A STUDY OF THE REDUCING ACTION
of
MAGNESIUM AMALGAM AND METALLIC MAGNESIUM
upon
AROMATIC NITROCOMPOUNDS

by

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of the requirements for the degree of
Doctor of Philosophy

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Abbreviations

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A.Ch.	Annales de Chemie et de Physique.
B.	Berichte der deutschen chemischen Gesellschaft.
Bl.	Bulletin de la societe chemique de Paris
C.	Chemisches Centralblatt.
J.Pr.	Journal fur praktische Chemie.
J.r.	Journal der russichen chemischen Gellschaft.
M.	Monatshefte fur Chemie. - Wien
R.	Recueil des travaux chimiques des Pays - Bas.
Soc.	Journal of the Chemical Society. - London
Z.	Zeitschrift fur Chemie von Beilstein, Fettig, und Hubner.

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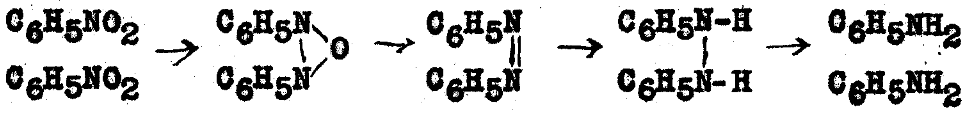
A STUDY OF THE REDUCING ACTION
of
MAGNESIUM AMALGAM
upon
AROMATIC NITROCOMPOUNDS

INTRODUCTION

The reduction of aromatic nitro-compounds has been the subject of much investigation. The reasons for this are apparent. In the first place the aromatic nitro-compounds present in themselves a large class of bodies. Again, there are many methods of reduction which may be applied to them, and, finally, as the result of this, there are obtained various classes of reduction-products that are of great theoretical and practical importance.

The reduction of aromatic nitro-compounds is generally accomplished either in acid or alkaline solution, or electrolytically. Generally speaking, reductions in acid solutions lead to the formation of amines while the use of alkaline reducing agents results chiefly in the formation of intermediate products such as the azoxy-, azo-, and hydrazo-compounds. This well known process is illustrated as follows:



$$\begin{array}{c}C_6H_5NO_2\\C_6H_5NO_2\end{array} \rightarrow \left.\begin{array}{l}C_6H_5N\\ \;|\\C_6H_5N\end{array}\right\rangle O \rightarrow \begin{array}{c}C_6H_5N\\ \;\;\|\\C_6H_5N\end{array} \rightarrow \begin{array}{c}C_6H_5N\text{-}H\\ \;|\\C_6H_5N\text{-}H\end{array} \rightarrow \begin{array}{c}C_6H_5NH_2\\C_6H_5NH_2\end{array}$$

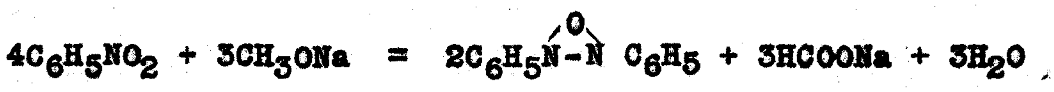
Reductions in acid solution are generally brought about by the action of iron or tin and hydrochloric acid upon nitro-compounds. Stannous chloride and hydrochloric acid may also be employed. These reactions are illustrated as follows:

$$C_6H_5NO_2 + 3Fe + 6HCl = 3FeCl_2 + 2H_2O + C_6H_5NH_2$$

$$2C_6H_5NO_2 + 3Sn + 12HCl = 2C_6H_5NH_2 + 3SnCl_2 + 4H_2O$$

$$C_6H_5NO_2 + 3SnCl_2 + 6HCl = C_6H_5NH_2 + 3SnCl_4 + 2H_2O ,$$

Alkaline reducing agents are milder in their action than acid reducing agents. Hence they are employed in the preparation of azoxy-,azo-, and hydrazo-compounds. In reducing nitro-compounds to azoxy-compounds the most important reducing agents are the alkali alcoholates and sodium amalgam. The reducing action of the alcoholates depends upon their capability of being oxidized by nitro-compounds. Thus, for instance, sodium methylate is oxidized to sodium formate by nitro-benzene with the production of azoxybenzene:



$$4C_6H_5NO_2 + 3CH_3ONa = 2C_6H_5\overset{O}{N-N}C_6H_5 + 3HCOONa + 3H_2O ,$$

By the addition of undissolved sodium or sodium amalgam to an alcoholic solution of a nitro-compound, a reaction mixture is obtained which is far more energetic in its reducing action than a previously prepared alcoholate. This is due to the fact that when sodium or sodium amalgam reacts with an alcohol, nascent hydrogen is evolved and plays a part in the reduction in addition to the reducing action of the alcoholate which is also formed. By this means azo-compounds are generally prepared. They may also be obtained by the action of alkaline stannous chloride (sodium-stannous-oxide) upon nitrocompounds:

$$2C_6H_5NO_2 + 4Sn(ONa)_2 = C_6H_5N{=}NC_6H_5 + 4SnO(ONa)_2 ,$$

Finally, azo-and hydrazo- compounds are obtained by the action of zinc dust and alkali hydroxides upon alcoholic solutions of nitro compounds. In such cases the reduction is due to the evolution of nascent hydrogen in accordance with the reaction:

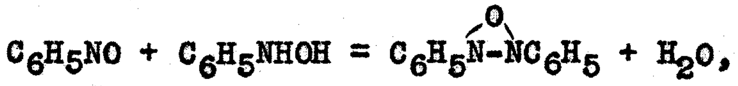
$$Zn + 2NaOH = Zn(Ona)_2 + 2H.$$

By means of the electro-reduction of aromatic nitro-compounds many of the syntheses just noted have been improved upon, and new syntheses have been effected. Electro-reductions are generally carried out in either acid or alkaline alcoholic solution, and here also the nitro-compounds ultimately yield amines, but a number of intermediate reduction-products can be isolated. The primary reduction process is illustrated as follows:

$$C_6H_5NO_2 \rightarrow C_6H_5NO \rightarrow C_6H_5NHOH \longrightarrow C_6H_5NH_2$$

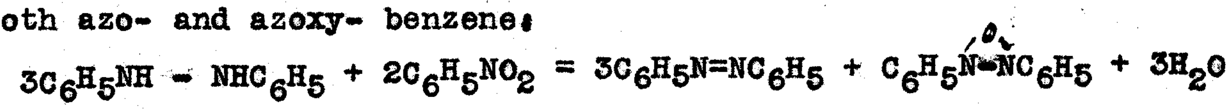
The relative yields of these various products depend upon the degree of acidity and concentration of the solution subjected to electrolytic reduction.

In alcoholic alkaline solutions of nitro compounds the electro-reduction may be accomplished by two secondary processes. Thus, for example, in the case of nitro-benzene, nitroso-benzene reacts with phenyl hydroxylamine to form azoxy-benzene in accordance with the reaction:



$$C_6H_5NO + C_6H_5NHOH = C_6H_5\overset{O}{N-N}C_6H_5 + H_2O,$$ and

hydrazobenzene is attacked by unreduced nitrobenzene to produce both azo- and azoxy- benzene:



$$3C_6H_5NH - NHC_6H_5 + 2C_6H_5NO_2 = 3C_6H_5N{=}NC_6H_5 + C_6H_5\overset{O}{N-N}C_6H_5 + 3H_2O$$

These wellknown examples simply serve to illustrate the more common methods employed in the reduction of aromatic nitro-compounds, and to indicate the reduction products generally resulting therefrom.

Hitherto, the reduction of aromatic nitro-compounds by means of magnesium amalgam has not been investigated, nor has there been any account given of the reducing action of metallic magnesium and methyl alcohol upon aromatic nitro compounds. Before taking up these subjects, a few words concerning magnesium amalgam will not be out of place.

MAGNESIUM AMALGAM

Magnesium amalgam was prepared in 1866 by Wanklyn and Chapman who made it by introducing magnesium ribbon into mercury which had been heated almost to boiling temperature. Klauer prepared magnesium amalgam by the action of potassium amalgam upon crystallized magnesium sulphate. In general, the amalgam can be made by bringing pure magnesium and mercury into intimate contact. In the cold, amalgamation takes place slowly but can be readily effected by warming. If the temperature be raised to the fusing point of magnesium the amalgamation takes place almost instantaneously and must be conducted in an inert atmosphere otherwise the magnesium will burn.

A satisfactory method of preparing magnesium amalgam, (5% Mg.), was found to consist first in warming a porcelain mortar by burning a few cubic centimeters of alcohol in it, then adding mercury and rubbing in the magnesium powder in small portions with a pestle. The magnesium combines with the mercury with the evolution of much heat to form a fluid amalgam which solidifies to a hard crystalline mass upon cooling. It is then broken up into small pieces and kept in tightly stoppered bottles in order to avoid decomposition by means of the moisture in the air.

Magnesium amalgam readily decomposes water with the evolution of hydrogen and the precipitation of magnesium hydroxide and mercury in a fine state of subdivision. Wanklyn and Chapman state that a one percent magnesium amalgam decomposes water more readily than a one percent sodium amalgam.

S. Muenier* has shown that when magnesium amalgam reacts with absolute ethyl alcohol, magnesium ethylate $Mg(OC_2H_5)_2$ is formed and hydrogen is evolved. He has also effected the synthesis of diphenylmethane through the action of magnesium amalgam upon an equimolecular mixture of benzyl chloride and mono brombenzene** and prepared the mono- and di-alkyl derivatives of malonic ester by the action of magnesium amalgam and alkyl halides upon malonic ester. In these respects magnesium amalgam acts similarly to sodium. With magnesium amalgam as a reducing agent Muenier has converted alkyl iodides to saturated hydrocarbons, and reduced acetaldehyde to β·γ· dioxybutane.

