in order that equal volumes of the two solutions would completely reduce equal volumes of Fehling's solution.

Summary

Methylation of glucose with methyl sulfate and sodium hydroxide at a temperature of 30° in a solution kept alkaline to brom thymol blue and acid to phenolpthalein resulted in a product which definitely gave a positive response to several common tests for an active or gamma sugar.

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THE PREPARATION OF TRIPHENYLMETHYLMAGNESIUM CHLORIDE

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Introduction

In connection with studies[1] involving triphenylmethylmagnesium chloride, it was necessary to develop a procedure for the preparation of this Grignard reagent in consistently high yields. We have had indifferent success, for some time, in preparing this reagent by methods commonly employed for the preparation of typical RMgX compounds.

The method described at this time gives excellent yields (96% and higher). These yields have been checked by different workers in this Laboratory so that the preparation is not as erratic as formerly. Our acid method of titration was used in determining the optimal factors reported at this time. The method of titration is very probably sound, and the high yields are unquestionably real because carbonation of the triphenylmethylmagnesium chloride has given yields of triphenylacetic acid as high as 91%.[2]

Experimental Part

The general procedure followed was that described recently by Gilman, Zoellner and Dickey[3] for the determination of yields of a variety of Grig-

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[1] (a) Gilman and Jones, THIS JOURNAL, **51**, 2840 (1929); (b) Gilman and Fothergill, *ibid.*, **51**, 3149 (1929).

[2] Unlike some other directions on optimal conditions for the preparation of unusual Grignard reagents reported from this Laboratory [such as allylmagnesium bromide by Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928), and *tert.*-butylmagnesium chloride and *tert.*-amylmagnesium chloride by Gilman and Zoellner, *Rec. trav. chim.*, **47**, 1058 (1928)], considerable work has been done by others on triphenylmethylmagnesium chloride, particularly in connection with free radicals. Among such earlier work are the following important references: Schmidlin, *Ber.*, **39**, 628, 4183 (1906), and Chichibabin, *ibid.*, **40**, 3965 (1907); *ibid.*, **42**, 3469 (1909). These authors have reported unusually high yields of products from triphenylmethylmagnesium chloride.

[3] Gilman, Zoellner and Dickey, THIS JOURNAL, **51**, 1576, 1584 (1929).

nard reagents. Before describing a typical experiment for the preparation of triphenylmethylmagnesium chloride, a short discussion will be given of the effect of some factors on the yield of this Grignard reagent.

The quantities of materials used in our present optimal conditions (in the titration studies) were as follows: 2.79 g. (0.01 mole) of triphenylchloromethane, 0.5 g. (0.021 atom) of magnesium of 80–200 mesh; 0.32 g. (0.025 atom) of iodine, and 40 cc. (0.39 mole) of anhydrous ether. The equivalent molecular (or atomic) ratios of these reactants are 1.0 of triphenylchloromethane, 2.1 of magnesium, 0.25 of iodine and 39.0 of ether.

Halide.—The triphenylchloromethane as finally used was the pure compound obtainable from the Eastman Kodak Company. Despite the fact that some of the samples have a distinct odor of hydrochloric acid, the chloride evidently is of high purity for the present purpose. Samples of the chloride frequently contain two distinct kinds of crystals, white and yellow, each variety melting at 110–112°. Experiments were carried out with samples of each and no essential difference in yield was noted.

Magnesium.—The magnesium was of 80–200 mesh. Ordinary magnesium turnings may be used, but optimal yields (under our conditions) with such magnesium require that 1.5 g. or 6.3 atom equivalents (instead of 2.1 with the 80–200 mesh magnesium) be taken. The yield varies with the quantity of magnesium (80–200 mesh), decreasing with small quantities of magnesium. It should be understood that the reacting ratio of magnesium is greater than one, inasmuch as a part of the 2.1 atom equivalents is used up not only by the triphenylchloromethane but also by the 0.25 equivalent of iodine. Several experiments with 30–80 mesh magnesium showed no essential difference in yield.

Iodine.—The iodine was dried in a desiccator over sulfuric acid and need not, of course, be powdered. The quantity of iodine has a marked effect on the yield. A progressive decrease in yield, under our conditions, was noted when less than 0.25 atom equivalent of iodine was used. Apparently, the yield is not improved by using more than 0.25–0.30 atom equivalent of iodine. The function of the excess magnesium and excess iodine in this preparation is made clear in the preliminary paper by Gilman and Fothergill[1b] on the dissociation of triphenylmethylmagnesium chloride. Actually, when the triphenylmethylmagnesium chloride is prepared by means of this relatively large quantity of iodine, there may be present, at the end of the reaction, some triphenylmethylmagnesium iodide.[4]

Ether.—The ether must be dry. Ether dried over sodium and kept over sodium was found to produce a turbidity in the mere transferal on a *humid* day. On such days the ether was distilled from sodium directly into the special reaction flask[3] for our quantitative studies. This extra refinement is unnecessary for ordinary purposes. The 39 molecular equivalents used in our determinations is unquestionably greater than that required. Ordinarily no more than 6–8 equivalents of ether are needed for the preparation of Grignard reagents.[2,3] This large quantity was used to prevent the triphenylchloromethane from splashing on the sides of the flask and so being removed, in part, from reaction with the magnesium. The large quantity of ether is desirable in effecting reactions of this Grignard reagent because of its sparing solubility in ether.

The benzene used to dissolve the RMgX compound so that aliquots could be removed for titration was dried over sodium. Such solution is unnecessary in the carbonation leading to the preparation of triphenylacetic acid, and the high yields of acid were obtained from the suspension of the RMgX compound in ether. However, the

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[4] Gilman and St. John, *Rec. trav. chim.*, **48** (1929).

benzene–ether solution of triphenylmethylmagnesium chloride may be desirable, if not necessary, for the preparation of other compounds from this Grignard reagent. Also, solution in an ether–benzene mixture may be necessary in separating the Grignard reagent from the excess of magnesium, for special reactions wherein the magnesium is harmful.

