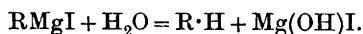


VII.—*The Direct Interaction of Aryl Halides and Magnesium.*

By JAMES FREDERICK SPENCER AND ELEANOR MARGUERITE STOKES.

IN the course of a series of reactions involving the use of the Grignard reagent, we obtained evidence which led us to doubt the necessity of the presence of ether or any catalyst in the preparation of magnesium aryl halogen compounds. Preliminary experiments showed that aryl iodides and magnesium react, on heating, with the formation of magnesium aryl iodides, which in view of the subsequent action of water must be constituted according to the type $R \cdot Mg \cdot I$.

The reaction took place with the evolution of a large amount of heat, and was generally complete in two to three minutes; on the addition of water, after cooling, the parent hydrocarbon was regenerated with the evolution of heat:



The ease with which the combination occurred indicated that this was possibly a reaction suitable for removing halogens from cyclic compounds, and so capable of being used as a means of orientation in the case of substituted compounds.

With the object of testing the suitability of the reaction for such determinations, we have studied the action of magnesium with a number of aromatic halogen substitution products, and have found that it is possible to remove iodine and bromine from such compounds almost quantitatively, and to obtain a large yield of the parent substance as product of the reaction.

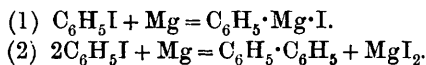
Thus *m*-bromoaniline gave a yield of 90 per cent. of the theoretical quantity of aniline, and *p*-bromophenol gave 40—50 per cent. of the theoretical yield of phenol.

Halogen acids and nitro-compounds containing halogens did not yield the corresponding acids and nitro-hydrocarbons. In the case of the acids, carbon dioxide was evolved, and with the nitro-compounds, nitrogen peroxide was evolved, which immediately reacted with the magnesium, giving rise to so much heat that the compound was completely charred, and, indeed, in one experiment the test-tube melted.

Halogen derivatives of naphthalene react in the same way with magnesium, α -bromonaphthalene yielding 70—80 per cent. of naphthalene.

Similarly, monobromoacenaphthene gave a yield of about 50 per cent. of the theoretical quantity of acenaphthene when treated in the same way.

This reaction does not seem to be general for chloro-substitution products; out of six substances investigated, namely, benzylidene chloride, *o*- and *p*-chlorophenol, α -chloronaphthalene, *p*-chlorotoluene, and *o*-chloroaniline, a reaction was found to take place only in the case of *o*-chloroaniline; in this instance, a large yield of aniline was obtained. Iodobenzene and bromobenzene require special note, for with these compounds it was found that the initial reaction proceeded in two directions, as indicated by the equations :



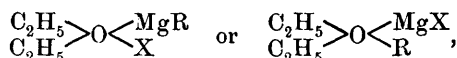
The products, benzene and diphenyl, were present in quantities which indicated that the reaction represented by (1) had taken place with about 45 per cent. of the iodobenzene, and the reaction represented by equation (2) with about 55 per cent. of the iodobenzene. The formation of diphenyl was observed by Tissier and Grignard (*Compt. rend.*, 1901, 132, 32) when carrying out the Grignard reaction under ordinary conditions.

We have done little up to the present with aliphatic compounds, but preliminary experiments have shown that methyl iodide, methylene iodide, trimethylene iodide, and *isopropyl* iodide do not react at all with magnesium when the two substances are heated together. Monobromosuccinic acid, however, does react, and the action commences without initial heating after the substances have been mixed for about two minutes. The product on treatment with water yields succinic acid.

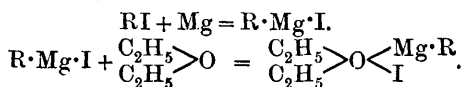
On treating the magnesium aryl compounds with water, we obtained derivatives which may be used for deciding the position of

substituting groups; they can, however, also be used for purposes of synthesis. For example, magnesium phenyl iodide, prepared by the method indicated, was ground in a mortar with a little absolute ether and an excess of solid carbon dioxide for about five minutes, the product of this treatment yielded about half the theoretical quantity of benzoic acid on the addition of dilute hydrochloric acid. In the absence of ether, the yield of benzoic acid was much reduced.

This reaction, effected without the use of a catalyst, indicates that ether is not absolutely necessary for the reaction, and the Grignard compounds are not necessarily formed through oxonium compounds of the type:



but rather, the view put forward by Tschelinzeff (*Ber.*, 1905, 38, 3664) is the more correct one, namely, that the addition occurs first between the iodide and the magnesium, and this then forms an addition compound with ether:



EXPERIMENTAL.

