the greatest external surface and, therefore, capable of the greatest anabolic activity and evaporation, while the large proportion remaining in the cotyledons points to the activity of this part of the mineral matter in promoting the catabolic change occurring therein.

The use of paraffined paper cups has proved very satisfactory for growing seedlings under exclusion of extraneous mineral matter and the method developed seems well suited for the further investigation of this subject.

We hope from this experiment and others in progress to throw further light on the physiology of germination and the nutrition of the embryos of plants and since these figures show that the fixation of carbon was considerably less than the loss apparently caused by oxidation it would be of interest to determine the means whereby they would be made to function normally as carbon fixers.[1]

LEXINGTON, KENTUCKY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE PRESIDENCY COLLEGE AND THE UNIVERSITY COLLEGE OF SCIENCE.]

HALOGENATION. XVII. THE ACTION OF HALOGENS ON THE GRIGNARD REAGENT AND THE REPLACEMENT OF HALOGEN ATOMS BY ONE ANOTHER.

BY RASIK LAL DATTA AND HARAPARBUTTY KUMAR MITTER.

Received December 2, 1918.

The action of halogens on the Grignard reagent has not been much studied. Grignard and Courtot[2] investigated the action of bromine and iodine on α-indenyl magnesium bromide with the formation of α,β,γ-tribromoindane and α,α-diindenyl, respectively, among other minor products. The action of cyanogen haloids on the Grignard reagent has been studied by Grignard and Courtot[3] and also by Grignard, Bellet and Courtot.[4] It has been shown by them that with cyanogen chloride, the nitrite is the chief product, while with cyanogen bromide and iodide mainly the corresponding halogen derivatives are formed. This has led Grignard to conclude that the cyanogen bromide and iodide act in the carbylamine form.

It has been found as a general reaction that one halogen is able to displace the other halogens from the Grignard reagent with the production of the corresponding haloid derivatives. The yield of haloid derivatives is much influenced by the nature of the halogen and also by the conditions of the experiment. These reactions are sometimes accompanied by secondary reactions due to the union of the Grignard residues.

When iodine is added to magnesium phenyl bromide, there are obtained

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[1] Acknowledgment is due Dr. A. M. Peter of this Station for this interpretation of these figures for the loss in weight of the air-dried material.

[2] *Compt. rend.*, 154, 361 (1912).

[3] *Bull. soc. chim.*, 17, 228 (1915).

[4] *Ann. chim.*, [9] 4, 28 (1915).

phenyl iodide in 25 to 30% yield, benzene in 30 to 40% yield and also a small quantity of diphenyl, but if magnesium phenyl bromide is added to an ethereal solution of iodine, phenyl iodide is formed in 90% yield. By the action of iodine on magnesium phenyl iodide, phenyl iodide, benzene and diphenyl are formed. In this case the yield of phenyl iodide and benzene is quite small, the main product being diphenyl. By the action of iodine on magnesium-*o*-bromotoluene, *o*-iodotoluene is obtained in 80% yield. From *m*-bromotoluene, *m*-iodotoluene is obtained in 76% yield besides a little unchanged *m*-bromotoluene. From *p*-bromotoluene, besides a little unchanged substance, *p*-iodotoluene is obtained in 74% yield. By the action of iodine on magnesium ethyl iodide, a low yield of ethyl iodide is obtained.

In a similar manner, by the action of bromine on magnesium phenyl iodide, benzene and bromobenzene are the main products, the yield of the latter being 30 to 40%. A small quantity of diphenyl is also formed. From magnesium phenyl bromide, phenyl bromide is obtained in 30 to 40% yield. By the action of bromine on magnesium ethyl iodide is obtained. From *n*-propyl iodide, propyl bromide has been obtained in 30 to 40% yield.

By the action of chlorine on magnesium phenyl bromide, a product is obtained which explodes with great violence; with magnesium phenyl iodode, a small yield of phenyl chloride is obtained. From *p*-bromotoluene, *p*-chlorotoluene is obtained in 20% yield.

