

is present along with other volatile hydrocarbons subject to attack by concd. sulfuric acid.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

SOME REARRANGEMENT REACTIONS OF ALPHA-NAPHTHYLMETHYLMAGNESIUM CHLORIDE

BY HENRY GILMAN AND JAMES E. KIRBY

RECEIVED JUNE 27, 1929

PUBLISHED NOVEMBER 8, 1929

Introduction

In continuation of investigations¹ concerned with so-called rearrangements of some organomagnesium halides, a study has been made of the reactions of α -naphthylmethylmagnesium chloride (α -C₁₀H₇CH₂MgCl). It is known that some RMgX compounds (in particular, benzylmagnesium chloride and triphenylmethylmagnesium chloride) react both normally and abnormally with some reagents, especially with aldehydes.² We wished to ascertain whether such abnormal reactions were characteristic

of organomagnesium halides with the grouping $\text{>C}=\overset{\text{CH}_2\text{MgX}}{\text{C}}$. The results of the present study show that α -naphthylmethylmagnesium chloride does behave abnormally with some compounds that give rise to rearrangement products with a type like benzylmagnesium chloride. Accordingly, mechanisms to be offered² for such rearrangements must include α -naphthylmethylmagnesium chloride.

The preparation of α -naphthylmethylmagnesium chloride by earlier investigators has been attended with more than ordinary difficulties. Weitzenböck and Lieb³ had no success in the synthesis of ethyl α -naphthylacetate from α -naphthylmethylmagnesium chloride and ethyl chlorocarbonate. They probably did not have any of the desired Grignard reagent in hand. When they treated α -naphthylmethyl chloride (prepared by the direct chlorination of α -methylnaphthalene)⁴ with magnesium they had difficulty in getting the magnesium to react, and after treating their reaction mixture with ethyl chlorocarbonate, the only product they isolated was di- α -naphthylethane formed as a result of a coupling reaction.⁵ Then Mayer and Sieglitz⁶ found that magnesium was used up to only a

¹ Gilman and Harris, *THIS JOURNAL*, **49**, 1825 (1927).

² A later report will describe many other reagents that react abnormally with such types.

³ Weitzenböck and Lieb, *Monatsh.*, **33**, 554 (1912).

⁴ Scherler, *Ber.*, **24**, 3930 (1891); Wislicenus and Wren, *ibid.*, **38**, 506 (1905).

⁵ Gilman and Fothergill, *THIS JOURNAL*, **50**, 3334 (1928).

⁶ Mayer and Sieglitz, *Ber.*, **55**, 1835 (1922). They prepared their bromide by the direct bromination of α -methylnaphthalene.

slight extent in its reaction with α -naphthylmethyl bromide, and they also obtained only the coupling product (di- α -naphthylethane) in a reaction with acetaldehyde. More recently, Conant, Small and Sloan⁷ had better success with their chloride prepared by the method of v. Braun and Moldaenke.⁸ However, their chloride reacted slowly with magnesium and the reaction was about complete at the end of three hours; their yield of crude α -naphthylmethylxanthenol from xanthone was about 15%.

Our chloride, prepared from α -naphthylcarbinol and thionyl chloride, reacted with comparative ease with ordinary magnesium turnings to give quite satisfactory yields⁹ of several products. Abnormal reactions were observed with ethyl chlorocarbonate and formaldehyde, the products having the carboxyethyl and carbinol groups, respectively, in the β - and not in the α -position. Normal products were obtained with carbon dioxide, dimethyl sulfate and phenyl isocyanate.

One reaction was carried out between the relatively inaccessible and expensive β -naphthylmethylmagnesium bromide and carbon dioxide, and the expected β -naphthylacetic acid was obtained.

Experimental Part

Preparation of α -Naphthylmethyl Chloride.—First, α -naphthylcarbinol was prepared in 50–53% yield in accordance with the method of Ziegler¹⁰ by the action of gaseous formaldehyde on α -naphthylmagnesium bromide. Then, to 25 g. (0.15 mole) of the carbinol dissolved in 100 cc. of dry toluene was added 25 g. of thionyl chloride in small quantities. A reaction set in at once and after the spontaneous reaction ended the solution was refluxed gently until evolution of gases ceased. This required about three hours. The toluene and thionyl chloride were removed under reduced pressure and fractional distillation of the residue gave 23.2 g. or a 79% yield of the chloride boiling at 135–139° (6 mm.).