Magnesium amalgam has had very little application as a reducing agent in organic chemistry, in fact, its reducing action upon aromatic nitro-compounds has hitherto been neglected. Dr. Thomas Evans in a paper on "Magnesium Amalgam" read before the Cincinnati Section in 1901, and later published in the Journal of the American Chemical Society (September 1904), described for the first time the reduction of an aromatic nitro compound by means of magnesium amalgam. In this instance a concentrated solution of nitro benzene in ethyl alcohol, 15.26 grams of the former to 50 cubic centimeters of the latter, was treated with more than enough megnesium amalgam (10% Mg.) to convert the nitrobenzene to phenylhydroxylamine. There resulted from this reduction 10.8 grams of azobenzene, a yield of 95.66 percent of the theory.

*Comptes Rendus.1902:134.pp.472-473
**Comptes Rendus.1903:137. pp.714-715

At the suggestion of Dr. Evans, reductions of nitrobenzene by means of magnesium amalgam were made, first, in a large excess of ethyl alcohol as solvent for the nitro-compound, and second, with a like excess of methyl alcohol as solvent. In the first instance the reduction product obtained was azoxybenzene in quantity equal to 89.9 percentof the theory. In the second case the reduction product was azobenzene in quantity equal to 88.53 percent of the theory. These surprising results, namely, that magnesium amalgam reduced nitrobenzene in ethyl alcohol to azoxybenzene, and in methyl alcohol to azobenzene prompted a study of "The Reducing Action of Magnesium Amalgam upon Aromatic Nitro-Compounds" in these solutions.

THE REDUCING ACTION OF MAGNESIUM AMALGAM
upon
AROMATIC NITRO-COMPOUNDS

In making reductions of various aromatic nitro-compounds by means of magnesium amalgam the general method of reduction and subsequent recovery of the reduction-products was as follows: The nitro-compound was dissolved in a large excess of the solvent contained in a deep cylindrical glass jar. During the addition of the powdered magnesium amalgam, the solvent was kept in active agitation by means of an efficient mechanical stirrer. It was necessary to add the amalgam in very small portions and at intervals in order to avoid a too rapid evolution of hydrogen. A five percent amalgam was used in each reduction and the amount added was a small excess over that required to reduce all the nitro-groups in the compound to amino-groups. Thus, for example, if dinitrobenzene were being reduced the quantity of magnesium amalgam added would be the equivalent of the hydrogen necessary to reduce the body to diaminobenzene, $C_6H_4(NO_2)_2 \rightarrow C_6H_4(NH_2)_2$.

After the requisite amount of amalgam had been added and the evolution of hydrogen had ceased, stirring was discontinued and the reaction mixture was poured into a large round bottomed flask. A return condenser was then attached to the flask and the reaction mixture heated upon an actively boiling water-bath for fifteen hours at the end of which time the condenser was turned down and the alcohol allowed to distil off. The residue was then transferred to an evaporating dish and the last minute traces of alcohol were driven off by heating upon a boiling water-bath. After thoroughly pulverizing the dry residue, the reduced compounds contained therein were completely removed by prolonged extractions with some suitable solvent such as ligroin or ether. Finally, by concentration of the combined extracts, by crystallization and recrystallization, the reduction products were obtained in pure form and subsequently identified.

In the first reductions ethyl alcohol was used as the solvent in which the aromatic nitro-compounds were reduced.

NITROBENZENE IN ETHYL ALCOHOL

25 grams of nitrobenzene were dissolved in 1 1/4 litres of 93 percent ethyl alcohol. The amount of 5 percent magnesium amalgam necessary to reduce 25 grams of nitrobenzene to aniline is 295 grams. In order to have a slight excess, 300 grams of magnesium amalgam were added in very small portions and at frequent intervals. About one hour was required for the addition of the amalgam. At each addition there was a rapid evolution of hydrogen accompanied by a precipitation of magnesium hydroxide and mercury in a fine state of division. The solution darkened slightly and the temperature rose from 15°C to 45°C during the reaction. When all of the amalgam had been decomposed and the temperature began to fall, the thinly fluid greenish gray reaction mixture was transferred to a flask provided with a return condenser and heated on a water bath for fifteen hours.

, The ethyl alcohol was then distilled off and the residue consisting of magnesium hydroxide, mercury and the reduction product, was dried in an evaporating dish upon a water bath. The light yellow mass so obtained was repeatedly extracted with boiling ligroin until the extracts were colorless after which they were combined and concentrated to 30 cubic centimeters. After standing for twelve hours the solution had solidified to a mass of light red needles. While these crystals were recrystallized from ether, it was found impossible to free them completely from ligroin. Purification was finally accomplished by dissolving the reduction-product in a small quantity of methyl alcohol and inducing crystallization by directing a stream of dry air upon the solution until a few crystals had formed when crystallization proceded rapidly. These were filtered off and recrystallized in the same manner. The compound thus obtained was insoluble in water, but readily soluble in the usual organic solvents and melted at 36°C thus proving itself to be azoxybenzene. Hence, the reduction of nitrobenzene in ethyl alcohol by means of magnesium gave azoxybenzene.

METADINITROBENZENE IN ETHYL ALCOHOL

Fifty grams of metadinitrobenzene were dissolved in 2 1/2 litres of 90 percent ethyl alcohol and 869 grams of 5 percent magnesium amalgam, sufficient to reduce the dinitrobenzene to phenylenediamine were added as described in the previous reduction.

The darkening of the solution was more marked in this reduction than in the reduction of nitrobenzene. The temperature also rose higher, this time going to 55°C. When no further action of the amalgam was perceptible the brownish red reaction mixture was heated for fifteen hours on the water bath. The boiling liquid and accompanying solid were poured upon a large Buchner filter and suction applied. As the filtrate cooled, a voluminous flocculent precipitate of light brown color settled out and was filtered off. Upon concentration of the filtrate more of this same compound was precipitated.

The residue upon the original filter was repeatedly extracted with boiling alcohol until the extracts were colorless. The compound was so insoluble that fifteen extractions with 500cc each of alcohol were necessary to dissolve it all out. Purification of the reduction product was effected by repeated recrystallization from alcohol. The purified compound consisted of light tan microscopic needles, slightly soluble in ether somewhat more soluble in benzene, toluene, and boiling alcohol, and readily soluble in chloroform. The melting point was 141°-142°C. These properties agree very well with those of metadinitroazoxybenzene as given by Klinger and Pitschke*.

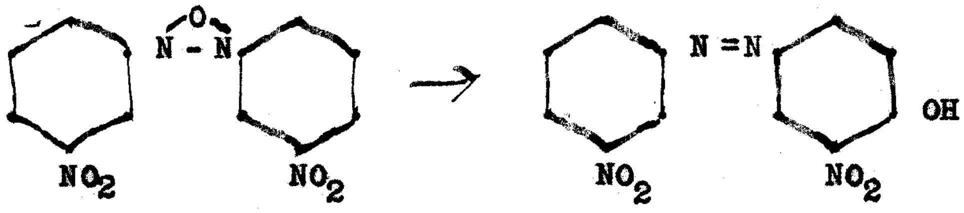
For more complete identification a nitrogen determination was made:

Weight of substance	0.1805 gm
No.cc of nitrogen evolved	32.00
Barometric reading	710.80mm
Temperature	16°C
Found-nitrogen	19.34 percent
Calculated-nitrogen	19.48 percent

Additional evidence as to the identity of the substance is based upon the fact that azoxy-compounds when heated for some time with concentrated sulphuric acid are converted into their isomers, the oxyazo-compounds. Thus for instance if the

* Ber. d. chem. Ges. 18: 2552 (1885)

substance in question were metadinitroazoxybenzene it should be converted to paraoxymetadinitroazobenzene:



Accordingly 5 grams of the reduction product were heated with 50cc of concentrated sulphuric acid, (Sp.G.-1.84), for one hour at 140°C. After cooling, the deep red reduction mixture was poured into a large volume of water, whereupon a light reddish yellow flocculent substance was precipitated. This substance was filtered off and recrystallized from alcohol in which it was sparingly soluble. When treated with sodium hydroxide solution the body immediately changed to a deep red colored compound which was soluble in water and when dilute sulphuric acid was added there occured a reprecipitation of the original oxy-azo compound. Its melting point was 172°-173°C, the melting point of paraoxymetadinitrobenzene. A nitrogen determination was made as follows:

Weight of substance	0.2408 gm
Nitrogen evolved	41.00cc
Barometric reading	731.30 mm
Temperature	16°C
Found-nitrogen	19.30 percent
Calculated nitrogen	19.48 percent

Theoretically the percentage of nitrogen is the same for both azoxy- and ozyazo-compound. Experimentally this was verified, and in connection with the properties already cited is conclusive evidence that metadinitrobenzene in excess of ethyl alcohol is reduced to metadinitroazoxybenzene by 5 percent magnesium amalgam. The yield was 30 grams, or 70 percent of the theoretical.

ORTHONITROTOLUENE IN ETHYL ALCOHOL

25 grams of orthonitrotoluene were dissolved in 1 1/4 litres of ethyl alcohol and 300 grams of 5 percent magnesium amalgam were added in the manner previously described. The solution became yellow in color and after all the amalgam had been added the reaction mixture was transferred to a round bottomed flask and heated with reflux condenser upon a boiling water bath for fifteen hours. The alcohol was then distilled off and the residue dried in an evaporating dish at water bath temperature. It was then repeatedly extracted with boiling ligroin until a colorless extract was obtained. The combined extracts were concentrated to a volume of 50cc and set aside. In the course of three or four days a mass of yellowish red monoclinic prisms had crystallized out. One of these crystals was exceptionally large being 2.5cm long, 1.0cm wide and 2.5cm thick.

