XXXVII.—*Different Methods of Applying the Grignard Reagents.*

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IN all those very numerous reactions in which the magnesium alkyl or aryl compounds, discovered by Grignard, are employed for synthetical purposes, the preparation of an ethereal solution of the reagent seems to be generally regarded as a necessary preliminary operation. In most cases this is a very easy task, but the quantity of pure ether required is considerable, and, particularly in the case of some of the aryl halides, the secondary formation of hydrocarbons not only causes loss of material, but often also very great inconvenience in the isolation of the compound which is afterwards prepared.

In synthesising some of the alkyl derivatives of silicon recently described, these disadvantages were overcome entirely, or to a very great extent, by omitting the preliminary preparation of the magnesium compounds. Benzylethylsilicon dichloride, for example, was obtained by gradually adding benzyl chloride to ethylsilicon trichloride in the presence of magnesium and ether (Luff and Kipping, *Trans.*, 1908, **93**, 2006), and the mono-, di-, and tri-benzyl derivatives of silicon tetrachloride were prepared in a similar

manner from benzyl chloride, magnesium, and an ethereal solution of the silicon compound (Martin and Kipping, *Trans.*, 1909, **95**, 306).

In order to ascertain whether this modification of the usual method could be advantageously applied in other cases, a few experiments have been made on the preparation of carbinols from aldehydes, ketones, and esters (Grignard, *Compt. rend.*, 1900, **130**, 1322). The results have shown that in these reactions, also, the preliminary preparation of the magnesium compound is unnecessary, and that a good yield of the desired product is obtained by gradually adding a mixture of the alkyl or aryl halogen compound with the aldehyde, ketone, or ester, to the theoretical quantity of magnesium, which is covered with a little ether. The only instance in which this modified method was found to fail was in the case of acetone; that the process is capable of very general application is shown by the fact that it may serve in the synthesis of compounds, not only of carbon and of silicon, but also of tin.

A direct comparison of the yields obtained by the two methods in a given preparation has not been instituted (except in the case of some silicon compounds, *loc. cit.*), and it may be that sometimes the one, sometimes the other, procedure will give the better results, according to the nature of the interacting substances. It seems, however, that unless such a comparison has been made in a particular case, there is no reason for abandoning the method originally employed by Barbier (*Compt. rend.*, 1899, **128**, 110) in favour of that which is now so generally or universally adopted. In some appropriate instances, in fact, the desired substance may be prepared with the aid of magnesium and the halogen derivative, even when the corresponding Grignard compound cannot be obtained; thus, as Jaworsky has recently shown (*Ber.*, 1909, **42**, 435), many unsaturated alcohols may be prepared by treating ketones with magnesium and allyl bromide or iodide in presence of ether, although magnesium allyl halides of the usual type are unknown.

It need hardly be added that no claim is here made for the discovery of the method which has been studied, but it is hoped that the publication of this note will save time and trouble to many who are working with the Grignard reagents.

EXPERIMENTAL.

In preparing the carbinols by the modified method, the formation of a very small quantity of the Grignard compound was first started in the flask containing the magnesium and anhydrous ether; a mixture consisting of the aldehyde, ketone, or ester with the halogen compound, and diluted with an equal volume of ether, was then

added gradually from a tap funnel, the mixture in the flask being vigorously stirred, and cooled if necessary. The products were isolated in the usual manner.

Most of the experiments concern the use of benzyl chloride, because the preparation of magnesium benzyl chloride is more troublesome than that of the majority of the Grignard reagents.

Phenylethylcarbinol was prepared from benzaldehyde and ethyl bromide. The reaction proceeded without difficulty, and no secondary or decomposition products appeared to be formed; almost the whole of the crude product distilled constantly at 131—132°/50 mm., leaving very little residue; the yield of the carbinol was nearly theoretical. During the distillation the formation of water was not observed, and even when distilled under 750 mm. pressure, the carbinol boiled constantly at 210—211° without decomposing.

Benzylmethylethylcarbinol was prepared from methyl ethyl ketone and benzyl chloride; only small quantities were used, but the yield seemed to be satisfactory. On distillation under 747 mm. pressure, the carbinol decomposed, giving off water, and boiling at 215—225°. It has been described by Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 228).

Triethylcarbinol was obtained from diethyl ketone and ethyl bromide. During the preparation, colourless crystals, doubtless the additive compound, separated on the sides of the flask. The crude product distilled at 130—140°/747 mm. without decomposing, and the yield was at least 60 per cent. of the theoretical. It is described as an oil boiling at 140—142° under atmospheric pressure.

Benzylphenylmethylcarbinol was prepared from magnesium ($1\frac{1}{4}$ atoms), benzyl chloride ($1\frac{1}{4}$ mols.), and acetophenone (1 mol.) in dry ethereal solution. A gentle reaction set in, and continued until all the metal had disappeared. After the ether had been removed, the additive compound was decomposed with water, and the product was distilled under 30 mm. pressure; it did not boil at a constant temperature, but passed over from 170° to 200°, and appeared to be a mixture of the carbinol and the unsaturated hydrocarbon (α -methylstilbene) derived from it. After several redistillations, however, a large proportion of it solidified on being kept for some time, giving the desired carbinol, which was easily obtained in a pure condition by recrystallisation from light petroleum. The compound has been described by Hell (*Ber.*, 1904, **37**, 457).

Benzylethylpropylcarbinol, $C_6H_5 \cdot CH_2 \cdot CEtPr \cdot OH$, was prepared by the interaction of ethyl propyl ketone and benzyl chloride; the yield was only about 60 per cent. of the theoretical, since, besides the carbinol, a rather large proportion of the unsaturated hydro-

carbon, derived from the carbinol by loss of water, was obtained. The carbinol boils at $186^{\circ}/90$ mm., and a sample of the pure compound gave, on analysis, the following results:

0.1824 gave 0.5442 CO_2 and 0.1729 H_2O . $\text{C}=81.3$; $\text{H}=10.5$.

