0.2931 gave 0.1849 AgI; calc. for $C_9H_7NHI.2AgI$, Ag = 29.51; found 28.99.

Tetrapropylammonium Silver Iodide, $2N(C_3H_7)_4I.3AgI$.—With tetrapropylammonium iodide, quite a distinct type of salt is obtained, *viz.*, $2NR_4I.3AgI$, whereas in the case of other salts, the type $NR_4I.2AgI$ is produced. The latter type is the one usually formed whereas the former type is only exceptional, being obtained mainly with the heavy bases. The salt is obtained as a white precipitate by adding a solution of silver nitrate to tetrapropylammonium iodide. The precipitate is washed and dried at 100°.

0.2533 gave 0.1324 AgI; calc. for $2N(C_3H_7)_4I.3AgI$; Ag = 24.32; found 24.02.

Investigations on similar lines are being continued.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

A STUDY OF THE MECHANISM OF THE GRIGNARD REACTION.

BY LAMBERT THORP AND OLIVER KAMM.

Received March 17, 1914.

Introduction.

Ever since the time when Grignard pointed out that the reaction between magnesium and alkyl or aryl halides was much facilitated if the latter were dissolved in ether, various opinions have, from time to time, been promulgated concerning the role of the solvent in the reaction. Evidence appears to be at hand pointing to the conclusion that the ether forms one or more definite compounds with the magnesium alkyl (or aryl) halide. Thus, in the case of methyl iodide, Grignard observed that an addition product of the formula $(C_2H_5)_2O.MgCH_3I$ was left, after the excess of ether had been removed in a vacuum. Grignard at first held the view that this molecule of ether functioned as ether of crystallization. Further evidence regarding the existence of definite compounds of ether and magnesium alkyl halides has been furnished by Tschelinzeff,[1] who showed that the addition of ether to a benzene solution of magnesium alkyl halide caused the evolution of definite and equal amounts of heat for each of the first two molecular quantities of ether added. Such an addition product would thus correspond to Zelinsky's compound $2(C_2H_5)_2O.MgI_2$.

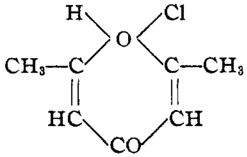
A definite idea regarding the distribution of valences in the ether addition products was first put forward by Baeyer and Villiger,[2] who, with the work of Collie and Tickle[3] in mind, believed that they had in this class of compounds further evidence to strengthen their belief in the existence of tetravalent oxygen. Three years previously Collie and

[1] *Ber.*, **37**, 2084 (1904); *Ibid.*, **37**, 4534 (1904); *Ibid.*, **39**, 773 (1906).

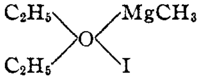
[2] *Ibid.*, **35**, 1201 (1902).

[3] *J. Chem. Soc.*, **75**, 710 (1899).

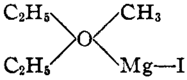
Tickle[1] had found that dimethyl pyrone formed a well defined addition product with hydrogen chloride to which they assigned an oxonium structure:



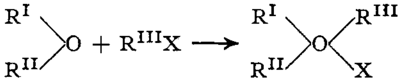
Accordingly, Baeyer and Villiger represented the substance $(C_2H_5)_2O.$-$MgCH_3I$ by a somewhat analogous oxonium arrangement:



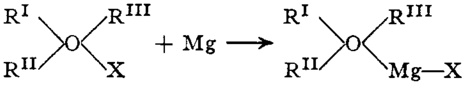
Grignard himself finally adopted an oxonium structure, but distributed the four valences of the oxygen in a different manner:



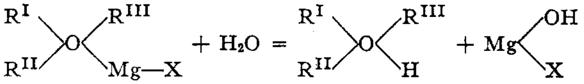
Recently, G. Stadnikoff[2] has undertaken to defend the view of Grignard regarding the oxonium structure of the addition products of ethers and magnesium alkyl halides. His theory concerning the mechanism of the reaction involves first the formation of an oxonium compound through the reaction between the ether and the alkyl halide:



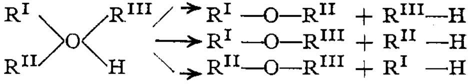
This product is then acted upon by the magnesium to form a monoetherate:



Upon treatment with water this latter compound is decomposed in the sense of the following requation to give another oxonium derivative:



Being very unstable this substance may break up in several directions:



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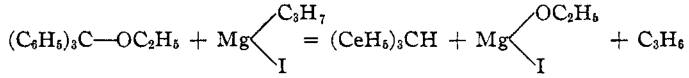
[1] *Loc. cit.*

[2] *J. Russ. Phys. Chem. Soc.*, 43, 1244 (1911); *C. A.*, 6, 1434 (1912); *J. Russ. Phys. Chem. Soc.*, 44, 1219, 1256 (1912); *C. A.*, 7, 983, 984 (1913); *Centr.*, 1, 21, 22 (1913); *J. Russ. Phys. Chem. Soc.*, 44, 1247 (1912); *Ber.*, 44, 1157 (1911); *Ibid.*, 46, 2496 (1913); *J. prakt. Chem.*, [2] 88, 1 (1913).