After filtering off the large crystals, the filtrate was concentrated upon a water bath until a dark red oil remained. This was dissolved in a small quantity of absolute alcohol and the solution was subjected to cold rapid evaporation by directing a blast of dry air upon its surface, stirring rapidly at the same time. Small light yellow crystals separated out in a short time, were filtered off, washed with alcohol and dried, and the process was repeated with the filtrate and washings. This treatment of the mother liquid was continued as long as the crystals were obtained. The substance after purification by recrystallization from absolute alcohol was found to be readily soluble in the common organic solvents and melted at 59°-60°C. This in connection with the other noted properties identifies the body as orthoazoxytoluene. In other words orthonitrotoluene is reduced in large excess of ethyl alcohol to orthoazoxytoluene by means of 5% of magnesium amalgam. The yield was 10 grams or 50.00 percent of the theoretical.

The red oil (from mother liquor) upon distillation with steam yielded 9 grams of orthonitrotoluene. This amount not being reduced by the amalgam accounts for the low yield of orthoazoxytoluene, namely 50 percent of the theoretical.

PARANITROTOLUENE IN ETHYL ALCOHOL

Twenty five grams of paranitrotoluene were dissolved in 1 1/4 litres of ethyl alcohol and 300 grams of 5 percent magnesium amalgam added in the usual manner. The reaction mixture which was of a yellowish gray color was heated upon the water-bath for fifteen hours, and after distilling off the alcohol, the residue was dried and then completely extracted with boiling ligroin. The combined extracts upon evaporating to dryness gave a solid mass of fine red-yellow crystals. Upon purification by recrystallization from methyl alcohol beautiful hair like yellow crystals were obtained melting at 75°C and soluble in all of the usual organic solvents. These properties identify the reduction product as paraazoxytoluene. The yield was 18 grams or 90.00 percent of the theoretical.

SUMMARY: Nitrobenzene, metadinitrobenzene, orthonitrotoluene and paranitrotoluene when reduced in ethyl alcohol solution by 5% magnesium amalgam yielded the corresponding azoxybodies namely, azoxybenzene, metadinitroazoxybenzene, orthoazoxytoluene and paraazoxytoluene.

The nitrocompounds just considered were also reduced in methyl alcohol solution according to the general method previously described.

NITROBENZENE IN METHYL ALCOHOL

Twenty-five grams of nitrobenzene were dissolved in 1 1/4 litres of 95 percent methol alcohol and treated with 300 grams of 5 percent magnesium amalgam. After the addition of a dew portions of the amalgam it was apparent that its action with methyl alcohol was different from that with ethyl alcohol. There did not appearto be any precipitation of magnesium hydroxide mixed with finely divided mercury for the amalgam collected in the bottom of the cylinder,despite the active stirring, and in a few minutes became liquid. The solution became light reddish yellow in color and the temperature rose to 45°C in about twenty minutes. When about one half of the calculated amount of magnesium amalgam had been added the reaction mixture began to thicken and in a short time was of the consistency of a heavy gelatinous syrup. It became much thicker as the final portions of the amalgam were added and the temperature rose to 50°C. The contrast between this yellow-red gelaninous solution and the gray thinly fluid one obtained with ethyl alcohol was striking, and was explained by the supposition that a methylate of magnesium was formed in one instance and that no corresponding ethylate was produced from the other. This will be referred to later.

The reaction-mixture was transferred to a round-bottomed flask and boiled on a water-bath with return condensor for fifteen hours, at the end of which time the odor of nitrobenzene was no longer discernible. During this prolonged heating there was a change from light reddish yellow to an orange red color and the mixture became more thinly fluid. The methyl alcohol was then distilled off leaving an orange yellow granular mass behind. This was further dried upon the water-bath and after thoroughly pulverizing, it was completely extracted with boiling ligroin. The extracts were combined and concentrated to a volume of 30cc which, after standing for several days, gave a crystalline mass of beautiful red plates. After recrystallization from methyl alcohol the reduction-product was found to melt sharply at 68°C, the melting point of azobenzene. The yield was 15.5 grams, or 88.53 percent of the theoretical.

METADINITROBENZENE IN METHYL ALCOHOL

Twenty-five grams of metadinitrobenzene were dissolved in 1 1/4 litres of methyl alcohol (95 percent) and 450 grams of magnesium amalgam were used for the reduction. During the action of the amalgam the formation of the gelatinous solution was again noticed and the solution which was at first colorless became chocolate brown. As in the reduction of nitrobenzene the temperature rose to 50°C. During the subsequent heating upon the water bath the reaction mixture seemed to darken in color and became more thinly fluid. The mixture while still boiling was poured into a large Buchner filter connected with a filter pump. A dark red filtrate was obtained which when heated upon a water bath to distil off the methyl alcohol, left a residue of 11. grams of an almost black oil.

The precipitate in the Buchner filter was dried and then dissolved in 300cc of glacial acetic acid which took into solution the magnesium compounds and the reduction-product leaving the mercury unattacked. After filtering to remove the mercury, the deep red filtrate solution was poured into two litres of water, whereupon a voluminous brown precipitate was formed. This was filtered off, washed with water and recrystallized from alcohol. Its melting point was 140°-142°. This and other properties identified it as metadinitroazoxybenzene. The yield was 11 grams or 54.37 percent of the theoretical.

The filtrate from which the reduction-product was separated was found to consist of a solution of magnesium acetate slightly colored by traces of organic matter. The tarry oil obtained from the original alcoholic solution seems to contain the corresponding azo-compound, but its separation and purification have proved to be so difficult that it has not been positively identified.

ORTHONITROTOLUENE IN METHYL ALCOHOL

Twenty-five grams of orthonitrotoluene were dissolved in 1 1/4 litres of methyl alcohol and 300 grams of 5 percent amalgam were added in the customary manner. In this instance also the gelatinous solution was formed and upon heating for fifteen hours it bacame more thinly fluid and changed from light yellow to orange-red in color. After distilling off all the alcohol and evaporating the residue to dryness, the reduction-product was extracted with boiling ligroin. The combined extracts were concentrated to a small volume which upon standing for several days deposited a mass of red monoclinic prisms, varying in length from two to ten millimeters. They were filtered off, washed with methyl alcohol, and dried, and found to melt at 55°C. The filtrate, upon addition of a small quantity of methyl alcohol, was subjected to rapid evaporation with a blast of dry air and yielded small crystals having the same melting point, namely 55°C. This reduction-product agrees with the orthoazotoluene of Klinger and Pitschke* in its properties. The yield was about 12.5 grams, or 66.50 percent of the theoretical.

* Ber.d. chem. Ges., 18, 2555 (1885)

PARANITROTOLUENE IN METHYL ALCOHOL

Twenty-five grams of paranitrotoluene were dissolved in 1 1/4 litres of methyl alcohol and 300 grams of magnesium amalgam were added in the usual manner. Again the gelatinous solution resulted. After heating for fifteen hours upon the water-bath the odor of paranitrotoluene was plainly evident thus showing that complete reduction of the nitrocompound had not yet been effected. Notwithstanding this, the methyl alcohol was distilled off and the residue dried upon the water-bath. After thoroughly extracting the residue and evaporating the combined extracts to dryness there resulted 19.5 grams of fine light yellow oily crystals.

This mass of crystals was dissolved in ethyl alcohol and upon evaporation there was obtained a quantity of short thick, orange colored needles. These were filtered off and when purified by recrystallization from ethyl alcohol yielded fine orange red needles melting at 144°C. They were paraazotoluene*. The yield was 4.5 grams or 23.90 percent of the theoretical.

The filtrate from the paraazotoluene was distilled in order to expel the alcohol. Fifteen grams of a red oil were left which was subjected to steam distillation. The distillate had the odor of paranitrotoluene while the non-volatile residue was odorless. The distillate was extracted with ether, and after evaporating off the solvent a mass of reddish yellow crystals were obtained which upon recrystallization from alcohol became almost colorless and melted at 54°. This was unchanged paranitrotoluene and weighed 9.5 grams.

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* Janovsky and Werigo. Jahresb., 1864, p.527

The residue from the steam distillation was also extracted with ether, evaporated to dryness and the yellow mass of crystals thus obtained were purified by recrystallization from ethyl alcohol. In this way fine light yellow crystals, melting at 75°C, were obtained. The yield was 5.5 grams or 22.2 percent of the theoretical yield of paraazoxytoluene.

The result of the reduction of paranitrotoluene in methyl alcohol was, paraazotoluene, 23.9 percent; paraazoxytoluene, 22.2 percent, while 38 percent of the original paranitrotoluene was recovered unchanged.

In summing up the reductions in dilute methyl alcohol solutions it is seen that nitrobenzene and orthonitrotoluene yield the corresponding azo-compounds, namely azobenzene and orthoazotoluene, while paranitrotoluene was reduced to both azo- and azoxytoluene. The chief exception to the behavior of the other nitrocompounds was found to be metadinitrobenzene which gave 54.37 percent of the theoretical quantity of metadinitroazoxybenzene. The extreme insolubility of this compound may explain why more of it was not reduced to the corresponding azo-derivative.

A summary of the various reductions with 5 percent magnesium amalgam and dilute solutions is given in the table on page 33.