Interaction of Iodobenzene and Magnesium.—Dry iodobenzene (40 grams) was mixed with dry magnesium powder (9 grams) in a small, hard, round-bottomed flask fitted with an air condenser. The mixture was carefully warmed over a free flame to the boiling point of the iodobenzene; after boiling for about a minute, the reaction commenced, and proceeded without any additional heating. The product was a light grey, homogeneous mass, which was slowly decomposed by the moisture of the air, forming benzene. When the mass had cooled, cold water was slowly added to it; this brought about a decomposition which was accompanied by the evolution of heat. As soon as the decomposition was complete, the products were distilled with steam, when benzene, diphenyl, and unchanged iodobenzene were found in the distillate. The yield of benzene was 44 per cent., and of diphenyl 54 per cent., of that required by theory.

The melting point of the diphenyl (70°) was unchanged after mixture with an equal weight of pure diphenyl.

Interaction of Bromobenzene and Magnesium.—In this case, the reaction did not occur at all readily, it being necessary to boil the mixture of bromobenzene and magnesium for about fifteen minutes before combination took place. The organic products and yields were the same as in the case of iodobenzene.

Interaction of p-Iodotoluene and Magnesium.—*p*-Iodotoluene (15 grams) and magnesium powder (2 grams) were mixed and gently warmed in a hard glass flask fitted with an air condenser. As soon as the boiling point of the iodotoluene was reached, the reaction also commenced, and proceeded without further heating; it was, however, not as violent as with iodobenzene. The product was a light grey mass, which was treated with water and distilled in steam. The distillate was extracted, dried, and fractionated, and shown to consist of toluene. The yield was 87 per cent., and a small quantity of unchanged *p*-iodotoluene was also recovered.

Interaction of o-Bromotoluene and Magnesium.—The interaction of these two substances took place in exactly the same way as in the case of *p*-iodotoluene. The product was the same, and the yield was equally good.

Interaction of m-Bromoaniline and Magnesium.—Dry *m*-bromoaniline (15 grams) was mixed with magnesium powder (4 grams) and heated in the same way as the foregoing mixtures; after two minutes, a most violent reaction took place. A yellow, solid mass was obtained, which reacted so violently with water that the liquid boiled. The whole mass was then distilled in steam, and the oil which passed over was extracted and fractionated. A yield of 90 per cent. of aniline was obtained.

Interaction of o-Chloroaniline and Magnesium.—This reaction took place extremely readily when heat was employed, and a good yield of aniline was produced.

Interaction of p-Bromophenol and Magnesium.—*p*-Bromophenol (8 grams) was mixed with magnesium powder (2 grams) and heated, the reaction commencing suddenly after about two to three minutes' heating. The product, a light grey, solid mass, was treated with water and distilled in steam, when a yield of 40 to 50 per cent. of phenol was obtained.

When tribromophenol was substituted for phenol, the reaction took place with extreme violence and evolution of heat, causing the tube to soften. The products contained less bromine than the original tribromophenol, for on the addition of bromine water to the solution a yellowish-white precipitate of tribromophenol was formed, but further identification was impossible, nor could the vigour of the reaction be lessened.

Interaction of α -Bromonaphthalene and Magnesium.— α -Bromonaphthalene (20 grams), mixed with magnesium powder (4 grams), was heated to boiling point, when a vigorous reaction commenced, which completed itself without any further heating. The product was a white and apparently crystalline mass. When cold, the addition of water was attended by great evolution of heat, and the presence of

naphthalene was at once evident from its odour. The mass was then distilled in steam, when a 72 per cent. yield of naphthalene was obtained. The yield was improved by the use of excess of magnesium; thus, whilst one atomic proportion of magnesium furnished a yield of 44 per cent. of the theoretical, from three times the quantity a yield of 72 per cent was obtained. The change in the yield is due to the smaller amount of the bromo-compound escaping reaction.

Interaction of Bromoacenaphthene and Magnesium.—About 1 gram of bromoacenaphthene was mixed with excess of magnesium powder and heated over the free flame. The reaction did not commence for about five minutes, and then proceeded quietly. Water was then added to the product, but action took place only on warming. This was in all probability due to the fact that the magnesium acenaphthyl bromide was protected from its action by being coated with unchanged bromoacenaphthene. The products after treatment with water were extracted with alcohol, and the acenaphthene formed crystallised out in good yield.

The investigation of this reaction is being continued.

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