What lends apparent strength to the hypothesis of Stadnikoff, is this very multiplicity of products, as a concrete example of which might be cited the following case: Upon decomposing, by means of dilute sulfuric acid, the reaction product from magnesium, propyl iodide and diphenylmethyl butyl ether, he obtained symmetrical tetraphenyl ethane, 1,1-diphenyl-butane, hydrogen, and diphenylmethyl propyl ether.

A. I. Gorski,[1] in his criticism of the work of Stadnikoff, has pointed out the possibility of interpreting his results on the basis of hydrolysis and reduction, or of direct reduction, of the ethers from analogy to the behavior of zinc alkyls:

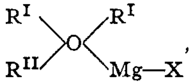


$$(C_6H_5)_3C—OC_2H_5 + Mg\begin{matrix}C_3H_7\\ I\end{matrix} = (CeH_5)_3CH + Mg\begin{matrix}OC_2H_5\\ I\end{matrix} + C_3H_6$$

His argument is further strengthened by a consideration of the results of his work upon the behavior of organo-magnesium compounds towards other oxygenated substances.

Theoretical.

Upon the basis of the conception of Stadnikoff, regarding the constitution of the addition products resulting from the action of ethers upon organomagnesium compounds, it should be possible to arrive at any given oxonium structure by employing two different combinations of ether and halogen derivative; that is to say, for example, it should be possible to generate the oxonium compound,



from the two combinations: (1) $R^I—O—R^I.R^{II}X$ and (2) $R^I—O—R^{II}.$-R^IX. The evidence as to whether or not identical addition products had been formed in the two cases could be furnished by a consideration of the nature of the decomposition products. Thus, upon treatment with dilute acids and carbon dioxide, respectively, the hydrocarbons, $R^I—H$ and $R^{II}—H$, and the acids $R^I—COOH$ and $R^{II}—COOH$ should not only be generated in both cases, but their ratios should be equal. It is the object of the present work to test this deduction from Stadnikoff's oxonium hypothesis by employing first, the combination, diethyl ether and phenyl bromide, and second, phenetole and ethyl bromide.[2]

Upon decomposing, by means of dilute sulfuric acid, the product resulting from the reaction of magnesium upon a mixture of diethyl ether and bromobenzene, a yield of benzene amounting to 61% of the theoretical

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[1] *J. Russ. Phys. Chem. Soc.*, **44**, 581 (1912); *Chem. Centr.*, **2**, 1527 (1912); *J. Russ. Phys. Chem. Soc.*, **45**, 163 (1913); *J. Chem. Soc.*, **104**, 1, 462 (1913).

[2] It is here assumed that the excess of ether used as a solvent does not change the nature of the decomposition products. It is our purpose to investigate the influence of this factor.

was obtained, as well as a considerable quantity of diphenyl and a small volume of gas. This gas, upon examination, proved to be a mixture of ether vapor, hydrogen, air, a hydrocarbon (or hydrocarbons) insoluble in fuming sulfuric acid, and possibly some ethylene. Upon treatment of an ethereal solution of phenyl magnesium bromide with carbon dioxide, the sole product was benzoic acid, whereas the hypothesis demands the simultaneous formation of propionic acid.

In the case of the combination, phenetole, ethyl bromide and magnesium, the decomposition products with dilute sulfuric acid and carbon dioxide were ethane and propionic acid, respectively. Neither benzene nor benzoic acid could be detected. The yield of ethane, based upon the magnesium in solution, was 97% of the theoretical, whereas in the case of bromobenzene and diethyl ether the yield was less than 0.2%.

Experimental.

Diethyl Ether, Bromobenzene and Magnesium.

Decomposition with Dilute Sulfuric Acid.—The solution of phenyl magnesium bromide was prepared in the usual manner from 12.2 g. (0.5 mol) of magnesium ribbon, 79 g. (0.5 mol) of bromobenzene and 100 g. of anhydrous ether. At the end of 2.5 hours 0.3 g. of magnesium remained undissolved; and the solution was made up to 250 cc. by the addition of a sufficient amount of anhydrous ether.