NITROCOMPOUND	SOLVENT	REDUCTION PRODUCT	YIELD PERCENT OF THEORETICAL
Nitrobenzene	Ethyl Alcohol	Azoxybenzene	89.90%
	Methyl Alcohol	Azobenzene	88.53%
Metadinitrobenzene	Ethyl Alcohol	Metadinitroazoxybenzene	70.00%
	Methyl Alcohol	Metadinitroazoxybenzene	54.37%
Orthonitrotoluene	Ethyl Alcohol	Orthoazoxytoluene	50.00%
	Methyl Alcohol	Orthoazotoluene	66.50%
Paranitrotoluene	Ethyl Alcohol	Paraazoxytoluene	90.00%
	Methyl Alcohol	Paraazoxytoluene Paraazotoluene	22.22% 23.90%

In the reductions of any one of the nitrocompounds considered the amount of the solvent, of ethyl alcohol and of methyl alcohol, was the same, as was also the quantity of magnesium amalgam added. This being the case it appears that the reduction-product obtained depends upon the solvent, for in dilute methyl alcohol solutions the tendency was towards the formation of azo compounds, while in dilute ethyl alcohol solutions azoxy compounds alone resulted. In parallel with this result it was noticed that when methyl alcohol was used as a solvent, the addition of magnesium amalgam produced a thick gelatinous syrup, which was not formed when ethyl alcohol was used. This naturally suggested the thought that magnesium methylate was formed and that it, like its analogue, sodium methylate, might act as a reducing agent upon the nitro-compound and thus aid the reduction to go further than it would in ethyl alcohol solution where no corresponding ethylate of magnesium was formed. In other words, were the reductions in methyl alcohol solutions due to the combined effects of nascent hydrogen and methylate of magnesium, while in ethyl alcohol solutions the only reducing factor was the evolved hydrogen? Before taking up this question it was first necessary to isolate and determine the nature of the gelatinous product previously mentioned.

MAGNESIUM METHYLATE

Absolute methyl alcohol was prepared from Kahlbaum's best methyl alchol by prolonged heating over quicklime. This was followed by distillation and subsequent digestion with anhydrous barium oxide until the solution became yellowish in color. Then upon distillation over more barium oxide, absolute methyl alcohol was obtained.

Two hundred grams of 5 percent magnesium amalgam were added to 500cc of absolute methyl alcohol in a 1 litre round bottomed flask which was provided with a return condensor and heated upon the water-bath until no evolution of hydrogen was perceptible. A gray gelatinous reaction mixture resulted which while boiling hot was poured into a large Büchner filter and suction applied. A clear liquid of syrupy consistency and of a faint yellow color filtered through. Upon standing over night the filtrate deposited a mass of semi-transparent prismatic crystals varying in length from 5 to 10 millimeters.

These crystals were very soft and jelly like in consistency. Upon agitating the flask they broke up to form a pulverulent jelly. The mass was then filtered off on the pump and dried in an air tight bath at 100°C. A white granular powder resulted which when heated upon a platinum foil burned for a short time as would alcohol, leaving a perfectly white residue which proved to be magnesium oxide. From this it was evident that the magnesium of the amalgam had reacted with methyl alcohol to form a compound soluble therein. After drying the compound for two hours longer at 110°C the percentage of magnesium oxide was determined:

Weight of substance	Weight of MgO	Calculated MgO in $Mg(OCH_3)_2$ percent	Found MgO percent
0.7456	0.3393	46.69	45.50
0.6373	0.2898	-----	45.49

The percentage of magnesium oxide in magnesium hydroxide is 71.42. Hence it is justifiable to conclude that the compound formed is not magnesium hydroxide.

If a drop of a solution of the supposed methylate of magnesium in methyl alcohol be added to two or three cubic centimeters of water, magnesium hydroxide is thrown down as a thick gelatinous precipitate, and the reaction is accompanied by a marked liberation of heat. This reaction is analagous to that which occurs when methylate of sodium or potassium is treated with water:

$$NaOC_2H_5 + HOH = NaOH + CH_3OH$$

$$Mg(OCH_3)_2 + 2HOH = Mg(OH)_2 + 2CH_3OH$$

Magnesium methylate is decomposed upon heating forming the oxide. It absorbs carbon dioxide from the air as was proved by exposing the dry compound to the atmosphere and then treating with dilute hydrochloric acid, when an appreciable amount of carbon dioxide was evolved. As evidence of change in the composition of the compound successive analyses during continued exposure gave decreasing percentages of magnesium oxide, namely:

1.	Magnesium oxide	44.80 percent
2.	" "	44.01 "
3.	" "	43.90 "
4.	" "	43.60 "

Hitherto magnesium methylate had not been prepared in this manner, namely by the action of magnesium amalgam upon absolute methyl alcohol. Emerich Szawasy* prepared magnesium methylate by the action of magnesium nitride upon methyl alcohol, and also by heating magnesium ribbon and the corresponding alcohol under pressure, in accordance with the following reactions:

$$Mg_3N_2 + 6CH_3OH = 3Mg(OCH_3)_2 + 2NH_3 \;;$$
$$Mg + 2CH_3OH = Mg(OCH_3)_2 + H_2$$

The compounds thus obtained are identical in properties.

When magnesium amalgam reacts with ethyl alcohol that is not anhydrous, no ethylate of magnesium is formed. However L. Muenier** has shown that when magnesium amalgam reacts with absolute ethyl alcohol the corresponding ethylate of magnesium is formed.

These facts seem to indicate that the reason for the reductions going one step further in dilute methyl alcohol than in dilute ethyl alcohol was that the formation of magnesium methylate in the former served as an additional factor in those reductions. The investigation of the reducing action of magnesium methylate alone upon an aromatic nitro-compound will be taken up later.

* Ber. d. Chem. Ges. 30; 806, 1836

** Comptes Rendus. 1902: 134, pp. 472-473

THE ACTION OF MAGNESIUM UPON METHYL ALCOHOL

The fact has been noted that Szawasy caused metallic magnesium to react with methyl alcohol under the combined influence of heat and pressure. I found that there was no reaction between magnesium and methyl alcohol under the influence of heat alone, but that as soon as a particle of iodine or magnesium iodide was added to the mixture, reaction began immediately and proceeded with increasing energy and an abundant evolution of hydrogen. The reaction ceased after all of the magnesium had combined with the methyl alcohol. Upon the addition of more magnesium the same energetic reaction was renewed. This furnished a new and convenient method for the preparation of magnesium methylate and may be carried out as follows:

One fourth of a gram molecule of powdered magnesium (6.1 gram) was added to 300cc of absolute methyl alcohol contained in a one litre round bottomed flask equipped with a return condensor. The contents of the flask were heated to boiling but no reaction ensued until a very small particle of iodine was added whereupon reaction began immediately and continued without further application of heat. In the course of ten minutes the reaction had become so energetic that the flask had to be submerged in cold water. A gray granular gelatinous precipitate was formed and in five minutes more all traces of metallic magnesium had disappeared and the evolution of hydrogen had ceased.

The condensor was then turned down and the methyl alcohol was completely distilled off leaving a granular white powder which was thoroughly dried at 100°C and then analysed for the content of magnesium oxide. The results were as follows:

Weight of substance	Weight of MgO	Calculated MgO in $Mg(OCH_3)_2$ percent	Found MgO percent
0.3887	0.1841	46.67	47.36
0.4080	0.1931	----	47.32

The yield was 21.5 grams or 99.62 percent of the theoretical for magnesium methylate. The reaction in this case is perfectly analagous to that of metallic sodium upon methyl alcohol:

$$Na + CH_3OH = NaOCH_3 + H$$

$$Mg + 2CH_3OH = Mg(OCH_3)_2 + H_2$$

The apparently catalytic action of the very small particle of iodine or magnesium iodide in causing the complete reaction of magnesium and methyl alcohol to form magnesium methylate has not yet been investigated. I also found that if a small quantity of an aromatic nitrocompound be added to a mixture of finely powdered magnesium and methyl alcohol reaction begins even in the cold and proceeds with increasing energy with the formation of magnesium methylate, an evolution of hydrogen, and reduction of the aromatic nitrocompound. Here too the aromatic nitrocompound seems to act as a catalytic agent in bringing about the reaction between the magnesium and the alcohol, but since hydrogen is evolved the nitrocompound consequently suffers reduction. It is not necessary that the methyl alcohol be absolute to accomplish this reaction.

These facts furnish the basis for a Study of the Reducing Action df Metallic Magnesium upon Aromatic Nitrocompounds.

A STUDY OF THE REDUCING ACTION OF METALLIC MAGNESIUM upon AROMATIC NITROCOMPOUNDS

When Evans and Fetsch[*] reduced nitrobenzene by means of magnesium amalgam in ethyl alcohol solution the reaction-product obtained was azobenzene. In this instance the reduction was carried out in a concentrated solution of the nitrocompound, namely, 1 gram of nitrobenzene to 5 cubic cemtimeters of solvent. Later, while pursuing the study of the reducing action of magnesium amalgam upon nitrocompounds in dilute alcoholic solutions[**] it was found that nitrobenzene, in a solution of 1 gram of nitrocompound to 50 cubic centimeters of ethyl alcohol was reduced to azoxybenzene, while in a methyl alcohol solution of the same concentration, azo benzene was the chief reduction product. These facts indicate that the nature and extent of the reduction of an aromatic nitrocompound depends not only upon the kind of solvent but also upon the degree of concentration of the solution subjected to reduction.

Accordingly, in the following reductions by means of metallic magnesium in methyl alcohol solutions, in order to secure comparative results, each nitrocompound considered was reduced, first, in a solution of concentration of 1 gram of solute to approximately 20 cubic centimeters of solvent, and then in a solution of double this concentration, namely 1 gram of solute to approximately 10 cubic centimeters of solvent.

[*] Journal American Chem. Soc. Vol. XXVI 9. p. 1158

[**] " " " " " XXVI 9. p. 1158

The general method of carrying out the reductions was as follows: The nitrocompound was dissolved in the requisite amount of Kahlbaum's best methyl alcohol contained in a large round bottomed flask equipped with a long return condensor. Finally powdered magnesium was then added either in aliquot portions or all at once in quantity sufficient to theoretically reduce the nitro-compound to the corresponding amino-compound. Reaction generally began without any application of heat and continued in most cases with such energy that cooling was necessary by submerging the flask containing the reaction mixture in a large vessel of cold water. By this means the reaction could be conveniently controlled. In each reduction the temperature rose to the ebullition point and there was an abundant formation of the thick gelatinous methylate of magnesium. The time for the completion of the reactions varied from five to forty-five minutes, the reductions being more rapid in concentrated than in dilute solutions.