Preparation of the Grignard Reagent.—In a first experiment we used α -naphthylmethyl chloride prepared by the direct chlorination of α -methylnaphthalene.⁴ Although we obtained the Grignard reagent from this chloride, the reaction was unsatisfactory. In all subsequent experiments we used the chloride prepared from the corresponding carbinol. With this chloride reaction set in as readily as with bromobenzene and magnesium when the usual small crystal of iodine was used as a catalyst.

In some preliminary experiments the reagent was prepared in a test-tube in connection with the color test of Gilman and Schulze.¹¹ It was observed that once the

⁷ Conant, Small and Sloan, *THIS JOURNAL*, **48**, 1743 (1926).

⁸ V. Braun and Moldaenke, *Ber.*, **56**, 2165 (1923).

⁹ No study was made of optimal conditions for the preparation of the α -naphthylmethylmagnesium chloride. It is highly probable, however, that yields of about 90% or more can be obtained by following the directions of Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928), for the preparation of allylmagnesium bromide. Judging by the yields of some of the products obtained from α -naphthylmagnesium chloride it is fair to state that this Grignard reagent was obtained in the present study in yields of at least 80%. See Gilman and St. John, *Rec. trav. chim.*, **48**, 593 (1929).

¹⁰ Ziegler, *Ber.*, **54**, 737 (1921).

¹¹ Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925); *Bull. soc. chim.*, **41**, 1479 (1927).

reaction started it continued in the presence of the Michler's ketone to give a pronounced characteristic color test on subsequent hydrolysis. Of course the same test was obtained in another test-tube experiment when the ketone was added after the reaction between the chloride and magnesium was complete.

In the subsequent reactions, 10 g. (0.057 mole) of the α -naphthylmethyl chloride in 50 cc. of ether was added slowly to 1.38 g. (0.057 atom) of magnesium turnings covered with 85 cc. of ether.¹² The RMgCl solution was of a yellowish-green color.

Carbon Dioxide.— α -Naphthylacetic acid was prepared in the customary manner¹³ from carbon dioxide. A negative color test¹¹ was obtained at the end of twenty minutes. The yield of acid from 0.057 mole of chloride was 59.4%.⁹ It was characterized both by its melting point and the melting point of α -naphthylacetamide¹⁴ prepared from it.

Dimethyl Sulfate.—The reaction between the Grignard reagent (0.057 mole of chloride) and dimethyl sulfate was carried out in accordance with the general directions of Gilman and co-workers.¹⁵ The yield of α -ethylnaphthalene was 55.1%. It distilled at 247–249° (742 mm.) and was identified as the picrate, which melted at 98–99°. The melting point of the picrate as reported by Carnelutti¹⁶ is 98°.

Phenyl Isocyanate.—A vigorous reaction took place when 10 g. (0.08 mole) of phenyl isocyanate in ether was added slowly to the Grignard reagent prepared from 17.6 g. (0.1 mole) of α -naphthylmethyl chloride. After working up the reaction product in a customary manner,¹⁷ 9.3 g. or a 36% yield of α -naphthyl acetanilide was obtained. The compound melted at 155° when crystallized from alcohol and its identity was confirmed by a mixed melting point determination with the anilide prepared from α -naphthylacetyl chloride¹⁸ and aniline.

In a preliminary experiment it was noticed that phenyl isocyanate stopped a reaction between α -naphthylmethyl chloride and magnesium. This reaction could not be induced to start again either by warming or by the addition of iodine. A similar case of negative catalysis with phenyl isocyanate was noted earlier by Gilman and Kirby¹⁹ with benzohydrylmagnesium chloride (C_6H_5)₂CHMgCl. In another experiment a small quantity of an as yet unidentified solid melting at 136–137° was obtained. This may be a rearrangement product.

Ethyl Chlorocarbonate.—The Grignard reagent prepared from 0.095 mole of the chloride was rapidly decanted from unused magnesium into a separatory funnel, and then added slowly to 43 g. (0.4 mole) of ethyl chlorocarbonate in ether. On working up the reaction products in a customary manner, subsequent to hydrolysis by iced dilute hydrochloric acid, a 41% yield of ester distilling at 145–150° (3 mm.) was obtained. The ester was hydrolyzed by heating with alcoholic potash and the acid obtained from the hydrolysis melted at 174°. It may be crystallized from either hot water or benzene.

