

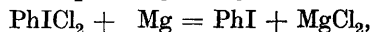
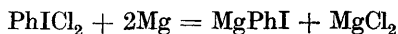
CXXXIX.—*The Action of the Grignard Reagent on certain Tervalent Organo-iodo-compounds.*

By HARRY HEPWORTH.

LACHMANN (*Ber.*, 1897, **30**, 887) studied the action of zinc ethyl on iodobenzene dichloride, doubtless in the hope of isolating a mixed aliphatic aromatic iodonium compound. The reaction was very vigorous, but no iodonium compound was produced.

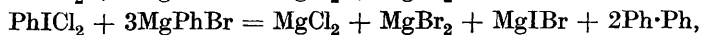
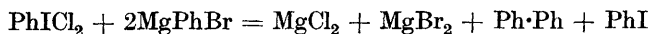
Willgerodt (*Ber.*, 1897, **30**, 56; 1898, **31**, 915) investigated the action of mercury phenyl and mercuric phenyl chloride on iodo-chlorides, both in the presence and the absence of water. Three compounds were formed, diphenyliodonium chloride, mercuric phenyl chloride and a double compound of diphenyliodonium chloride with mercuric chloride. Mercury ethyl was substituted for mercury diphenyl in the hope of obtaining a phenylethyl-iodonium chloride, but this aspiration was not realised, the products of reaction being ethyl chloride, iodobenzene, and either mercuric ethyl chloride or mercuric chloride.

In the experiments described in this paper the action of magnesium, magnesium ethyl bromide, and magnesium phenyl bromide on iodobenzene dichloride, iodosobenzene, iodoxybenzene, and the corresponding toluene compounds is described. In the first instance, the action of magnesium powder on iodobenzene dichloride and *p*-iodotoluene dichloride was investigated. The addition of a crystal of iodine to the ethereal suspension of the dichloride, and a little magnesium powder catalyses the reaction, which proceeds vigorously, the products being magnesium chloride, benzene or toluene, iodobenzene or *p*-iodotoluene, and a little diphenyl. The reaction is best represented as follows :

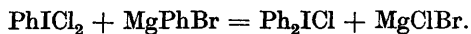


both reactions taking place concurrently.

Iodobenzene and diphenyl are the principal products of the reaction between magnesium phenyl bromide and iodobenzene dichloride, whilst diphenyliodonium chloride is formed in small quantities. The principal reaction is represented by the equation :

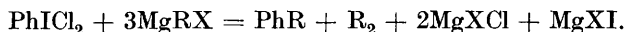


and to a smaller extent :



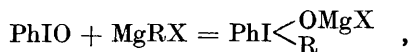
Similar compounds were obtained by the action of magnesium phenyl bromide on *p*-iodotoluene dichloride.

Magnesium alkyl haloids and iodobenzene dichloride gave the corresponding paraffin hydrocarbons and alkyl derivatives of benzene. No iodonium bases were formed in these reactions.



Corresponding compounds were obtained from *p*-iodotoluene dichloride.

The reaction between Grignard compounds and iodoso-compounds in suspension in ether and toluene is very slow. Magnesium ethyl bromide and iodobenzene gave iodobenzene only, whilst magnesium phenyl bromide gave iodobenzene and a little diphenyl-iodonium hydroxide. The normal reaction,



only takes place even partly in the case of magnesium phenyl bromide. Magnesium alkyl haloids reduce iodoso-compounds to iodo-compounds.

In contrast with the iodoso-compounds, the iodoxy-compounds react readily with organo-magnesium compounds, but in all cases the latter act as reducing agents, the original iodo-compounds being regenerated and no iodonium bases being formed.

It will thus be seen that whilst small quantities of diphenyl-iodonium and phenyl-*p*-tolyl-iodonium bases may be obtained by the action of magnesium phenyl bromide on the corresponding iodo-dichlorides and iodoso-compounds, no indications of mixed aliphatic aromatic iodonium bases have been obtained by the action of magnesium alkyl haloids on the same compounds, and that these organo-metallic compounds simply function as reducing agents to iodoso- and iodoxy-compounds.

In view of the fact that the chlorine atoms in iodo-dichlorides are ionisable and readily removed, it is suggested that the formula (R.I.).....Cl₂ represents their behaviour better than the older formula.

EXPERIMENTAL.

Action of Magnesium Powder on Iodobenzene Dichloride and p-Iodotoluene Dichloride.