Three cubic centimeters of the above solution were introduced into a buret filled with 70% sulfuric acid at a temperature of 50°. The ether was readily absorbed, a layer of benzene separated on the surface of the acid, and approximately 1 cc. of gaseous product was obtained.

In order to examine the latter, 100 cc. of the original solution were decomposed in the same way. The resulting gas measured 27.55 cc., which, after treatment with fuming sulfuric acid, decreased to 21.45 cc. An alkaline pyrogallol solution reduced this volume to 21.10 cc. After the addition of 18.8 cc. of oxygen to 11.2 cc. of the residual gas, and explosion of the mixture, the volume of gaseous product was 15.5 cc. After treatment with a solution of caustic potash the resulting gas measured 12.10 cc., and the contraction, 3.4 cc., represents the volume of carbon dioxide. If we assume the hydrocarbon present to be ethane, the data indicate that only 1.7 cc. were formed from the decomposition of approximately one-tenth of a mol of the Grignard solution, while the amount of hydrogen was 6.8 cc. The benzene was found to be soluble in fuming sulfuric acid without leaving any residual gas.

The benzene obtained from a second 100 cc. portion of phenyl magnesium bromide solution was dried over calcium chloride, purified by shaking with concentrated sulfuric acid, and distilled. Nine grams (b. p. 78–82°) were obtained. The residue in the distilling bulb yielded upon distillation 1 g. of pure diphenyl. The above weight of benzene, based upon the bromobenzene, and corrected for the amount of diphenyl formed, corresponds to 61% of the theoretical.

Decomposition with Carbon Dioxide.—A current of dry carbon dioxide was passed for 3 hours into 50 cc. (0.1 mol) of the cool Grignard solution prepared above. At the end of this time the viscous mass was decomposed by means of dilute sulfuric acid, and then extracted with ether six times, the total volume of ether extract amounting to 350 cc. Since hydrobromic acid could not be detected in this extract, it was possible to determine the total acidity, due to organic acids, by direct titration after evaporation of the ether. Ten cubic centimeters of the ether solution required 29.00 cc. $Ba(OH)_2$ (0.0281 *N*).

A second (50 cc.) portion of the ether extract was evaporated on the water bath, and the acid taken up with 100 cc. of hot water. The solution was allowed to cool to room temperature (22°), and the excess of benzoic acid filtered off. The filtrate, a saturated solution of benzoic acid, and suspected to contain some propionic acid, was subjected to distillation. An equal volume of a solution of benzoic acid, saturated under the same conditions was distilled at the same time. The results are tabulated below, column A containing the values for the acid solution resulting from the decomposition of the Grignard compound, and column B the values for the blank saturated solution of benzoic acid.

	(0.0281 *N*). Cc. $Ba(OH)_2$. A.	(0.0281 *N*). Cc. $Ba(OH)_2$. B.
1st 10 cc. distillate	1.60	1.72
2nd 10 cc. distillate	1.95	2.05
3rd 10 cc. distillate	2.10	2.05
4th 10 cc. distillate	2.32	2.25
5th 10 cc. distillate	2.55	2.55

Ten cubic centimeters of the saturated benzoic acid solution were found to be equivalent to 7.95 cc. $Ba(OH)_2$ solution. A comparison of the above values for benzoic acid with the Duclaux constants for propionic acid indicates that the latter acid distils in a current of steam five times as rapidly as benzoic acid, and we should, therefore, expect a large per cent. of the propionic acid to be found in the first portions of the distillate. Calculations show that the above method, allowing an error of 0.1 cc. in the values for the $Ba(OH)_2$ titrations, is capable of detecting as little as 0.0015 g. of propionic acid in 100 cc. of solution. The close agreement obtained between the values for the two solutions indicates that propionic acid was absent. The yield of benzoic acid obtained amounted approximately to 50% of the theoretical.

Phenetole, Ethyl Bromide and Magnesium.

Decomposition with Dilute Sulfuric Acid.—A mixture of 60 g. of phenetole, 2.4 g. of magnesium in the form of ribbon, 12 g. of ethyl bromide and a crystal of iodine was warmed until solution of the greater part of the magnesium had been effected. The reaction was considerably more sluggish than in the former case. Butane was evolved, and a precipitate of magnesium iodide separated.