$\text{C}_{13}\text{H}_{20}\text{O}$ requires $\text{C}=81.2$; $\text{H}=10.4$ per cent.

Benzyltrimethylcarbinol could not be obtained by treating magnesium with a mixture of acetone and benzyl chloride, for although acetone reacts vigorously with a prepared solution of a Grignard compound, the presence of the ketone seems to retard or prevent the formation of magnesium benzyl chloride. This preparation was attempted several times, using acetone which had been dried with calcium chloride during several days, and then distilled, and also samples which had been first treated with a small quantity of a solution of the Grignard compound and then decanted; only negative results were obtained. In other experiments the formation of the Grignard compound was first started by the addition of a little benzyl chloride, and then the mixture of acetone and benzyl chloride was added, drop by drop, to the magnesium, but the vigorous action which was in progress soon ceased after a small proportion of the acetone had been added, and could not be made to start again. In a similar manner, the addition of acetone to an ethereal solution of magnesium ethyl bromide, which is reacting vigorously with magnesium, soon brings the interaction to a standstill.

Phenyldibenzylcarbinol was prepared from ethyl benzoate (1 mol.) and benzyl chloride (2 mols.) in presence of magnesium, the reaction proceeding without difficulty. The product was distilled under diminished pressure, and the distillate readily solidified to a hard, pale yellow cake. On recrystallisation from light petroleum, the carbinol was obtained in colourless needles; the yield was 60 per cent. of the theoretical. The compound has been described by Klages (*Ber.*, 1904, **37**, 1456). An attempt was made to prepare phenyl ethyl ketone by adding a mixture of ethyl benzoate (1 mol.) and ethyl bromide (1 mol.) to magnesium, but the product appeared to be a mixture of unchanged ethyl benzoate and phenyldiethylcarbinol.

Dibenzylethylcarbinol, $\text{CEt}(\text{CH}_2\cdot\text{C}_6\text{H}_5)_2\cdot\text{OH}$, was prepared from ethyl propionate and benzyl chloride in presence of magnesium and ether. When the ingredients had been mixed, the solution was heated under a reflux condenser for a short time, the ether was distilled off, and the residue heated at 100° during about two hours. The product was isolated in the usual manner, and the yield was good:

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0.1717 gave 0.5337 CO_2 and 0.1308 H_2O . $\text{C}=84.8$; $\text{H}=8.5$.

$\text{C}_{17}\text{H}_{20}\text{O}$ requires $\text{C}=85.0$; $\text{H}=8.3$ per cent.

Dibenzylethylcarbinol is a colourless, viscous liquid, boiling at $193^\circ/12$ mm. When cooled in a freezing mixture, it becomes very viscous, but does not crystallise, and when boiled under atmospheric pressure it decomposes slowly with elimination of water.

Diethylstannic Chloride, SnEt_2Cl_2 .

Stannic chloride (1 mol.) was treated with ethyl bromide (1 mol.) in presence of magnesium and ether under the usual conditions with the intention of obtaining a mono-alkyl derivative of tin, but a compound of this type seemed not to be formed, or was produced in small quantities only. The principal product was diethylstannic chloride, which has been described by Pfeiffer (*Ber.*, 1902, **35**, 3306), and which was identified by its melting point as well as by analysis.

α -Bromo- $\alpha\alpha$ -dibenzylpropane, $\text{C}_6\text{H}_5\text{CH}(\text{Br})\text{CH}_2\text{C}_6\text{H}_5$.

For a purpose outside the scope of this investigation, experiments were made on the preparation of α -bromo- $\alpha\alpha$ -dibenzylpropane, and on the conversion of this compound into $\gamma\gamma$ -dibenzyl-*n*-hexane; as the former operation is successful only under particular conditions, the results are here recorded. Dibenzylethylcarbinol (15 grams) is dissolved in dry ether (80 c.c.), and phosphorus tribromide (35 grams) is added gradually to the solution; the mixture, which becomes warm, is kept at the ordinary temperature for about twenty-four hours, then boiled under a reflux condenser for about an hour; finally the ether is distilled, and the residue is heated at 100° for about two hours. The product, when cold, is poured on ice, the bromide is extracted with ether, and the extract is washed with sodium carbonate solution, which removes phosphorus compounds. From the crude preparation which is obtained by the evaporation of the ethereal solution, the pure bromide is easily isolated by crystallisation from light petroleum. The yield is at least 85 per cent. of the theoretical.

The combined bromine was estimated by boiling the sample with an alcoholic solution of silver nitrate:

0.2861 gave 0.1765 AgBr . $\text{Br}=26.1$.

$\text{C}_{17}\text{H}_{19}\text{Br}$ requires $\text{Br}=26.4$ per cent.

α -Bromo- $\alpha\alpha$ -dibenzylpropane forms large, colourless prisms, and melts at $58-59^\circ$. It rapidly loses hydrogen bromide when it is heated at about 115° , and it cannot be distilled even under 13 mm. pressure.

Many unsuccessful attempts were made to prepare $\gamma\gamma$ -dibenzyl-*n*-hexane. The bromide was treated with magnesium propyl bromide, and also with propyl bromide and magnesium in presence of ether, but in both cases the qualitative and quantitative analysis of the product showed it to consist principally, if not entirely, of an unsaturated hydrocarbon. An ethereal solution of the bromide was also heated with propyl bromide and sodium, but only the propyl bromide was attacked, and the α -bromo- $\alpha\alpha$ -dibenzylpropane was recovered unchanged.

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