Iodobenzene dichloride was prepared by leading a current of dry chlorine into an ice-cold solution of iodobenzene in dry chloroform according to the method of Willgerodt (*J. pr. Chem.*, 1886, [ii], **33**, 154), whilst *p*-iodotoluene dichloride was prepared in a similar manner from *p*-iodotoluene. Willgerodt (*Ber.*, 1893, **26**,

357) states that *p*-iodotoluene dichloride deposited from a chloroform solution melts at 85°, but the compound obtained by the author melted at 104—105°. This is in close agreement with the melting point obtained by Ortoleva (*Gior. Soc. Sci. Nat. Econ.*, 1900, 23), who found that *p*-iodotoluene dichloride melted at 105—106° independent of the solvent from which it was crystallised.

A preliminary experiment showed that iodobenzene dichloride and *p*-iodotoluene dichloride only underwent very slight decomposition when heated in ethereal suspension for several hours.

On adding a trace of magnesium powder to an ethereal suspension of 5 grams of *p*-iodotoluene dichloride in 30 c.c. of dry ether, and heating on a water-bath, no evident reaction took place. The mixture was allowed to cool and a minute crystal of iodine added, when reaction proceeded in the cold and the ether ultimately boiled. Magnesium powder (1.25 grams) was added in small quantities from time to time and the mixture was stirred continuously. After about two hours, when about half the magnesium had been added, the reaction became very feeble, and the mixture was warmed on a water-bath. The rest of the magnesium was added during the course of an hour and the heating continued; at the end of five hours, a little unchanged magnesium was still present. The mixture was allowed to settle, the clear superincumbent ethereal solution filtered through dry asbestos, and the residue washed four times with 20 c.c. of dry ether. On adding water to the residue, there was a slight momentary reaction, thus showing that a little magnesium *p*-tolyl iodide was still present. The aqueous solution was filtered and found to contain 1.3 grams of magnesium chloride.

The ethereal solution was decomposed with water, when a vigorous reaction ensued. The ethereal layer was separated and the aqueous portion extracted twice with ether. After drying and distillation of the ether, 1.1 grams of toluene (b. p. 109—110°) and 1.2 grams of *p*-iodotoluene (m. p. 35°; b. p. 210—212°) were obtained by fractionation. The *p*-iodotoluene was separated from traces of *pp'*-ditolyl by crystallisation from alcohol.

In a similar experiment with 5.5 grams of iodobenzene dichloride and 1.3 grams of magnesium powder, 1.2 grams of magnesium chloride, 1.1 grams of iodobenzene (b. p. 187—189°), and traces of benzene and diphenyl were obtained.

Action of Magnesium Ethyl Bromide and Magnesium Phenyl Bromide on Iodobenzene Dichloride and p-Iodotoluene Dichloride.

A preliminary experiment showed that magnesium methyl iodide reacted vigorously with iodobenzene dichloride with the evolution

of a gas. In an experiment in which excess of magnesium methyl iodide in anisole solution was added to 0.1 gram of iodobenzene dichloride in 10 c.c. of anisole, 7 c.c. of ethane were collected over dry mercury.

Iodobenzene dichloride (5.5 grams) was added, a little at a time, to a solution of magnesium ethyl bromide prepared from 0.8 gram of magnesium, 3.4 grams of ethyl bromide, and 50 c.c. of dry ether. A vigorous reaction ensued, the mixture became homogeneous and the ether boiled, but after the addition of about 3 grams of the iodo-chloride very little further reaction took place. After an hour much magnesium chloride had separated. The mixture was kept overnight and then cautiously decomposed with ice-cold water. After extraction, removal of the ether, and repeated fractionation, 0.9 gram of ethylbenzene (b. p. 134—136°) and 1.2 grams of iodobenzene (b. p. 187—189°) were obtained. The identity of the product, b. p. 134—136°, with ethylbenzene was further established by its oxidation with permanganate to benzoic acid. No iodonium base was found in the aqueous solution after decomposition of the product with water, and it is evident that insufficient magnesium ethyl bromide had been employed to react with the whole of the iodobenzene dichloride.

In a second experiment in which 2.5 mols. of magnesium ethyl bromide were employed, the sole products of reaction were ethylbenzene and a little iodobenzene.

Experiments were carried out in which magnesium and ethyl bromide were added from time to time to a well-stirred emulsion of iodobenzene dichloride and ether cooled in ice, but again no iodonium base was formed, the principal product being ethylbenzene. With 3.5 mols. of magnesium ethyl bromide, ethylbenzene was almost the sole product of reaction.

