

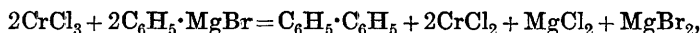
CII.—*The Action of Chromic Chloride on the Grignard Reagent.*

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THE object of this investigation was to obtain organo-metallic derivatives of chromium. With this end in view, the anhydrous chloride, CrCl_3 , was treated with the Grignard reagent, and the product worked up in the usual way. When the anhydrous chloride was added to the ethereal solution of the Grignard reagent, a vigorous reaction took place, but the desired product, an organo-metallic compound of the type CrR_3 (or possibly CrR_2Cl or CrRCl_2) was not isolated. This is, however, in harmony with the fact pointed out by one of us recently (P., 1914, 30, 4) that elements

in even series and in sub-group A of the Periodic Classification are unable to form organo-metallic derivatives.

The reaction first studied, namely, that between chromic chloride and magnesium phenyl bromide, proved to be of considerable interest from another point of view. It was found that diphenyl had been produced in considerable quantity. The only way in which it has been found possible to account for this is to assume that the chromic chloride is reduced to chromous chloride according to the equation:



and experiments in which the chromous salt was estimated (by adding an excess of standard potassium dichromate solution and titrating with ferrous ammonium sulphate solution) show that this explanation is probably correct. The actual weight of diphenyl obtained was larger than that required by the above equation, but it is well known that a certain amount of diphenyl is always produced in the preparation of magnesium phenyl bromide, and it was thought that this fact would account for the excess of diphenyl isolated.

In order to settle this point, and to test whether the chloride had any catalytic effect, two parallel experiments were carried out under exactly similar conditions, equal weights of magnesium phenyl bromide being prepared in each case, to one of which one-third of an equivalent of chromic chloride was added, but to the other none.

The difference between the weights of diphenyl obtained in the two cases corresponded (within the limits of experimental error) with the weight of chromic chloride used, on the basis of the above equation; the latter thus receives additional support, and catalytic action on the part of the chromic chloride is shown to be out of the question.

The reducing action of the Grignard reagent has been observed in several cases, notably in the case of azobenzene, which is reduced to hydrazobenzene (Franzen, *Ber.*, 1905, **38**, 2716).

In view of the extreme simplicity and rapidity of the reaction thus discovered, it was deemed probable that it would be of general practical value. When magnesium benzyl bromide was used instead of the phenyl compound an excellent yield of almost pure *s*-diphenylethane (dibenzyl) was obtained within a few hours of commencing the preparation.

Grignard reagents from α -bromonaphthalene and *p*-iodotoluene similarly gave almost theoretical yields of $\alpha\alpha$ -dinaphthyl and 4:4'-dimethyldiphenyl.

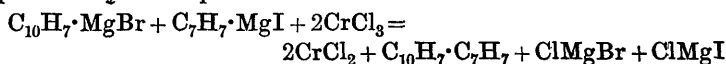
Whilst the expensiveness of the chromic chloride is a drawback,

the extreme simplicity with which it has been possible to obtain good yields of the diphenyl type of hydrocarbon must be taken into consideration. It is indeed doubtful whether by any other method such comparatively pure products are obtainable in a short time.

Among aliphatic compounds, *iso*amyl iodide has alone been made use of, but further experiments will be made in this direction. The yield of di*iso*amyl was unsatisfactory.

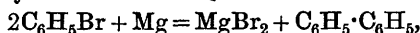
One strange anomaly has been met with which remains totally unexplained. The Grignard reagent prepared from *o*-iodotoluene appeared to react with the chromic chloride in the usual way, but no 2:2'-dimethyldiphenyl could be isolated. Two repetitions of this experiment, using *o*-iodotoluene and *o*-bromotoluene respectively, gave similar negative results.

Finally, an attempt was made to prepare unsymmetrical hydrocarbons by a similar process; for example, Grignard reagents obtained from α -bromonaphthalene and *p*-iodotoluene were mixed and treated with the chloride in the hope that the reaction expressed by the equation:



would occur. No definite evidence was obtained of the production of anything but the two simpler hydrocarbons, dinaphthyl and dimethyldiphenyl; and an attempt to prepare propylbenzene on similar lines was scarcely more successful.

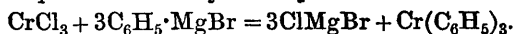
It was thought possible that anhydrous ferric chloride might react in a similar manner with the Grignard reagent. The analogous reaction does not, however, occur in this case, since the diphenyl actually isolated is easily attributable to the reaction:



which always occurs to some extent during the preparation of aromatic Grignard reagents. No organic derivative of iron was isolated, and the reaction products have not been examined further.

EXPERIMENTAL.

Preliminary Experiment.—In this experiment the quantities used were those required to satisfy the equation:



7.2 Grams of magnesium turnings were dissolved in 50 grams of bromobenzene and 200 c.c. of dry ether, and treated with 15 grams of chromic chloride with continual shaking and cooling. After the vigorous reaction had subsided, the mixture was heated on the water-bath for an hour and a-half and left overnight. The

product was decomposed with ice-cold water and dilute acid, extracted repeatedly with ether, and the latter filtered, dried, and evaporated. 14.4 Grams of diphenyl (m. p. 70—71°) were obtained. (Found, C=93.35; H=6.69. Calc., C=93.46; H=6.54 per cent.)