After all traces of magnesium had disappeared and the evolution of hydrogen had ceased the return condensor was turned down and the methyl alcohol was distilled off over an actively boiling water-bath. The contents of the flask was then transferred to an evaporating dish and dried over the water-bath and thoroughly pulverized. The reduction-products containing any unreduced nitrocompound were completely extracted from the residue of magnesium methylate by means of some suitable solvent, generally ether. The combined extracts were concentrated to a small volume which was subjected to steam distillation. By this means the nitrocompounds which were volatile with steam could be separated from the reduction-products. Extraction of the steam distillate with ether and subsequent freeing of the extract from ether by means of distillation yielded the unreduced nitrocompound.

The steam distillation residue was then dissolved in some suitable solvent and by means of fractional crystallization the reduction-products were recovered therefrom. After purification by recrystallization they were identified by their melting points and other wellknown properties.

A. NITROBENZENE IN METHYL ALCOHOL. DILUTE SOLUTION

One-fourth of a gram molecule of nitrobenzene (31 gm) was dissolved in 620 cubic centimeters of methyl alcohol contained in a 2 litre round bottomed flask equipped with a return condensor. 18 grams of powdered megnesium was added and the reaction began immediately without any application of heat and continued with increased energy so that cooling was necessary. The reaction mixture became yellow-red in color and was of a thick gelatin consistency. In the course of about 30 minutes all traces of magnesium had disappeared. The reaction mixture had a slight odor of nitrobenzene. It was accordingly heated on an actively boiling water-bath for 15 hours, and at the end of this time the nitrobenzene odor was still perceptible.

The condensor was then turned down and all the methyl alcohol was distilled off. After transferring the contents of the flask to a large evaporating dish in which they were thoroughly dried and pulverized, the reduction-products were completely extracted with boiling ether and the extracts were concentrated to a small volume which was subjected to steam distillation.

Azobenzene was found to be volatile with steam but some azoxybenzene is carried over with it. Hence the steam distillate contained an excess of azobenzene and some azoxybenzene which were extracted by shaking up several times with ether, combining the extracts and distilling off the ether leaving a **mixture** of azo- and azoxybenzene. By dissolving this residue in methyl alcohol and subjecting the solution to rapid cold evaporation the azobenzene was made to crystallize before the azoxybenzene. By repetition of this process the azobenzene was separated from the azoxybenzene.

The steam-distillation residue was dissolved in methyl alcohol and from this solution azoxybenzene was obtained by rapid cold evaporation. After filtering off the crystals of azoxybenzene and repeating this process with the filtrate, more azoxybenzene was obtained. Finally a small amount of black tarry oil was left in the last filtrate from which no more crystals could be obtained.

The yield of azobenzene was 10 grams, or 43.95 percent of the theoretical. The yield of azoxybenzene was 7.8 grams or 31.30 percent of the theoretical.

B. NITROBENZENE IN METHYL ALCOHOL. DILUTE SOLUTION

In the preceding reduction (A) of nitrobenzene in methyl alcohol the reaction-mixture was purposely boiled for 15 hours upon the water-bath. In order to determine what effect if any this process of boiling has upon the final yield of reduction-products, the reduction was repeated as previously described using the same quantities of nitrobenzene, methyl alcohol and magnesium, but omitting the boiling of the reaction-mixture. The yields of the reduction-products were as follows:

Azobenzene,	10 grams;	43.95 percent of the theoretical
Azoxybenzene,	8 "	32.00 " " " "

In the preceding reduction the yields were:

Azobenzene,	10 grams;	43.95 perſent of the theoretical
Azoxybenzene	7.8 "	31.30 " " " "

From these results it must be concluded that the process of boiling the reaction mixture has no appreciable effect upon the final yield of reduction-products. This however does not afford any evidence as to what effect the magnesium methylate produced in the reaction has upon the nitrocompound present or te reduction products formed. This forms the next topic of investigation.

THE ACTION OF MAGNESIUM METHYLATE UPON NITROBENZENE

Nitrobenzene is reduced by sodium methylate in methyl alcohol solution to azoxybenzene in accordance with the following reaction:

$$4C_6H_5NO_2 + 3CH_3ONa = 2C_6H_5\overset{O}{N\text{-}N}C_6H_5 + 3HCOONa + 3H_2O$$

In reducing nitrocompounds in methyl alcohol solution by means of magnesium amalgam or metallic magnesium the methylate of magnesium is formed. Now if magnesium methylate acts similiarly to sodium methylate, as was previously suggested, then an explanation is afforded as to why the reductions go one step further in methyl alcohol solutions than in ethyl alcohol solutions where the ethylate of magnesium was not formed.

9 grams of powdered magnesium were brought into reaction with 300 cubic centimeters of methyl alcohol as previously described in the preparation of magnesium methylate. After the reaction

was completed 15.5 grams of nitrobenzene were addedto magnesium methylate in methyl alcohol and the mixture was heated at boiling temperature (with reflux condensor) on the water-bath for fifteen hours. During the heating there was no perceptible change in color.

The methyl alcohol was then distilled off an the residue completely extracted with ether. After distilling off the ether from the combined extracts there was obtained 15 grams of a dark yellow oil, smelling strongly of nitrobenzene, and distilling at 206°C. This identifies the recovered oil as nitrobenzene, and the amount recoveredwas 96.77 percent of the quantity started with.

This result would indicate that magnesium methylate has little if any reducing action at all upon nitrobenzene. Its action upon azoxybenzene was next investigated.

THE ACTION OF MAGNESIUM METHYLATE UPON AZOXYBENZENE

The amount of magnesium methylate here prepared was the quantity that would be formed inthe reduction of nitrobenzene in methyl alcohol, using sufficient magnesium to theoretically reduce the nitrocompound to aniline. One eighth gram molecule quantities were used, namely 9 grams of magnesium being converted into the methylate by its action with methyl alcohol, 300 cubic centimeters of which were used. After the magnesium was dissolved 12.5 grams of azoxybenzene were added to the magnesium methylate in methyl alcohol and the mixture was boiled on the water-bath for fifteen hours with return-condensor.

After this the condensor was turned down and the methyl alcohol was distilled off. Extraction of the residue and evaporation of the ether extracts to dryness gave 12.5 grams of azoxybenzene, the same quantity with which the experiment was started. The recovered azoxybenzene had a slight isonitrile odor. In Conclusion, magnesium methylate has no action upon azoxybenzene.

REDUCTION OF NITROBENZENE IN METHYL ALCOHOL CONCENTRATED SOLUTION

25 grams of nitrobenzene were dissolved in 250 cubic centimeters of methyl alcohol contained in a two litre round bottomed flask equipped with return condensor, and 14.8 grams of powdered magnesium were added. A violent reaction begam immediately, cooling by submersion of the flask containing the reaction mixture was at once necessary, and in the course of ten minutes the magnesium had entirely disappeared and there was left in the flask a thick red gelatinous paste. The odor of nitrobenzene had entirely disappeared.

The methyl alcohol was then distilled off and the residue was througly dried in an evaporating dish upon the water-bath, pulverized, and the reduction product extracted from the methylate of magnesium with ether. The extracts were combined and evaporated to dryness leaving a mass of red crystals. These were recrystallized from methyl alcohol in beautiful red plates having a melting point of 68°C. The reduction product was azobenzene; 18 grams in quantity, or 97.30 percent of the theoretical.

In the preceding reduction (concentration = 1 gram solute to 20cc of solvent) both azoxy- and azobenzene were obtained. In this last reduction of nitrobenzene (concentration = 1 gm. solute to 10cc of solvent) azobenzene alone was obtained. From these results it must be concluded that the extent of the reduction depends upon the degree of concentration of the solutions.

A. ORTHONITROTOLUENE IN METHYL ALCOHOL. DILUTE SOLUTION

One fourth of a gram molecule of orthonitrotoluene (34 gram) was dissolved in 680 cubic centimeters of methyl alcohol contained in a 2 1/2 litre round bottomed flask equipped with a return condensor. 18 grams of powdered magnesium was added and the reaction began at once and proceded quietly for ten minutes. Then cooling became necessary as the reaction was becoming vigorous. The reaction mixture became yellow-red in color and thickly gelatinous in consistency. In the course of half an hour the reduction was completed.

After distilling off the excess of methyl alcohol a pasty red residue was left. This was dried and pulverized and subjected to repeated extractions with ether until the extracts which were red in color at first had become colorless. The extracts were combined, concentrated to a small volume, and subjected to steam distillation. Steam-distillation was continued until the distillate no longer had the odor of nitrotoluene.

Extraction of the steam distillate with ether and distillation of the ether extract yielded 6.5 grams of orthonitrotoluene, the amount unattacked in the reduction.

The steam-distillation residue was also extracted with ether and upon allowing this extract to stand for several days a mass of red monoclinic prisms crystallized out. These were filtered off, washed with methyl alcohol and dried. The melting point was 55°C. This identified the reduction-product as orthoazotoluene. By concentration of the filtrate and rapid cold evaporation more azotoluene was obtained. The yield was 17 grams or 64.76 percent of the theoretical. 6.5 grams or 19.11 percent of orthonitrotoluene was recovered.

B. ORTHONITROTOLUENE IN METHYL ALCOHOL. CONCENTRATED SOLUTION

One fourth of a gram molecule of orthonitrotoluene, (34 grams) was dissolved in 340 cubic centimeters of methyl alcohol and 18 grams of magnesium were added. The reaction in this reduction was much more energetic then in the preceding reduction. This was due to the increased concentration of the solution of orthonitrotoluene. Cooling was necessary during almost the entire course of the reduction which was completed in about twanty minutes. The reaction-mixture was yellow-red in color and very thick in consistency.