EXPERIMENTAL.

Action of Iodine on Magnesium Phenyl Bromide.

When solid iodine is added to magnesium phenyl bromide, there is formed phenyl iodide in 25 to 30% yield and 30 to 40% of benzene is also formed. Some phenyl bromide is also obtained due to some unchanged phenyl bromide in the reagent. But if the Grignard reagent is added to an ethereal solution of iodine phenyl iodide is formed in 90% yield.

Magnesium phenyl bromide was prepared by adding 52.3 cc. of phenyl bromide mixed with 53 cc. of ether to 12 g. of magnesium. The reaction was not allowed to become too vigorous and the magnesium was made to dissolve as completely as possible with the gradual addition of 260 cc. of ether. Powdered iodine was gradually added in a reflux apparatus when it dissolved in the reagent with much vigor and with the disappearance of color. The total quantity of iodine taken up in this way amounted to 57 g. The reaction was allowed to take place in the cold and when it had subsided, ice-water was added drop by drop, whereupon a vigorous reaction took place with the appearance of a white, flocculent precipitate of magnesium hydroxide. When there was no further reaction with water, dil. hydrochloric acid was added until the precipitate of magnesium hydroxide dissolved. The ethereal layer was separated and distilled.

When nearly the whole of the ether had distilled over, the residual liquid was dehydrated over calcium chloride and redistilled. 20 cc. of liquid boiling between 75 and 90° was collected, 10 cc. boiling between 140 and 165°, and 18 cc. boiling between 165 and 193°. At the end the liquid in the distilling flask charred, and a small amount of high boiling liquid came over which at once solidified. This on recrystallization from hot benzene was found to melt at 70° and was identified as diphenyl. The separate fractions were purified by fractionation and 25 to 30% phenyl iodide, 10 to 20% phenyl bromide due to unchanged phenyl bromide in the reagent, and 30 to 40% of benzene were obtained.

When magnesium phenyl bromide was added to an ethereal solution of iodine, phenyl iodide was formed in 90% yield. The ethereal solution of the Grignard reagent obtained from 9 g. of magnesium and 39.4 cc. of phenyl bromide was added drop by drop to 64 g. of iodine dissolved in a fairly large quantity of ether. During the addition of the first portions of the reagent there was no noticeable change, but with the addition of more, some portions of the iodine solution gradually became colorless with the separation of a heavy layer of thick, black oil. On constant shaking the black oil dissolved. When nearly the whole of the magnesium phenyl bromide had been added, the color of the iodine solution was discharged. Ice-water was then added to the colorless solution when a vigorous reaction set in and the liquid became cloudy. Dil. hydrochloric acid was then added in small quantities at a time until the cloudiness disappeared. The upper ethereal layer gave an oil which when washed, dried and distilled yielded 5 cc. of benzene, 5 cc. of phenyl bromide due to unchanged phenyl bromide in the magnesium phenyl bromide, and 24 cc. of phenyl iodide. Allowing for the unchanged phenyl bromide, the yield o phenyl iodide was 90%.

Action of Iodine on Magnesium Phenyl Iodide.

Phenyl iodide was prepared according to the method of Datta and Chatterjee[1] by the action of iodine on benzene in the presence of nitric acid. Magnesium phenyl iodide was prepared from 6 g. of magnesium and 20.4 cc. of phenyl iodide exactly as before. The only peculiarity in preparing this reagent is that the reaction between phenyl iodide and metallic magnesium takes place quite readily, and hence special care must be taken to prevent too violent a reaction. Powdered iodine was added through the top of a reflux condenser in very small quantities at a time. About 45 g. of iodine was taken up by the reagent and the product on subsequent hydrolysis with water and then with dil. hydrochloric acid, yielded an oil which on fractional distillation gave 10 cc. of benzene, 3 cc. of phenyl iodide, and a high boiling solid residue which on crystallization from boiling benzene was found to melt at 70° and was

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[1] THIS JOURNAL, 39, 437 (1917).

identified as diphenyl. Here the main product of the reaction was diphenyl.

