixed solvent was cooled to 0° in a 2-liter three-necked flask, which was fitted with a stirrer and reflux condenser, and surrounded by a bath of ice and salt. The solution of monochloroamine, cooled to −60° in a bath of carbon dioxide-snow and acetone, was added dropwise to the organomagnesium compound solution which was stirred continuously. A white precipitate was formed. The organomagnesium compound was used in excess, being in the proportion of three moles or more of *n*-butylmagnesium halide or the equivalent of di-*n*-butylmagnesium to one mole of monochloroamine. After the addition of the monochloroamine, the reaction mixture was stirred for an hour and then decomposed by addition of dilute sulfuric acid. The aqueous layer was neutralized and steam distilled into dilute hydrochloric acid. The distillate was evaporated to dryness on a steam-bath and placed in a desiccator. The amine hydrochloride was separated from the ammo-

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(9) Coleman and Johnson, "Inorganic Syntheses," McGraw-Hill Book Company, N. Y., 1939, Vol. I, p. 59.

(10) The presence or absence of combined solvent was not determined.

nium chloride by means of *n*-butyl alcohol. The two products were dried to constant weight in a vacuum desiccator.

In the calculations the slight amount of ammonia in the monochloroamine solutions, as shown by the difference in analysis for nitrogen and chlorine, was subtracted from the amount of ammonium chloride obtained, to give the actual amount of ammonia formed in the reaction. Percentage yields were calculated on the basis of the chlorine analysis of the monochloroamine. These results are shown in Table I.

Monochloroamine with Dialkyl Magnesium Solutions (without Separation from Halide Precipitate).—The Grignard reagent was prepared and analyzed. The dioxane–ether precipitating solution was added. A slight increase over the usual amount was used to allow for dilution due to the addition of the monochloroamine solution. The amount of di-*n*-butylmagnesium in this mixture was calculated. Monochloroamine was added in the same proportion as before. The products were isolated in the usual manner. The results are shown in Table I.

The Addition of Anhydrous Magnesium Iodide to Organomagnesium Compounds and the Reactions of the Resulting Mixtures with Monochloroamine.—The ether solution of the Grignard reagent, or of di-*n*-butylmagnesium, was prepared with a minimum volume of ether and to this was added the ether solution of magnesium iodide in the calculated amount, based upon the analysis for iodine. Analysis before and after the addition of the magnesium iodide showed that there was no loss in the active reagent. This solution was cooled to 0° and stirred for an hour after which the ether solution of monochloroamine was added in the usual manner. The results are shown in Table I.

Summary

1. The reactions of monochloroamine with di-*n*-butylmagnesium and with Grignard reagents prepared from the *n*-butyl halides have been compared. A maximum yield of *n*-butylamine of 97% was obtained with di-*n*-butylmagnesium at $-60°$.

2. The effect on this reaction of adding various amounts of anhydrous magnesium iodide to the di-*n*-butylmagnesium has been determined.

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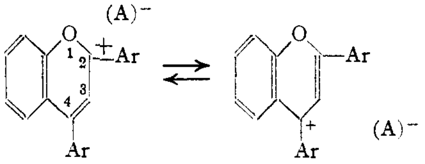
[Contribution from the Noyes Chemical Laboratory, University of Illinois]

Benzopyrylium Salts. III. Syntheses from Substituted Coumarins and Chromones

By R. L. Shriner and Robert Bruce Moffett

Previous studies of benzopyrylium salts[1] led to the suggestion that the carbon atoms 2, 3 and 4 in the heterocyclic ring represent a special case of the allylic three-carbon atom system and that these salts may tautomerize or resonate between the two structures I and II.



I II

(A = anion such as Cl^-, $FeCl_4^-$, ClO_4^-)

This viewpoint harmonized with the 2-carbonium salt structure proposed by Dilthey[2] and the 4-carbonium ion which Hill and Melhuish[3] pointed out must also be a possibility. Also, Löwenbein[4] had found that flavylium perchlorates undergo a coupling reaction with phenylmagnesium bromide, a reaction characteristic of allylic systems.[5]

Further evidence in favor of this viewpoint has now been obtained by demonstrating that the same benzopyrylium salt is obtainable from either a substituted coumarin or from a chromone by treatment with the appropriate Grignard reagent followed by reaction with an acid. The formation of flavylium salts by treatment of the carbinols obtained by the action of Grignard reagents on substituted coumarins is a well-known reaction introduced by Decker and Fellenberg[6] and used by Willstätter[7] for the synthesis of anthocyanidin salts. Heilbron and Zaki[8] prepared a 4-substituted benzopyrylium salt by the action of phenylmagnesium bromide on 2,3-dimethyl-7-methoxychromone but no comparison has been made of the salts obtained by these two different methods.

In the present work 3-phenyl-4-(*p*-tolyl)-6-

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(1) Shriner and Moffett, This Journal, **62**, 2711 (1940).

(2) Dilthey, *J. prakt. Chem.*, **94**, 53 (1916); *ibid.*, **95**, 107 (1917); *Ber.*, **53**, 261 (1920); *J. prakt. Chem.*, **131**, 1 (1931); *ibid.*, **138**, 42 (1933); *Ber.*, **64**, 2082 (1931).

(3) Hill and Melhuish, *J. Chem. Soc.*, 1161 (1935); *Chem. Rev.*, **19**, 27 (1936).

(4) Löwenbein, *Ber.*, **57**, 1517 (1924); Löwenbein and Rosenbaum, *Ann.*, **448**, 223 (1926).

(5) Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, 1938, Vol. I, p. 424.

(6) Decker and Fellenberg, *Ber.*, **40**, 3815 (1907); *Ann.*, **356**, 281 (1907).

(7) Willstätter and Schmidt, *Ber.*, **57**, 1945 (1924); Willstätter, Zechmeister and Kindler, *ibid.*, **57**, 1938 (1924).

(8) Heilbron and Zaki, *J. Chem. Soc.*, 1902 (1926).