The reduction product, chiefly orthoazotoluene, was recovered as described in the previous reduction. The yield was 18 grams or 68.57 percent of the theoretical. In addition to the orthoazotoluene there was also obtained from the final filtrate 4 grams of dark red oil from which no more crystals of orthoazotoluene could be obtained. From the steam distillate 2 grams or 5.88 percent of orthonitrotoluene was recovered.

The results of these two reductions of orthonitrotoluene in methyl alcohol solution; A, dilute solution; B, concentrated solution are:

A. Orthoazotoluene	64.76 percent of the theoretical
B. Orthoazotoluene	68.57 " " " "
A. Orthonitrotoluene (recovered)	19.11 percent
B. Orthonitrotoluene "	5.88 "

A. REDUCTION OF PARANITROTOLUENE IN METHYL ALCOHOL. DILUTE SOLUTION

One fourth of a gram molecule of paranitrotoluene (34 grams) was dissolved in 680 cubic centimeters of methyl alcohol and 18 grams of magnesium were added. The reaction began slowly but proceded with increasing energy and in the course of about fifteen minutes cooling was necessary. The reaction mixture rapidly became yellow in color and gelatinous in consistency. After all the magnesium had disappeared the methyl alcohol was distilled off and the residue was dried over the water-bath and then pulverized. The light yellow powder thus obtained had a slight odor of paranitrotoluene.

After thoroughly extracting with ether, combining the extracts and distilling off all of the ether there was left a solid mass of yellow-red crystals. These were transferred to a small flask and subjected to steam-distillation in order to free the reduction products from the unreduced paranitrotoluene which was volatile with steam.

Extraction of the steam distillate with ether and subsequent evaporation of the extract gave 2 grams or 5.88 percent of unreduced paranitrotoluene. The liquid reduction products in the flask became solid upon cooling. They were filtered off and dissolved in just enough boiling ethyl alcohol to take them completely into solution. Upon allowing this solution to cool slowly a mass of red fine needle shaped crystals separated out. These were filtered off and recrystallized from ethyl alcohol and were found to have a melting point of 144°C. This identifies the product as paraazotoluene.

By combination of the filtrates obtained from paraazotoluene with the first filtrate, concentration of the combined filtrates to a smaller volume, and subsequent cooling, there were obtained more crystals of paraazotoluene, but the quantity was very small. In this way 6 grams or 22.83 percent of the theoretical yield of paraazotoluene was obtained.

Upon repeated concentration of the filtrate from the parazotoluene and subsequent crystallization there was obtained 17 grams of fine light yellow crystals melting at 75°C. They were paraazoxytoluene. The yield was 60.53 percent of the theoretical.

The separation of paraazotoluene from paraazoxytoluene is easily effected since the former is difficultly soluble in ethyl alcohol. In some instances two crystallizations affected a complete separation of the azo- from the azoxycompound.

B. PARANITROTOLUENE IN METHYL ALCOHOL. CONCENTRATED SOLUTION

One fourth of a gram-molecule, 34 grams, of paranitrotoluene was dissolved in 340 cubic centimeters of methyl alcohol and 18 grams of magnesium were added. The reaction began at once and proceded with such violence that the flask had to be submerged in cold water during the reaction which was completed in about eight minutes. The reaction mixture was yellow in color and so thick that it could not be poured. After distilling off the methyl alcohol and drying the residue which was thoroughly extracted from ether, the reduction products were recovered as described in the preceding reduction of orthonitrotoluene in dilute methyl alcohol solution.

Only a trace of paranitrotoluene was recovered upon steam-distillation thus showing that this reduction was more complete than the preceding one.

Upon fractional crystallization of the steam distillation residue there was obtained 15 grams of paraazotoluene melting at 144°C. The yield was 57.14 percent of the theoretical. From the filtrates from the paraazotoluene 10 grams of fine light yellow crystals melting at 75°C, thus giving a yield of 35.39 percent of the theoretical for paraazoxytoluene.

The results of the reduction of paranitrotoluene in methyl alcohol, A, dilute solution, and B, concentrated solution are as follows:

A.	Paraazotoluene	22.85	percent of the theoretical
B.	Paraazotoluene	57.14	" " " "
A.	Paraazoxytoluene	60.53	" " " "
B.	Paraazoxytoluene	35.39	" " " "
A.	Paranitrotoluene (recovered)	5.88	percent
B.	Paranitrotoluene "	Trace	

Here again the results indicate that the reduction is more complete in concentrated than in dilute solution.

A. REDUCTION OF ORTHONITROANISOL IN METHYL ALCOHOL DILUTE SOLUTIONS

One fourth of a gram molecule (38 gram) of orthonitroanisol were dissolved in 640 cubic centimeters of methyl alcohol and 18 grams of magnesium were added. An energetic reaction began at once and continued with such violence that cooling was necessary during the entire course of the reaction which lasted fifteen minutes. A deep red colored gelatinous reaction-mixture resulted. The methyl alcohol was distilled off as usual and the residue was dried and completely extracted with ether. The ether extracts which were red became almost black in color upon standing in the air. This indicated the probable formation of a hydrazo-compound which is readily oxidizible to the deeply red colored azocompound. The combined ether extracts were concentrated to a small volume and subjected to steam-distillation until the odor of orthonitroanisol could no longer be detected in the volatile distillate. Extraction of the distillate with ether and subsequent distillation of the extract gave 10 grams or 26.31 percent of recovered orthonitroanisol.

The black tarry steam distillation residue was dissolved in boiling methyl alcohol and upon cooling very fine granular yellowish crystals separated out. These were filtered off and washed and found to melt at 103°C, the melting point of orthohydrazoanisol. Upon recrystallization they separated out in the form of small grayish leaflets which became black upon long exposure to the air, due to oxidation. The yield was 4 grams or 13.11 percent of the theoretical.

After no more crystals of hydrazoanisol could be obtained from the steam distillation residue there was left 10 grams of a thick black tar. This tar was treated with various solvents in the hope of isolating some reduction-product which proved unsuccessful.

B. ORTHONITROANISOL IN METHYL ALCOHOL. CONCENTRATED SOLUTION

One fifth of a gram molecule (30 grams) of orthotoluene was dissolved in 300 cubic centimeters of methyl alcohol and 14.5 grams of magnesium were added. The reaction in this instance went with almost explosive violence and all traces of magnesium had disappeared in four minutes. The reaction mixture was of a deep blood red color and so thick in consistency that it could not be poured.

After distilling off the methyl alcohol, drying the residue and completely extracting with ether, the residue was of a brownish red color. Upon treating the residue with dilute hydrochloric acid so as to dissolve the methylate of magnesium there was left 4.5 grams of a black tarry substance which was insoluble in the ordinary organic solvents.

The ether extracts were combined and concentrated to a small volume. Upon addition of methyl alcohol and rapid cold evaporation there were obtained 2.5 grams of red granular crystals. These were filtered off and recrystallized from methyl alcohol in the form of short fine needle crystals, deep red in color, and melting at 153°C, the melting point of orthoazoanisol. The yield was 2 grams or 8.26 percent of the theoretical.

The combined filtrates from the othoazoanisol were concentrated to a small volume and subjected to steam distillation until the odor of orthoanisol could no longer be detected in the volatile distillate. Extraction of the distillate with ether and subsequent distillation of the ether extract gave 7 grams or 23.33 percent of recovered orthonitroanisol.

The tarry steam distillation residue was dissolved in methyl alcohol and after repeated attempts at recrystallization only 2 grams of a product with a definite melting point could be obtained. The crystals thus obtained melted at 103°C and were identical with those of orthohydrazoanisol described in the preceding reduction. The yield was 8.16 percent of the theoretical.

The filtrates from the hydrazoanisol upon combination and evaporation to dryness gave 5.5 grams of tar, from which after various attempts no definite reduction product could be isolated. The total amount of tarry matter recovered was 10 grams.

The results of the reduction or orthonitroanisol in methyl alcohol, A, dilute solution; B, concentrated solution are as follows:

A. Ortho hydrazoanisol		13.11	percent	of	the	theoretical
B. Orthohydrazoanisol		8.26	"	"	"	"
A. Orthoazoanisol		-----	"	"	"	"
B. Orthoazoanisol		8.26	"	"	"	"
A. Orthonitroanisol,	(recovered)	26.31	"			
B. Orthonitroanisol	"	23.33	"			

The ratio of the amount of tarry products recovered in A to the amount recovered in B was as 4:5.

Here it is to be noted that the reduction of orthonitroanisol was more complete in concentrated than in dilute solution. Judging from the low yields of the reduction products and the large amounts of tarry substances produced, the reduction of orthonitroanisol in methyl alcohol solution by means of metallic magnesium is not a satisfactory process.

A. REDUCTION OF PARANITROANISOL IN METHYL ALCOHOL. DILUTE SOLUTION

One fourth of a gram molecule (38 grams) of paranitroanisol was dissolved in 640 cubic centimeters of methyl alcohol and 18 grams of magnesium were added. There was very little evidence of reaction, even after boiling the reaction-mixture. However, after heating for about twenty minutes the reaction began and proceeded with increasing energy so that cooling was necessary. In the course of twenty-five minutes the reaction was completed. The reaction-product was yellowish in color and thickly gelatinous in consistency.

After distilling off the methyl alcohol and drying the residue it was extracted continuously with boiling ligroin. These extracts when combined and evaporated to a small volume yielded beautiful flaky yellow crystals melting at 116°C, the melting point of para-azoxyanisol. Upon further extraction of the residue with ether, combination and concentration of the extracts, there was also obtained a mass of yellow needles which upon recrystallization were also found to melt at 116°. In this way 20 grams or 62.01 percent of the theoretical yield of paraazoxyanisol was obtained by extraction of the reduction mixture with the two solvents, ligroin and ether. The paraazoxyanisol was more soluble in ether than in ligroin, crystallizing from the former in yellow needles and from the latter in yellow flakes.