The neutralization equivalent (184.8, whereas the calculated value for $C_{12}H_{10}O_2$ is 186) showed it to be isomeric with α -naphthylacetic acid. It was definitely shown to be α -methyl- β -naphthoic acid by a mixed melting point determination with an

¹² For general directions on the preparation of Grignard reagents see Gilman, Zoellner and Dickey, *THIS JOURNAL*, **51**, 1576, 1583 (1929).

¹³ Gilman and Parker, *ibid.*, **46**, 2816 (1924).

¹⁴ Boessneck, *Ber.*, **16**, 641 (1883).

¹⁵ A recent leading reference is Gilman and Heck, *THIS JOURNAL*, **50**, 2223 (1928).

¹⁶ Carnelutti, *Ber.*, **13**, 1671 (1880).

¹⁷ Gilman and Furry, *THIS JOURNAL*, **50**, 1214 (1928).

¹⁸ Prepared from α -naphthylacetic acid and thionyl chloride by heating in a benzene solution. The acid chloride was not isolated.

¹⁹ Gilman and Kirby, *THIS JOURNAL*, **48**, 1734 (1926).

authentic specimen of the acid kindly provided by Professor v. Auwers.²⁰ This rearrangement product is remindful of a like rearrangement of benzylmagnesium chloride² which with ethyl chlorocarbonate gave both ethyl *o*-toluate and ethyl phenylacetate. The ester described above is undoubtedly chiefly ethyl α -methyl- β -naphthoate.

The anilide of α -methyl- β -naphthoic acid was prepared after the method¹⁸ used for the preparation of the anilide of α -naphthylacetic acid and melted at 217–218° after crystallization from alcohol.

No definite products were obtained in the attempts to oxidize α -methyl- β -naphthoic acid by alkaline permanganate and by chromic acid in acetic acid. Mayer and Schnecko²¹ also had no success in their attempts to oxidize the same acid to α,β -dicarboxynaphthalene.

Formaldehyde.—The reaction between gaseous formaldehyde and the Grignard reagent prepared from 0.1 mole of the chloride gave 6.4% of the coupling product (di- α -naphthylethane), an as yet unidentified small fraction distilling between 100–130° (6 mm.) and 2.6 g. of a yellow oil distilling at 167–170° (6 mm.) and melting at 121° when crystallized from benzene. It showed reactions of an active hydrogen compound and its phenylurethan (prepared from phenyl isocyanate in benzene) melted at 125°. No definite product was obtained in the attempted oxidation of the carbinol by means of alkaline permanganate to the corresponding acid. In this connection it is interesting to note that Ziegler and Tiemann²² were unsuccessful in their attempted oxidation of the isomeric β -methyl- α -naphthylcarbinol to the corresponding aldehyde. They used chromic acid; a part of their carbinol was completely oxidized and the remainder was unchanged. These difficulties in oxidation may be due to steric influences. Undoubtedly the carbinol is α -methyl- β -naphthylcarbinol formed as a result of a rearrangement reaction that has been confirmed by several with benzylmagnesium chloride and formaldehyde. None of the normal and known reaction product, α -naphthylethyl alcohol, has as yet been isolated.

The Reaction between β -Naphthylmethylmagnesium Bromide and Carbon Dioxide.—The reaction between β -naphthylmethyl bromide and magnesium in ether started easily with the aid of a crystal of iodine. The Grignard reagent was carbonated in the customary manner¹³ and the β -naphthylacetic acid obtained after crystallization from benzene melted at 138°. Its identity was confirmed by a mixed melting point determination with the acid prepared according to Blank²³ by the hydrolysis of β -naphthylacetoneitrile.

Summary

It has been shown that α -naphthylmethylmagnesium chloride can be readily prepared in satisfactory yields and that it reacts normally with carbon dioxide, dimethyl sulfate and phenyl isocyanate, but abnormally with ethyl chlorocarbonate and formaldehyde. The rearrangement reactions of this organomagnesium chloride can be correlated with like reactions shown by compounds with the $-\text{CH}=\text{CHCH}_2\text{MgX}$ grouping.

AMES, IOWA

²⁰ v. Auwers and Möller, *J. prakt. Chem.*, **109**, 124 (1925).

²¹ Mayer and Schnecko, *Ber.*, **56**, 1408 (1923).

²² Ziegler and Tiemann, *ibid.*, **55**, 3406 (1922).

²³ Blank, *ibid.*, **29**, 2372 (1896).