Three cubic centimeters of the clear solution were introduced into a buret filled with 5% sulfuric acid, and the resulting gas was drawn off by means of a mercury attachment and examined as described below. After purification by treatment with fuming sulfuric acid, the volume of gas was 35.9 cc. (13° and 727.5 mm.). The results of the explosion with an excess of oxygen indicate that the gas was pure ethane: 5.1 cc. gas produced 10 cc. CO_2, 4.9 cc. gas produced 10.1 cc. CO_2. In the dilute sulfuric acid which had been used for the decomposition of the phenetole solution the magnesium was determined as pyrophosphate. Wt. $Mg_2P_2O_7$ = 0.2004 g. The agreement between the volume of ethane, predicted upon the assumption that 22.4 liters of the gas are equivalent to 24.3 g. of magnesium, and the volume actually found, is shown in the following table:

	Cc.
Volume ethane (0 : 760 mm.)	32.8
Volume ethane (0 : 760 mm.): soluble in 3 cc. phenetole	7.4
Total volume ethane	40.2
Volume ethane equivalent to 0.2004 g. $Mg_2P_2O_7$	40.3

The yield of ethane is evidently about 99.7% of the theoretical. Assuming a maximum error of 1 cc. in the several determinations, the yield of ethane is still more than 97%.

Decomposition with Carbon Dioxide.—A current of dry carbon dioxide was passed into 50 cc. of the cool phenetole solution, prepared in the preceding experiment. After about two hours, ice water was added to the viscous mass, and then enough ammonium chloride to dissolve the magnesium hydroxide. After separation of the phenetole the aqueous layer was acidified with dilute sulfuric acid, and one-half of the solution (110 cc.) was distilled according to the method of Duclaux. The results were as follows:

1st 10 cc. distillate required 8.60 cc. KOH (0.115 *N*)
2nd 10 cc. distillate required 8.65 cc. KOH (0.115 *N*)
3rd 10 cc. distillate required 6.85 cc. KOH (0.115 *N*)
4th 10 cc. distillate required 5.98 cc. KOH (0.115 *N*)

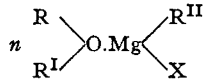
Not a trace of halogen acid could be detected in any portion of the distillate before the fifth.

In order to test for benzoic acid the second half of the solution was made strongly alkaline with potassium hydroxide, evaporated on the water bath to small bulk, cooled, acidified with dilute sulfuric acid, and extracted repeatedly with ether. The ether was distilled, and the residue taken up with 30 cc. of hot water. Upon cooling, no benzoic acid separated out.

For the purpose of detecting minute traces of benzoic acid, an aqueous solution of copper propionate was employed. Preliminary tests had shown that this reagent was capable of giving a distinct precipitate in a neutral solution of benzoic acid at a dilution of 1 : 10,000. Since no precipitate was formed in the 30 cc. portion of neutral solution, benzoic acid, if produced at all in the reaction, must have been present in an amount less than 0.006 g.

Conclusions.

1. The action of an alkyl (or aryl) halide upon magnesium in the presence of an ether results in the formation of certain addition products which may be represented by the general formula



$$n\,\frac{R}{R^{I}}\!>\!O.Mg\!<\!\frac{R^{II}}{X}$$

2. The Grignard-Stadnikoff oxonium structure predicts that a given etherate may be prepared by either of two methods. Experimental data, however, indicate that the compounds formed are not identical—in fact all the evidence obtained is contrary to the theory of Stadnikoff.

3. It is unnecessary to assume any oxonium structure for the Grignard compounds in order to account for the decomposition products obtained with the common ethers (diethyl and phenyl-ethyl). If, however, the assumption of an oxonium structure is desired, the Baeyer-Villiger formula is to be preferred.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

SOME TRANSFORMATIONS OF RICINOLEIC AND OLEIC ACIDS.

[SECOND PAPER.]

ACTION OF MONOPOTASSIUM ANILIDE AND POTASSIUM PHENOLATE UPON DIBROMOHYDROXYSTEARIC AND DIBROMOSTEARIC ACID.

BY B. R. HONOVSKI.

Received March 5, 1914.

In my previous paper[1] it was shown that ricinoleic acid was changed to diiodostearic by the action of hydriodic acid. This acid upon reduction with nascent hydrogen is changed quantitatively to stearic acid. This reaction makes it certain that the iodine atoms in diiodostearic acid are not added to two neighboring carbon atoms:

$$CH_3(CH_2)_5CHI—CH_2—CHI—CH_2(CH_2)_7COOH,$$

$$CH_3(CH_2)_5CHI—CH_2—CH_2—CHI(CH_2)_7COOH,$$

otherwise, upon reduction with nascent hydrogen, an unsaturated acid would be obtained, similar to the dihalogen oleic, elaidic, fumaric, and maleic acids, which, upon reduction of their respective dihalogen-deriva-

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[1] *Ber.*, 42, 3339 (1909).