The filtrates from the paraazoxytoluene, from which no more of the azoxycompound could be obtained, were combined and concentrated to a small volume which was subjected to steam distillation, which was continued until the volatile distillate no longer had the odor of paranitroanisol. Upon extraction of the steam distillate with ether and subsequent distillation of the ether extract there was obtained 4 grams or 10.51 percent of recovered paranitroanisol.

B. PARANITROANISOL IN METHYL ALCOHOL. CONCENTRATED SOLUTION

One fourth of a gram molecule of paranitroanisol (38 grams) was dissolved in 320 cubic centimeters of methyl alcohol and 18 grams of magnesium were added. The reaction began at once and proceeded with almost explosive violence. Notwithstanding the fact that the flask containing the reaction mixture was submerged completely in ice cold water, part of the contents of the flask were thrown out through the long condensor. In the course of five minutes all traces of magnesium had disappeared, and a yellow pasty, almost solid reaction-mixture resulted. This was dried and extracted completely with ether. From the combined ether extracts there was obtained 20 grams of yellow needle crystals melting at 116°C, thus identifying the reaction product as paraazoxyanisol. The yield was 62.01 percent of the theoretical.

Upon concentration of the filtrates from the paraazoxyanisol and subsequent steam distillation as previously described there was obtained 2.5 grams or 6.58 percent of recovered paranitroanisol.

The results of reduction of paranitroanisol in methyl alcohol, A. dilute solution, B, concentrated solution, are as follows:

A,	Paraazoxyanisol	62.01 percent of the theoretical
B.	Paraazoxyanisol	62.01 " " " "
A.	Paranitroanisol (recovered)	10.51 percent
B.	Paranitroanisol "	6.58 "

In those reductions, while the peecentage yields of azoxy-compound are the same, it is to be noted that a larger amount of paranitroanisol was reduced in the concentrated than in the dilute solution and the amount of tarry matter formed was also greater in the concentrated than in the dilute-solution-reductions.

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A complete summary of the reductions of nitrobenzene, orthonitrotoluene, paranitrotoluene, orthonitroanisol and para-nitroanisol in methyl alcohol solutions, dilute and concentrated, by means of metallic magnesium in proportionately equivalent quantities, is found in the following table.

Nitrocompound	Reduction-products A. Dilute solution	Theoretical yield percent	Nitrocompound recovered percent	Reduction-products B. Concentrated solution	Theoretical yield percent	Nitrocompound recovered percent
Nitrobenzene	Azobenzene Azoxybenzene	43.95 31.30	----	Azobenzene Azoxybenzene	97.30 -----	---
Orthonitrotoluene	Orthoazo-toluene	64.76	19.11	Orthoazo-toluene	68.57	5.88
Paranitrotoluene	Paraazotoluene Paraazoxytoluene	22.85 60.53	5.88	Paraazotoluene Paraazoxytoluene	60.53 35.39	Trace
Orthonitroanisol	Orthohydrazo-anisol Orthoazoanisol	13.11 -----	26.31	Orthohydrazo-anisol Orthoazoanisol	8.16 8.26	23.33
Paranitroanisol	Paraazoxyanisol	62.01	10.51	Paraazoxyanisol	62.01	6.58

From a comparison of the results thus far obtained it is evident that the nature and extent of the reduction of a nitrocompound in methyl alcohol by means of metallic magnesium is dependent upon the degree of concentration of the solution. It is also to be noted that in the reductions of ortho-nitrocompounds no corresponding azoxy-compounds were obtained. On the other hand it is seen from the percentages of nitrocompounds recovered that in both dilute and concentrated solutions, the para nitrocompounds were more completely attached then were the orthonitrocompounds.

It has been shown that the methylate of magnesium, formed in these reductions when previously prepared, has no reducing action upon nitrobenzene or azoxybenzene. This was further verified by carrying out reductions of nitrobenzene, where in one instance the reaction-mixture was heated upon the water bath at boiling temperature for 15 hours, while in the other instance, the process of boiling was omitted. In each case the percentage yields of the reduction products were practically the same. These experiments were repeated with both ortho-and paranitrotoluene and again the percentage yields of reduction products were the same.

Since, in these reductions, metallic magnesium does not react with methyl alcohol until the aromatic nitrocompound has been added, it may be possible that the methylate of magnesium in its state of formation has some reducing action upon the nitrocompound which is present. This point will be investigated at some future time.

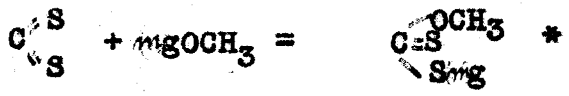
A NEW SYNTHESIS OF ETHYL METHYL XANTHIC ESTER

The fact has been pointed out that metallic magnesium and methyl alcohol do not react under the ordinary conditions of temperature and pressure, but upon the addition of a small particle of iodine, or a few drops of a nitrocompound, reaction begins, hydrogen is evolved and the methylate of magnesium is formed. Certain alkyl halides and even carbon bisulphide induce the reaction between magnesium and methyl alcohol.

It is the reaction between carbon bisulphide, methyl alcohol and magnesium that is now to be considered. While making preliminary tests a marked difference in the appearance of the reaction-product was noticed according as magnesium was allowed to react with a dilute or a concentrated solution of carbon bisulphide in methyl alcohol. In the case of the dilute solution the reaction product was light-yellow in color and very thickly gelatinous, this latter property being due to the supposed formation of magnesium methylate. On the other hand where carbon disulphide was present in excess, no precipitate was formed and the solution was of a deep blood red color.

These observations led to the conclusion that when magnesium reacts with a solution of carbon bisulphide in methyl alcohol, magnesium methylate tends to form, and this then in turn, in the presence of an excess of carbon disulphide, reacts to form magnesium methyl xanthate. These reactions may be represented as follows:

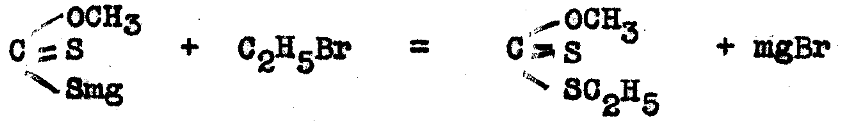
$$Mg + 2CH_3OH = Mg(OCH_3)_2 + H_2$$



$$C\begin{smallmatrix}S\\S\end{smallmatrix} + mgOCH_3 = C{=}S\begin{smallmatrix}OCH_3\\Smg\end{smallmatrix} \;*$$

* mg = 1/2 Mg

Now if magnesium methyl xanthate is thus formed it should in turn react with an alkyl halide, such as ethyl bromide, to form an ester of the hypothetical methyl xanthic acid, namely ethyl methyl xanthic ester, in accordance with the following reaction:



$$C\begin{array}{l}\nearrow OCH_3\\ = S\\ \searrow Smg\end{array} + C_2H_5Br = C\begin{array}{l}\nearrow OCH_3\\ = S\\ \searrow SC_2H_5\end{array} + mgBr$$

That such reactions do actually take place with the final production of ethyl xanthic ester is evident from the following experimental part.

EXPERIMENTAL PART

One half of a gram molecule (12 grams) of magnesium; 152 grams of carbon bisulphide, (twice the theoretical amount in order to insure an excess); and 500 cubic centimeters of methyl alcohol were placed in a two litre round bottomed flask equipped with a long reflux condensor. The reaction began immediately and proceded with increasing energy so that in the course of about ten minutes the contents of the flask were boiling violently. Five minutes later all of the magnesium had disappeared and the resulting reaction-mixture which was of a clear deep red brown color was heated to boiling temperature upon the water-bath for two hours in order to effect complete reaction between the carbon bisulphide and any magnesium methylate that was in solution.

After the contents of the flask had cooled down to the room temperature, 120 grams of ethyl bromide was added. This amount was a slight excess over that actually required to combine with the magnesium as methyl xanthate. As soon as the ethyl bromide was added the contents of the flask became warmer and in the course of a few minutes were boiling actively. The color of the solution rapidly changed from deep red brown to pale yellow. The reaction mixture was again boiled for two hours to insure complete reaction between the ethyl bromide and the magnesium methyl xanthate.

In order to obtain the ethyl methyl xanthic ester thus formed, a litre of water slightly acidified with sulphuric acid was added to the reaction mixture in the flask. A heavy yellow oil separated out and was extracted with ether in a separatory funnel. The ether solution thus obtained after being neutralized, washed with water, and filtered, was subjected to distillation.

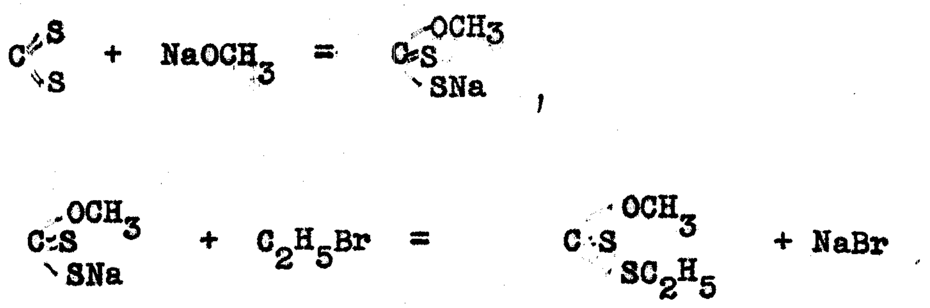
By distillation at boiling-water-bath temperature the ester was freed from ether, carbon-bisulphide, ethyl bromide, and methyl alcohol. Further distillation with direct flame yielded 85 grams of a light yellow oil, distilling at 184°C, the boiling point of ethyl methyl xanthic ester. The yield was 62.50 percent of the theoretical.

Further distillation to 200°C resulted in the decomposition of the residue in the distilling flask, a very small quantity of distillate passing over.

