[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

THE REACTION BETWEEN BENZHYDRYLMAGNESIUM CHLORIDE AND DIMETHYL SULFATE

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Introduction

It is necessary at times to carry out reactions with organomagnesium halides by preparing the RMgX compound in the presence of the compound with which it is to react. This is particularly the case with allylmagnesium halides, for diallyl and magnesium halides are formed when an allyl halide is added to magnesium and ether.[2] The same kind of coupling or Würtz reaction accompanies the formation, to a variable, but much less extent, of all RMgX compounds. This coupling reaction is significant generally, but not always, when the halogen in the RX compound is highly reactive. For example, large amounts of dibenzyl are formed when special precautions are not observed in the preparation of benzylmagnesium halides.[3]

The highly reactive halogen in benzhydryl halides ($(C_6H_5)_2CHX$) makes it necessary to carry out reactions with the corresponding RMgX compounds by preparing the benzhydrylmagnesium halide in the presence of the compound with which reaction is sought. Gomberg and Cone[4] observed that when benzhydryl bromide was added to magnesium a large amount of tetraphenylethane formed which covered the magnesium and so impeded reaction. To avoid this coupling reaction, they added activated magnesium in successive small parts to benzhydryl bromide and triphenylchloromethane so that a good yield (about 80%) of pentaphenylethane was obtained. Bert[5] in a like manner prepared diphenylacetic acid in a 14% yield by passing carbon dioxide into an ether solution of benzhydrylmag-

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[1] This paper is an abstract of a part of a thesis presented by James E. Kirby in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at Iowa State College.

[2] This coupling reaction is undoubtedly the resultant of several reactions. First, there may be a simple Würtz-Fittig reaction between the magnesium and halide, although it is probable that most such reactions take place as the result of the formation of an intermediate organometallic compound. Second, the RMgX compound is first formed and then reacts with RX compound to give the R—R compound and magnesium halide. [Compare (a) Späth, *Monatsh.*, **34**, 1965 (1913).] Third, the RMgX compound is first formed and then induces a coupling reaction between *two* molecules of halide. [Compare Ref. 2a and (b) Fuson, THIS JOURNAL, **48**, 830 (1926).]

Even when there is little danger of this coupling reaction it is desirable in some cases to add the halide and compound that is to enter into reaction to the magnesium in ether in order to get a selective reaction. [Compare (c) Davies and Kipping, *J. Chem. Soc.*, **99**, 296 (1911) and (d) Hepworth, *ibid.*, **119**, 251 (1921).]

[3] Gilman and McCracken, THIS JOURNAL, **45**, 2462 (1923).

[4] Gomberg and Cone, *Ber.*, **39**, 1461 (1906).

[5] Bert, *Compt. rend.*, **177**, 324 (1923).

nesium bromide during its formation and after the reaction had been started with ethyl bromide. However, under corresponding conditions they got no reaction with oxygen and with dimethyl sulfate. Inasmuch as Gilman and Hoyle[6] recommended dialkyl sulfates, particularly diethyl sulfate, as reagents for characterizing the —MgX group attached to carbon as well as to some other elements, a study has been made of the reaction of dimethyl sulfate and other compounds with benzhydrylmagnesium halides.

It has been shown that dimethyl sulfate does react in the general manner with benzhydrylmagnesium chloride to give *unsym.*diphenylethane: $2(C_6H_5)_2CHMgCl + (CH_3)_2SO_4 \longrightarrow 2(C_6H_5)_2CHCH_3 + MgSO_4 + MgCl_2$. However, the extent of this reaction is very decidedly limited, and a 95% yield of tetraphenylethane was obtained. Benzhydryl chloride was used in preference to the bromide because Gilman and McCracken[3] directed attention earlier to the improved yields of RMgX compounds that could be obtained when chlorides were used in preference to the corresponding bromides. This was borne out by experiment when a 32.5% yield of diphenylacetic acid was obtained from benzhydrylmagnesium chloride and carbon dioxide under conditions whereby Bert[5] obtained but a 14% yield using benzhydrylmagnesium bromide.

Benzhydrylmagnesium chloride can actually be prepared by adding benzhydryl chloride to magnesium and ether in which is dissolved a small crystal of iodine. This was shown by the characteristic color test for RMgX compounds described by Gilman and Schulze.[7] The benzhydrylmagnesium chloride obtained in this manner is quite unstable as was indicated by the decided weakening of the color test even after five minutes had elapsed. A like positive test is also obtained when either benzhydryl chloride or benzhydryl bromide is added *with* Michler's ketone to magnesium in ether containing a little iodine. However, when phenylisocyanate[8] was added with benzhydryl chloride to magnesium which had already entered into reaction with benzhydryl chloride alone, the reaction stopped, and none of the expected anilide was obtained. This result is somewhat surprising in view of the good yield of phenylacetanilide obtained when a mixture of benzyl chloride and phenylisocyanate was added to magnesium and ether.

Bert[5] got no reaction between benzhydryl bromide, dimethyl sulfate and

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[6] Gilman and Hoyle, THIS JOURNAL, **44**, 2621 (1922). This reaction was studied earlier by others. References to former work are given in a paper by Gilman and Beaber [*ibid.*, **47**, 518 (1925)]. Subsequent work on alkyl sulfates and the Grignard reagent has been done by Bert [*Bull. soc. chim.*, **37**, 1252 (1925)].