Estimation of Chromous Chloride produced in the Reaction.

In the following experiment all the operations were carried out in an atmosphere of hydrogen, to avoid the oxidation, by atmospheric oxygen, of the chromous chloride produced.

0.97 Gram of magnesium was dissolved in an ethereal solution of 6.9 grams of bromobenzene. 5.25 Grams of chromic chloride were added, and, after the reaction had subsided, the product was treated with water (free from air) and dilute acid, and finally a known excess of standard potassium dichromate solution. The dichromate was then titrated with ferrous ammonium sulphate solution.

CrCl_3 used = 5.25.

CrCl_2 calc. = 4.07. Found: (I) 2.8; (II) 3.4 grams.

Estimation of Diphenyl produced in the Reaction.

Two parallel experiments were performed.

Two equal quantities (5.7 grams) of magnesium were dissolved in two equal quantities (36.6 grams) of bromobenzene. To one of the solutions so obtained 5.3 grams of chromic chloride were added. Both mixtures were then heated under reflux on the water-bath for four hours, and the products worked up.

Experiment 1.—No CrCl_3 added. Benzene found = 14.4; diphenyl found = 5.3 grams.

Experiment 2.— CrCl_3 added. Benzene found = 7.8; diphenyl found = 7.7 grams.

The diphenyl due to the chromic chloride is therefore 2.4 grams, whereas the above equation requires 2.57 grams. The agreement is satisfactory, and it is also evident that no catalysis had occurred.

The details of the following experiments are all precisely similar, and need not be repeated in each case. The Grignard reagent was made up in the usual way, the powdered chromic chloride slowly added, with frequent shaking, and the flask finally heated on the water-bath for from one to two hours. The product was then decomposed with water and dilute acid, and isolated by extraction with ether.

s-Diphenylethane (Dibenzyl), $C_{14}H_{14}$.

5.25 Grams of magnesium, 50 grams of benzyl bromide, and 31.6 grams of chromic chloride gave 28 grams of *s*-diphenylethane, m. p. 52°. (Found, C=92.16; H=7.89. Calc., C=92.25; H=7.75 per cent.)

 $\alpha\alpha$ -Dinaphthyl, $C_{20}H_{14}$.

31.1 Grams of α -bromonaphthalene, 3.69 grams of magnesium, and 24 grams of chromic chloride gave 21.6 grams of crude $\alpha\alpha$ -dinaphthyl, which, on crystallisation, furnished colourless needles, melting at 154°. (Found, C=94.18; H=5.82. Calc., C=94.45; H=5.55 per cent.)

4:4'-Dimethyldiphenyl, $C_{14}H_{14}$.

21.3 Grams of *p*-iodotoluene, 2.2 grams of magnesium, and 14 grams of chromic chloride gave an 80—85 per cent. yield of pure 4:4'-dimethyldiphenyl, melting at 121°. (Found, C=92.18; H=7.89. Calc., C=92.25; H=7.75 per cent.)

For further identification this was converted into 4-methyldiphenyl-4'-carboxylic acid by oxidation with chromic acid. The white solid melted at 235° (uncorr.), whilst Carnelley (T., 1877, 32, 653) gives 245—250° (corr.). (Found [by titration with alkali], M.W.=201. Calc., M.W.=212.)

Diisoamyl, $C_{10}H_{22}$.

50.4 Grams of *isoamyl* iodide, 6.1 grams of magnesium, and 38 grams of chromic chloride gave 4.1 grams of a liquid boiling at 143—160°. On fractionation, 1.3 grams were obtained, boiling at 158—159°.

Attempt to prepare α -p-Tolylnaphthalene.

41.4 Grams of α -bromonaphthalene, 43.6 grams of *p*-iodotoluene, 9.73 grams of magnesium, and 63.2 grams of chromic chloride furnished a liquid which, on fractionation under diminished pressure, gave successively toluene, naphthalene, 4:4'-dimethyldiphenyl, and $\alpha\alpha$ -dinaphthyl. α -*p*-Tolylnaphthalene could not be identified.

n-Propylbenzene, C_9H_{12} .

47.5 Grams of bromobenzene, 19 grams of propyl bromide, 7.4 grams of magnesium, and 47.4 grams of chromic chloride gave 0.5 gram of a liquid boiling at 158—159° (*n*-propylbenzene boils at 158.5°), in addition to much diphenyl, hexane, and benzene.

Use of Ferric Chloride.

8.1 Grams of ferric chloride, 3.2 grams of magnesium, and 23.8 grams of bromobenzene (that is, three equivalents of the Grignard reagent) gave a brown liquid, which was shaken with benzene to precipitate ferric chloride, the benzene being evaporated and the residue distilled in a current of steam. 3.4 Grams of diphenyl were obtained in this way. The residue was dissolved in benzene, and repeatedly washed with water to remove ferric chloride; the solution was dried and evaporated, leaving 2.4 grams of a resinous solid, which has not yet been identified, but contains no organo-compound of iron.

In conclusion, we wish to express our thanks to Prof. J. T. Hewitt, F.R.S., for his interest in this work, and to the Research Fund Committee of East London College for defraying the cost of some of the materials used in this investigation.

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