Atmosphere.—The experiments were carried out in an atmosphere of pure dry nitrogen. In both of the larger-sized runs from which triphenylacetic acid was prepared and in the smaller analyses the trap of Gilman and Hewlett[5] was found eminently satisfactory and made it possible to dispense with a continuous stream of inert gas.

Preparation of Triphenylmethylmagnesium Chloride.—The 0.01 mole runs were carried out in special flasks of the kind described recently.[3] The 0.02 mole run was carried out in a 200-cc. and the 0.04 mole preparations in a 500-cc. three-necked flask provided with a mercury-sealed stirrer and a spiral water condenser the top of which was attached directly to the trap[5] after the flask was swept out by a stream of dry and oxygen-free nitrogen or hydrogen.

The magnesium, ether and iodine are added to the carefully dried flask, and when all of the iodine has reacted with the magnesium (as indicated by the disappearance of the iodine color)[6] the triphenylchloromethane is added as a solid and at one time. Partial solution is effected, during stirring, by directly heating the flask with a small flame for a few moments. With such heating a spontaneous reaction sets in, and as the halide reacts an insoluble complex forms. The reaction mixture is then refluxed moderately (in our experiments by heating with an electric hot-plate) for three hours.[7]

The following series of color changes occurs under anhydrous conditions during the course of heating. First, the greenish-yellow solution resulting on dissolution of the chloride turns brown about ten or fifteen minutes after the initial heating. Then, after thirty to forty minutes the solution becomes reddish-brown and the mixture contains little if any precipitate. During the next five or ten minutes the quantity of buff or fawn-colored precipitate increases markedly, and in some cases with distinct suddenness. The quantity of precipitate increases up to one and one-half hours of refluxing and then completely fills the solvent.[8] With refluxing beyond one and one-half hours the volume of precipitate frequently decreases somewhat. At the end of the three-hour (total) period of refluxing, the reaction is done,[9] and can be used directly for the prepa-

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[5] Gilman and Hewlett, *Rec. trav. chim.*, **48** (1929). By regulation of the trap it is an easy matter to distil off ether and replace it by benzene (or another solvent) without a continuous flow of inert gas.

[6] Stirring is started at once and the iodine disappears in a few minutes. At this stage, if the reagents and apparatus were dried carefully, the solution has only a very slight turbidity and with special care it is entirely clear. When anhydrous conditions are not present the yield is decreased at least 4–5%.

[7] In the smaller 0.01 runs the time of heating was one and one-half hours plus the twenty to thirty minutes of heating during the removal of ether prior to the addition of benzene to get soluble aliquots for analysis. In either the 0.01, 0.02 or 0.04 mole runs a two-hour period of heating is sufficient to give an excellent yield by titration; however, our best yields of acid (from carbonation of the Grignard reagent) were obtained after a three-hour period of heating. The yield of acid drops about 7% with a one and one-half to two hour period of heating.

[8] It is partly for this reason that the large volume of ether is desirable in order to facilitate completion of reaction. If stirring is interrupted at this stage, the precipitate settles somewhat, revealing a thin upper ethereal layer of a reddish color.

[9] Should it be desirable to remove aliquots for titration or to dissolve the Grignard reagent for a special subsequent reaction, the ether is removed by heating with a hot

ration of triphenylacetic acid and other derivatives, particularly those which form ether-soluble magnesium complexes.[10]

Summary

Conditions have been determined for the preparation of triphenylmethylmagnesium chloride in excellent yields.

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

THE REACTION BETWEEN ALKALI METAL ALKYLS AND QUATERNARY PHOSPHONIUM HALIDES

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The question of whether or not phosphorus ever has a valence of five is still open. It is generally accepted that in the phosphonium salts its valence is four and that the negative ion is held by a polar valence to the phosphonium ion. Lewis[1] believes that phosphorus shares five pairs of electrons with five chlorine atoms in phosphorus pentachloride and has therefore a valence of five. Langmuir[2] has said that the valence of phosphorus in this compound is four and that one chlorine atom is held by a polar valence. Prideaux[3] has presented the idea that three of the chlorine atoms are attached to the phosphorus atom by means of true covalences whereas the remaining two are joined by singlet linkages. Sugden[4] has advanced experimental evidence favoring this view.

Staudinger and Meyer[5] attempted to prepare penta-alkyl phosphorus compounds by the action of zinc ethyl on tetra-ethylphosphonium iodide. However, at low temperatures no reaction was noted and at higher temperatures they obtained triethylphosphine, butane and zinc iodide. The same investigators[6] have prepared the compound $(C_6H_5)_3P{=}C(C_6H_5)_2$, called by them triphenylphosphinediphenylmethylene, in which all of the valences of phosphorus are satisfied by carbon atoms. This compound

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water-bath (60–80°). Then the addition of a volume of benzene in slight excess of that of the ether removed dissolves the reagent. For titration purposes it is merely necessary to make several marks on the reaction flask in order to measure subsequently the total volume of Grignard solution.

[10] Details will appear shortly on some general preparations involving triphenylmethylmagnesium chloride.

[1] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Company, New York, **1923**, p. 102.

[2] Langmuir, THIS JOURNAL, **41**, 919 (1919).

[3] Prideaux, *Chem. Industry*, **42**, 672 (1923).

[4] Sugden, *J. Chem. Soc.*, 1174 (1927).

[5] Staudinger and Meyer, *Helv. Chim. Acta*, **2**, 612 (1919).

[6] Staudinger and Meyer, *ibid.*, **2**, 635 (1919).