[7] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

[8] Phenyl- and naphthylisocyanates are reagents for characterizing RMgX compounds by the formation of crystalline anilides in good yields, even though these reagents cannot be used for the quantitative estimation of RMgX compounds. [Compare Gilman, Wilkinson, Fishel and Meyers, *ibid.*, **45**, 150 (1923).]

magnesium because the dimethyl sulfate in all probability, like phenylisocyanate, acted in some anti-catalytic manner. In support of this it was noted that dimethyl sulfate when mixed with benzhydryl chloride actually stopped a reaction between benzhydryl chloride and magnesium. However, if the reaction between benzhydryl chloride and magnesium is carried out rapidly, and if dimethyl sulfate is added before coupling to tetraphenylethane is complete, some of the expected *unsym.*diphenylethane is obtained.

Experimental Part

Preparation of Benzhydryl Chloride.—A 93.3% yield of benzhydryl chloride was obtained when 40 g. of thionyl chloride was added slowly to a suspension of 60 g. of benzhydrol in 150 cc. of toluene. The mixture was refluxed until no sulfur dioxide or hydrogen chloride was evolved, about two to two and a half hours. The chloride distilled at 161–162° (13 mm.) and melted[9] at 18°. Benzhydryl chloride has been prepared by Montagne[10] in a 92% yield from benzhydrol by the use of the less expensive hydrogen chloride. However, Engler and Bethge,[11] who reported its preparation by a like reaction, give the melting point as 14°.

Benzhydrylmagnesium Chloride and Dimethyl Sulfate.—Forty g. (0.2 mole) of freshly prepared benzhydryl chloride dissolved in 200 cc. of dry ether was added during 20–25 minutes to 4 g. of magnesium and 50 cc. of ether containing a small crystal of iodine. Reaction commenced after the first addition of the chloride as was evidenced by the disappearance of the iodine color and the formation of a heavy, white precipitate of tetraphenylethane. A positive color test[7] was noted after the addition of about one-tenth of the chloride solution.

A slight heat of reaction was observed on the addition of 20 g. of dimethyl sulfate in ether. The reaction mixture was stirred and refluxed for four hours, and then allowed to stand overnight. After hydrolyzing the mixture with cold, dil. hydrochloric acid, it was filtered and gave 31.5 g. or a 95.5% yield of tetraphenylethane. The ether layer when dried and distilled in a vacuum gave 0.8 g. of an oil that came over at 148–153° (20 mm.). This was identified as *unsym.*diphenylethane by the preparation of the dinitro derivative according to the method of Anschütz and Romig.[12] A mixed melting point with an authentic specimen of the dinitro compound prepared from *unsym.*-diphenylethane[13] showed no depression.

Benzhydryl Chloride, Carbon Dioxide and Magnesium.—After reaction set in between a small amount of benzhydryl chloride and magnesium in dry ether, carbon dioxide was bubbled over the surface[14] of the ether during the addition of 40 g. of benzhydryl chloride. After the reaction mixture had been worked up in a customary manner, 13.8 g. or 32.5% of diphenylacetic acid was obtained.

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[9] The temperatures recorded in this paper are uncorrected.

[10] Montagne, *Rec. trav. chim.*, **25**, 379 (1907).

[11] Engler and Bethge, *Ber.*, **7**, 1125 (1874).

[12] Anschütz and Romig, *Ann.*, **233**, 340 (1886).

[13] Diphenylmethyl carbinol was prepared according to the method of Klages and Heilmann [*Ber.*, **37**, 1450 (1904)], and the carbinol was reduced by heating with hydriodic acid and glacial acetic acid according to the method of Chichibabin [*Ber.*, **44**, 441 (1911)].

[14] This reaction was carried out according to the optimal conditions for the preparation of *n*-valeric acid determined previously by Gilman and Parker, THIS JOURNAL, **46**, 2816 (1924).

Summary

Benzhydrylmagnesium chloride can be prepared in very low yields by adding benzhydryl chloride to magnesium in ether. It reacts normally with dimethyl sulfate to give *unsym.*diphenylethane.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

ALPHA-NAPHTHYLISOCYANATE AS A REAGENT FOR PHENOLS AND ALIPHATIC AMINES[1]

BY H. E. FRENCH AND A. F. WIRTEL

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This investigation of α-naphthylisocyanate as a reagent for phenols and aliphatic primary and secondary amines is a continuation of a similar study of that substance as a reagent for alcohols.[2]

On the whole, α-naphthylisocyanate proved to be a satisfactory reagent for phenols and aliphatic amines. The procedure used in the preparation of derivatives was very simple. In the cases of the phenols it consisted essentially in heating the two substances together for a few minutes. In the cases of the amines the application of heat was unnecessary, the reaction going at room temperature. The reaction was found to be a general one; of the thirty-two substances tried, only the polyhydroxy phenols failed to react. The derivatives were in all cases found to be easily purified. At the fairly high temperatures used, the α-naphthylisocyanate reacted readily with moisture, so that certain amounts of dinaphthyl-urea were always formed with the urethan. The dinaphthyl-urea, however, is very insoluble in boiling ligroin (b. p., 100–120°) while the urethans are in general, readily soluble so that the separation is easily accomplished. In this respect the α-naphthylisocyanate possesses certain advantages over the analogous phenylisocyanate. In the latter case the separation of the urethan from the diphenyl-urea is sometimes a matter of some difficulty, due to the solubility of the urea in organic solvents. The naphthylurethans crystallized well from ligroin and had sharp melting points. In general, very good yields of the urethans were obtained, so that from three to five drops of the phenol were usually found sufficient for identification purposes.

The reaction is catalyzed by trimethylamine or triethylamine dissolved in dry ether. The catalytic effect of the amine is shown by the following facts. *o*-Nitrophenol, heated repeatedly with α-naphthylisocyanate failed to produce a urethan. When this procedure was followed by the

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[1] This paper is an abstract of a thesis submitted by A. F. Wirtel in partial fulfilment of the requirements for the Professional degree in Chemical Engineering at the University of Missouri.

[2] Bickel with French, THIS JOURNAL, **48,** 747 (1926).