Action of Iodine on Magnesium *o*-Bromotoluene.

o-Bromotoluene was prepared from *o*-toluidine through the diazonium reaction, and the purified liquid boiling between 175 and 185° was used for the preparation of the reagent. Magnesium *o*-bromotoluene was prepared by the usual method from 9 g. of magnesium and 45.7 cc. of *o*-bromotoluene. A solution of 74 g. of iodine in ether was prepared and the reagent was gradually added to it. The colorless product was hydrolyzed by means of ice-water and the ethereal layer was separated and distilled on a water-bath. The residue on drying was distilled, and 8 g. of *o*-bromotoluene and 52 g. of *o*-iodotoluene were obtained; the yield of *o*-iodotoluene amounted to 80% of the theory.

Action of Iodine on Magnesium *m*-Bromotoluene.

m-Bromotoluene was prepared from *m*-toluidine by the diazonium reaction. Magnesium *m*-bromotoluene was prepared by the usual method from 9 g. of magnesium and 45.7 cc. of *m*-bromotoluene. A solution of 76.6 g. of iodine in ether was prepared and the Grignard reagent was added gradually to the iodine solution discharging the color. The product was hydrolyzed with ice-water as before, and, after removal of the ether, was subjected to fractional distillation. 9 g. of unchanged *m*-bromotoluene and 50 g. of *m*-iodotoluene were obtained. The formation of *m*-iodotoluene took place in this case with 76% yield.

Action of Iodine on Magnesium *p*-Bromotoluene.

p-Bromotoluene was prepared from *p*-toluidine by the diazonium reaction. The reagent which was prepared from 12 g. of magnesium and 61 cc. of *p*-bromotoluene, was made up to 200 cc., and gradually added to 93 g. of iodine dissolved in a large volume of ether, discharging its color. The product was next hydrolyzed with ice-water, and the resulting oil in the ethereal layer subjected to distillation, whereupon 20 cc. *p*-bromotoluene was obtained together with 48 g. of *p*-iodotoluene, corresponding to a yield of 74%.

Action of Iodine on Magnesium Ethyl Bromide.

Magnesium ethyl bromide was prepared from 6 g. of magnesium and 18.7 cc. of ethyl bromide. Iodine was gradually added to the reagent till no more was used up, 48 g. being required. The product was hydrolyzed by means of ice-water, and subjected to fractional distillation. As the differences in the boiling points of ether, ethyl bromide and ethyl iodide are not very great, a perfect separation could not be achieved, and hence only the low yield of 20% ethyl iodide was obtained, although in reality a much greater quantity was formed which distilled over as a mixture with ethyl bromide.

Action of Bromine on Magnesium Phenyl Iodide.

By the action of bromine on magnesium phenyl iodide, benzene was formed in 35 to 45% yield together with bromobenzene in 30 to 40% yield. A very small quantity of diphenyl was also formed. Magnesium phenyl bromide was prepared in the usual manner from 6 g. of magnesium and 20.4 cc. of phenyl iodide. Bromine was added in drops from a separatory funnel to the ethereal solution of the Grignard reagent and the mixture was kept cold. The product on hydrolysis in the usual way with ice-water yielded a liquid which on fractional distillation gave 12 cc. of benzene and 9 cc. of phenyl bromide. Hence there was a yield of about 35 to 45% of benzene and 30 to 40% of phenyl bromide. A small quantity of diphenyl was isolated from the last portions of the distillate.

Action of Bromine on Magnesium Phenyl Bromide.