In similar experiments with *p*-iodotoluene dichloride and magnesium ethyl bromide, *p*-ethyltoluene and *p*-iodotoluene were the principal products, whilst a gas, probably butane, was given off. The aqueous solution obtained on decomposing the preliminary products with water contained no organic matter.

With magnesium phenyl bromide and iodobenzene dichloride, diphenyl (m. p. 70.5°; b. p. 254°) and iodobenzene (b. p. 188°) were formed, whilst the filtered aqueous solution obtained after decomposing the product of reaction with water gave only a little diphenyliodonium iodide on the addition of an aqueous solution of potassium iodide.

Similar results were obtained with magnesium phenyl bromide and *p*-iodotoluene dichloride. A small quantity of phenyl-*p*-tolyl-iodonium iodide was obtained on treating the aqueous solution,

obtained on decomposing the product with water, with an aqueous solution of potassium iodide.

Action of Magnesium Ethyl Bromide and Magnesium Phenyl Bromide on Iodobenzene and p-Iodosotoluene.

Iodobenzene and *p*-iodosotoluene were obtained by the action of an aqueous solution of sodium hydroxide on the corresponding iodo-dichlorides, as described by Willgerodt (*Ber.*, 1892, **25**, 3494).

Four and a half grams of iodobenzene were added to an ethereal solution of magnesium ethyl bromide prepared from 0.8 gram (1.5 mols.) of magnesium, 3.6 grams of ethyl bromide, and 30 c.c. of dry ether. There was no evident reaction in the cold and the iodobenzene did not go into solution. After heating on the water-bath for three hours, the bulk of the iodobenzene still remained undissolved. The greater part of the ether was evaporated and 50 c.c. of toluene, which had been dried over sodium and distilled over phosphoric oxide, were added. The flask was now heated on a sand-bath for two days, when rather less than half of the iodobenzene reacted. On decomposing the mixture with water, a vigorous reaction ensued. The contents of the flask were extracted four times with ether, and after removal of the ether about 1 gram of iodobenzene (b. p. 186—189°) was obtained. The aqueous portion containing iodobenzene and magnesium hydroxide in suspension was filtered, but the clear filtrate contained no iodonium base. The residue contained no organic matter other than iodobenzene.

In a similar experiment in which 4.5 grams of iodobenzene, 0.8 gram (1.5 mols.) of magnesium and 5 grams of bromobenzene were used, 1.5 grams of iodobenzene and 3 grams of diphenyl were obtained, whilst a little diphenyliodonium iodide was obtained by treating the aqueous solution obtained on decomposing the reaction product with water, with an aqueous solution of potassium iodide.

Similar results were obtained on treating *p*-iodosotoluene with magnesium ethyl bromide. With magnesium phenyl bromide, a small quantity of phenyl-*p*-tolyliodonium iodide was obtained.

Action of Magnesium Ethyl Bromide and Magnesium Phenyl Bromide on Iodoxybenzene and p-Iodoxytoluene.

Iodoxybenzene and *p*-iodoxytoluene were prepared from the corresponding iodoso-compounds by distillation in steam in the usual manner.

p-Iodoxytoluene (2.25 grams) was added a little at a time to a solution of magnesium ethyl bromide prepared from 1.5 grams (3 mols.) of magnesium, 6.5 grams of ethyl bromide, and 30 c.c of dry ether, the whole being kept at room temperature. A vigorous reaction ensued, and on warming on the water-bath for half an hour almost the whole of the iodoxybenzene went into solution. The flask was kept overnight at room temperature, when an oil was observed at the bottom of the flask. The product was decomposed by ice-cold water and extracted three times with ether. After drying and removing the ether, 1.8 grams of iodobenzene (b. p. 186—188°) were obtained. The aqueous solution contained no iodonium base and the residue insoluble in water contained no organic matter.

Magnesium phenyl bromide reacted with iodoxybenzene much less readily, and after warming for eight hours on the water-bath, a little unchanged iodoxybenzene still remained. The sole products of reaction were diphenyl and iodobenzene and no iodonium base was present in the aqueous solution.

Similar results were obtained by the action of magnesium ethyl bromide and of magnesium phenyl bromide on *p*-iodoxytoluene.

The author is indebted to the Research Committee of Messrs. Nobel's Explosives Co., and particularly to Mr. Rintoul, for the facilities accorded him in carrying out this investigation.

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[Received, May 13th, 1921.]
