[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATION OF PHENYLMAGNESIUM CHLORIDE IN THE ABSENCE OF A SOLVENT

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Introduction

Phenylmagnesium chloride has been prepared in satisfactory yield by customary procedures in ether as a solvent.[1] However, because of the relative inertness of the chlorine in chlorobenzene, the time (but not the attention) required for an approximately complete reaction is inordinate.

Details are given at this time for the preparation of phenylmagnesium chloride in 85% yields. The reaction is effected by heating chlorobenzene with magnesium in a sealed tube at 150–160° for three hours. The solid, "individual" phenylmagnesium chloride obtained in this manner is soluble in ether or in an ether–benzene mixture, and in such solutions can be employed to carry out the usual reactions of Grignard reagents.

Experimental Part

The technique followed in this preparation is essentially that of Gilman and Brown[2] for the preparation of magnesium diphenyl.

Eleven and two-tenths grams (0.1 mole) of chlorobenzene and 3.6 g. (0.15 atom) of magnesium[3] are placed in a bomb tube which can be prepared from a conventional Carius tube. The tube is evacuated by means of a good water pump until the chlorobenzene boils and then is sealed off. After heating at 150–160° for three hours, the liquid disappears entirely[4] and the tube is about one-half filled with a light brown powder.

Using the technique and operations described for the related preparation of magnesium diphenyl,[2] the contents of the tube were first washed with dry benzene, and then the phenylmagnesium chloride was dissolved in about 100 cc. of a mixture of equal parts of benzene and ether. The solution was filtered in an atmosphere of nitrogen[2] to remove unaltered magnesium, and aliquots were taken for titration.[5] The yield determined in this manner was 85%.

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[1] Gilman and St. John, *Rec. trav. chim.*, **49**, June (1930). Very probably the time required for this preparation might be significantly reduced with the use of higher-boiling solvents.

[2] Gilman and Brown, *ibid.*, **49**, 202 (1930).

[3] The magnesium used in these experiments was of 30–80-mesh. However, it is highly probable that ordinary magnesium turnings will serve equally well. An excess of magnesium is unnecessary, but an excess of chlorobenzene may decompose the RMgX compound at elevated temperatures. This is strikingly illustrated in related experiments on the reaction between alkyl iodides and magnesium in the absence of a solvent.

[4] Heating at a higher temperature appears to be unsatisfactory because of a charring effect. Under our conditions, there appeared to be no reaction when the tube was heated at 140° for four hours.

[5] Gilman, Zoellner and Dickey, THIS JOURNAL, **51**, 1576 (1929). Earlier references to this method for the quantitative estimation of organometallic compounds are to be found in this article.

Discussion of Method

The special procedure used here for a quantitative study is, of course, quite unnecessary in the usual manipulation of such ether-free Grignard reagents. This method of preparation has a number of advantages over the customary procedure. First, it makes it possible to prepare Grignard reagents from the relatively less expensive RCl compounds.[6] Second, the quantity of ether required in subsequent operations can be drastically reduced,[7] or possibly replaced by other less expensive and less inflammable solvents. These two advantages, in particular, are largely of technical importance. For ordinary laboratory operations the best procedure is that involving the use of bromobenzene in ether. Third, the method should lend itself to the synthesis of RMgX compounds having alkyl or aryl groups, otherwise prepared with uncommon difficulty.[8]

The phenylmagnesium chloride prepared in this way is insoluble in benzene, but is soluble in ether or in an ether–benzene mixture. This significant observation should serve to correct numerous early observations on the chemistry of organomagnesium halides. Running through the literature of these compounds is the observation that once the ether has been expelled from the Grignard reagent (in high temperature reactions wherein a large part of the ether is replaced by a higher boiling solvent) it is difficult or impossible to again bring the RMgX compound into solution by means of ether. The insolubility referred to by such writers may be due to secondary reactions between the ether and RMgX and MgX_2 compounds, respectively. This remains to be determined.

We have mentioned that the Grignard reagent prepared in this manner should be brought into some sort of solution or suspension prior to its subsequent reaction with various reagents. This is quite necessary with dry gases, because the solid phenylmagnesium chloride appears not to react with carbon dioxide and gives but a small quantity of phenol in its reaction with oxygen.

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Summary

Directions are given for the satisfactory preparation of phenylmagne-

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[6] By this method it should be possible to obtain improved yields of RMgX compounds from such halides as *p*-bromodimethylaniline. Also, the yield of di-Grignard reagent from *p*-dibromobenzene should be significantly increased see [Gilman, Beaber and Jones, *Rec. trav. chim.*, **48**, 597 (1929)]. It is interesting to note that when fluorobenzene is heated with magnesium at about 300° for many hours, a small quantity of diphenyl is formed. This means unquestionably that phenylmagnesium fluoride was formed as an intermediate compound. It is almost certain that phenylmagnesium fluoride can be prepared in this manner by heating at a lower temperature for a longer time.

[7] Gilman and McCracken, *ibid.*, **46**, 463 (1927).

[8] A case in point is vinyl chloride. See also Ref. 6 of this paper, and Evans and Diepenhorst, This Journal, **48**, 715 (1926).

sium chloride in the absence of solvents. General applications and conclusions from this sealed-tube method of preparation have been discussed.

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OPTICALLY ACTIVE SALTS OF 2-NITRO-OCTANE

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In connection with the general theory of tautomerism the conversion of an optically active secondary nitro compound into salts of the aci-form which are also optically active is of considerable theoretical importance. Only one example is recorded in the literature at the present time, namely, Kuhn's studies on 2-nitrobutane.[1] Since this work represents the only experimental evidence against the classical formulas for the aci-form, it was thought that the preparation and further study of another secondary nitro compound would furnish confirmatory evidence and additional knowledge concerning the tautomerism of these types of compounds.

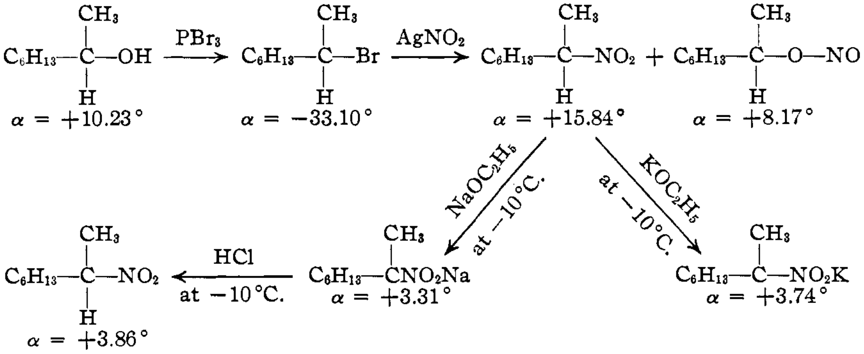
The following schematic diagram shows the preparation of the optically active 2-nitro-octanes and indicates the products obtained from them. It also lists the optical rotations of all the compounds and summarizes the results obtained during this investigation.

The dextro series represents the purer compounds. It is evident that a slight racemization took place during the preparation of the *l*-bromide from the *l*-octanol-2.

The above data fully confirm Kuhn and Albrecht's observation that the sodium salts of optically active secondary nitro compounds are also optically active. That this optical activity is actually due to the sodium salts was proved as follows.

(1) The optical rotation of equivalent amounts of the nitro compound

CHART I. DEXTRO SERIES



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[1] Kuhn and Albrecht, *Ber.*, **60,** 1297 (1927).