By the action of bromine on magnesium phenyl bromide, phenyl bromide was obtained in 30 to 40% yield. A small quantity of diphenyl was also formed. Magnesium phenyl bromide was prepared from 6 g. of magnesium and 26.1 cc. of phenyl bromide. When bromine was added from a graduated separatory funnel, vigorous reaction took place on the addition of each drop; and a total of 9.4 cc. was taken up. The reagent was kept cold by placing the vessel in ice-water. The product was next hydrolyzed with ice-water, and hydrochloric acid added to dissolve the flocculent precipitate of magnesium hydroxide. The oily layer after drying and distilling yielded 9 cc. of bromobenzene, corresponding to 30 to 40% yield. A small quantity of diphenyl was also formed.

Action of Bromine on Magnesium Ethyl Iodide.

Ethyl bromide was formed by the action of bromine on magnesium ethyl iodide, but the exact yield could not be ascertained, since it could not easily be separated from ether.

Action of Bromine on Magnesium *n*-Propyl Iodide.

By the action of bromine on magnesium *n*-propyl iodide, *n*-propyl bromide was formed in 30 to 40% yield. 6 g. of magnesium and 25 cc. of *n*-propyl iodide were used for the preparation of the reagent. About 10 cc. of bromine was taken up by the Grignard reagent. Excess of bromine was found to replace the iodine of the normal propyl iodide used in the preparation of the reagent. Ice-water was added to the reaction mixture, when a vigorous reaction took place with the separation of oil and the formation of magnesium hydroxide, which then was dissolved as usual by mineral acids. The ethereal layer was separated and subjected to distillation. After the distillation of ether, *n*-propyl bromide came over and was obtained in 30 to 40% yield.

Action of Chlorine on Magnesium Phenyl Bromide.

By the action of chlorine on magnesium phenyl bromide, a product was formed which on shaking exploded violently. Chlorine was passed through magnesium phenyl bromide prepared from 6 g. magnesium and 26 cc. phenyl bromide. The gas was generated by the action of hydrochloric acid on potassium permanganate and was carefully washed and dried by first passing through water and then through conc. sulfuric acid. The gas seemed to be absorbed with no special change, but after a long time a solid incrustation appeared. When the chlorine seemed to have no further action, the passage of the gas was stopped and the vessel taken out of the glass reaction chamber. Upon shaking the flask slightly to break the incrustation, it exploded with a loud report and a bright flash. The nature of the product could not, therefore, be ascertained on account of its great instability.

Action of Chlorine on Magnesium Phenyl Iodide.

By the action of chlorine on magnesium phenyl iodide a yield of 20 to 25% of phenyl chloride was obtained. Chlorine gas was passed through magnesium phenyl iodide prepared from 6 g. of magnesium and 20.4 cc. of phenyl iodide. The product was hydrolyzed with ice-water and, after the distillation of ether, was subjected to distillation, when phenyl chloride was obtained in 20 to 25% yield. The low yield was due to the fact that a considerable quantity of the reagent was decomposed by the chlorine.

Action of Chlorine on Magnesium *p*-Bromotoluene.

Chlorine gas was passed through magnesium *p*-bromotoluene, prepared from 6 g. of magnesium and 30 cc. of *p*-bromotoluene. After hydrolysis and fractional distillation of the product, magnesium *p*-chlorotoluene was obtained in 18 to 20% yield.

CALCUTTA, INDIA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY COLLEGE OF SCIENCE.]

HALOGENATION. XVIII. DIRECT IONIZATION BY MEANS OF IODINE AND NITRIC ACID.

BY RASIK LAL DATTA AND NIHAR RANJAN CHATTERJEE.

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In continuation of the researches on iodination by nitric acid[1] it has now been found that reaction takes place with considerable facility in the case of aromatic acids and aromatic haloid derivatives.

The following results have been obtained: *p*-Iodobenzene gives a good yield of *p*-diiodobenzene. It was noted in my previous communication on the subject[2] that a small quantity of trinitrophenol is formed as a result of the hydrolysis of iodobenzene and simultaneous nitration in the presence of nitric acid. In view of this reaction it was thought possible to develop a method for the catalytic preparation of trinitrophenol using

[1] Datta and Chatterjee, THIS JOURNAL, 39, 435 (1917).

[2] *Loc. cit.*