In conclusion metallic magnesium reacts with a solution of carbon bisulphide in methyl alcohol to form magnesium methyl xanthate which in turn reacts with ethyl bromide to form ethyl methyl xanthic ester, in accordance with the reactions previously indicated. Other alkyl halides were found to be applicable in the syntheses of analagous esters.

This synthesis affords an example of the analogy between magnesium and sodium or potassium methylates which later are commonly used in the preparation of various xanthic esters in accordance with the following analogous reactions:

$$Na + CH_3OH = NaOCH_3 + H;$$

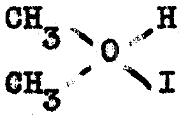


$$\mathrm{C}\begin{matrix}S\\S\end{matrix} + NaOCH_3 = \mathrm{C}\begin{matrix}OCH_3\\S\\SNa\end{matrix},$$

$$\mathrm{C}\begin{matrix}OCH_3\\S\\SNa\end{matrix} + C_2H_5Br = \mathrm{C}\begin{matrix}OCH_3\\S\\SC_2H_5\end{matrix} + NaBr$$

A NEW QUADRIVALENT OXYGEN COMPOUND

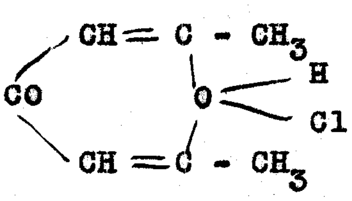
Compounds supposed to contain quadrivalent oxygen atoms have been known for sometime, and are termed oxonium salts. Friedel, who predicted the influence of temperature upon valence, first called attention to the fact that methyl ether and hydrochloric acid gas entered into combination. Since then dimethyl ether and hydriodic acid have been brought into reaction at low temperatures and a compound melting at -15°C was isolated as the product of the reaction. Upon careful analysis it was shown to have the constitution $C_2H_6O.HI$, which represented structurally would be:



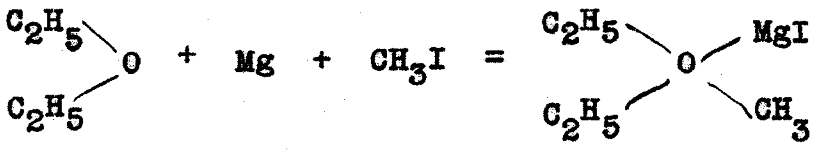
,

a compound containing one quadrivalent oxygen atom.

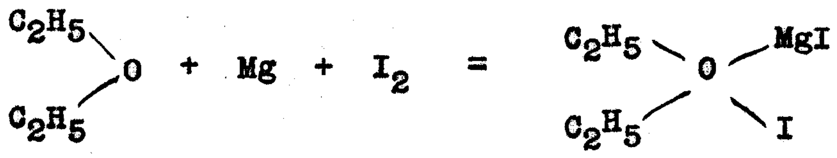
Another organic compound, dimethyl pyrone, is characterized by the formation of salts with acids, which are formed by dissolving dimethylprone in an aqueous solution of hydrocloric or oxalic acids. Collie and Tickle, the discoverers of these compounds accordingly assumed the tetravalency of the oxygen atom enclosing the carbon chain and attributed to dimethylprone the following constitution:



In addition to these examples, Bayer and Villiger have shown that compounds containing oxygen belonging to various classes of organic bodies, such as alcohols, aldehydes, esters, etc., are able to yield definite crystallized compounds with complex acids such as ferrocyanic acid, and they assume that the oxygen in these compounds is tetravalent. Baeyer and Villiger are also of the opinion that the Griguard ether compounds of alkyl magnesium halides are oxonium derivatives. Ether, absolutely anhydrous, is indispensible to the Griguard reaction, and is found to be held in combination with the magnesium and alkyl halide. This important and well known reaction is illustrated as follows:



This reaction suggested the idea that possibly free iodine and magnesium might react with absolute ether to form an analogous compound containing a quadrivalent oxygen atom, as follows:



Accordingly a small quantity of iodine was dissolved in a little absolute ether and upon the addition of a small portion of powdered magnesium, a vigorous reaction followed, and sufficient heat was evolved to cause the ether to boil. In a very short time the color of the iodine had entirely disappeared. The unattacked excess of magnesium was filtered off and upon evaporation of the filtrate, a solid white crystalline mass was obtained which was extremely deliquescent. Upon the addition of a few drops of water to the crystalline mass, violent decomposition of the compound resulted with a hissing sound and the evolution of ether vapor. This was evidence that magnesium, iodine and ether had reacted to form some compound. Accordingly the reaction was repeated upon a more complete scale.

A three litre round bottomed flask was equipped with a long reflux condensor and a glass stoppered droppong funnel. To the upper end of the condensor was fitted a calcium chloride tube to prevent moisture from entering the apparatus. One gram molecule (24.3 grams) of magnesium was placed in the flask and covered with 500 cubic centimeters of absolute ether. Then 253 grams of iodine, the equivalent of 1 gram molecule of magnesium, was dissolved in 1500 cubic centimeters of absolute ether, and this solution was added to the contents of the flask, thru the glass stoppered funnel, in portions of 50 cubic centimeters each. After each addition there was a vigorous reaction accompanied by boiling of the reaction mixture. In the course of a few minutes the color of the iodine disappeared, whereupon another portion of iodine solution was admitted thru the dropping funnel. At times the reaction was so energetic that the flask had to be submerged in cold water.

The last portions of the iodine solution that were added reacted very slowly, even when heat was applied, and not until an excess of magnesium was added did the color of the iodine solution entirely disappear, thus showing the completion of the reaction. The contents of the flask were allowed to cool and in the course of three hours the bottom of the flask was covered with a yellowish white crystalline mass from which extended in various directions spear-like crystals, varying from 2.5 to 8.0 centimeters in length and from 0.5 to 1.0 centimeters in thickness at the base, from which they tapered to a point.

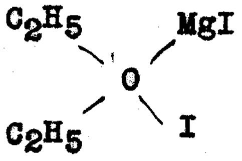
Upon standing in the light the compound turned brown in color, due to the separation of iodine. However upon boiling in ether with magnesium, the brown color disappeared. Upon cooling rapidly, the magnesium-ether-iodide compound separated out in small prismatic needles, which were filtered off on a Buchner funnel with suction and dried in a stream of air which was freed from carbon dioxide and moisture. This new compound, thus originally prepared, has been designated as magnesium-ether-iodide. It was extremely deliquescent. A small quantity placed in a watch glass in the open air soon becomes liquid. Upon the addition of a few drops of water the compound is violently decomposed with the evolution of heat, ether vapor, and a solution of magnesium iodide in water remains. When magnesium-ether-iodide is heated in a test tube it melts to a clear yellow liquid and ether is evolved. As heating is continued the liquid becomes dark brown in color, and when all of the ether is driven out of the compound, iodine fumes come off, and there is left a white solid residue. Magnesium-ether-iodide was soluble in anhydrous benzene, and upon boiling the solution the only change perceptible was a slight violet color of the benzene solution, due to partial dissociation of the iodine. Ether was not evolved upon boiling the benzene solution but the addition of a few drops of water caused an energetic decomposition with an evolution of ether vapor.

The analysis of the magnesium-ether-iodide was effected by decomposing the compound with water and precipitating the iodine by means of silver nitrate solution. The magnesium was precipitated as magnesium ammonium phosphate and weighed as pyrophosphate.

The results of the analyses were as follows:

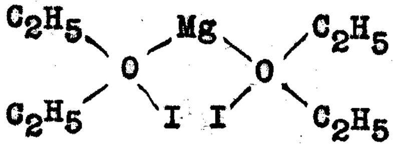
DETERMINATION OF MAGNESIUM	I.	II.
Weight of compound taken for analysis	1.3751 gm	1.4649 gm
Weight of $Mg_2P_2O_7$	0.3603 "	0.3935 "
Percent of Mg	5.66	5.81
DETERMINATION OF IODINE		
Weight of compound taken for analysis	1.6786 gm	1.7462 gm
Weight of AgI	1.8492 "	1.9170 "
Percent of I_2	59.52	59.31

Two possible formulae are suggested for the magnesium-ether-iodide, namely:



Formula I

and



Formula II

According to Formula I the compound should contain:

Mg, 6.90 percent I, 73, 71 percent

According the Formula II, the compound should contain:

Mg, 5.70 percent I, 59,53 percent Found,

Mg { 5.66 percent
5.81 "

I { 59.52
59.31

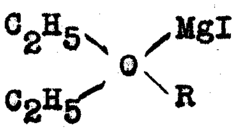
From these results it is evident that Formula II, $MgI_2 \cdot 2(C_2H_5)_2O$ undoubtedly is the correct one.

The determination of the percent of ether in magnesium ether iodide was a rather difficult problem. Owing to its being so extremely deliquescent it could not be weighed out directly into a platinum boat for subsequent combustion.

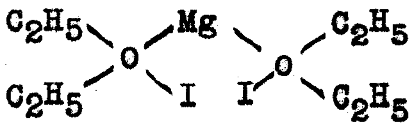
The percent of ether was determined directly by preparing a large quantity of the compound and weighing it in a closed distilling flask. This flask was then attached to a long condensor and upon the addition of water through a glass stoppered dropping funnel, the compound was decomposed with the liberation of ether which distilled off and was caught in a weighed receiver, submerged in a freezing mixture the temperature of which was -22°C. The last traces of ether were driven over by gently heating the distilling flask upon the water bath. The water-vapor which was volatile with the ether was frozen out, and the ether remaining was weighed in the sealed receiver. Two determinations were made in this manner, the first by decomposing the compound with water, and the second by direct heating of the compound in the distilling flask until no more ether was evolved and the compound began to dissociate giving off fumes of iodine. The results of these determinations were as follows:

DETERMINATION OF ETHER	I	II
Weight of compound	54.7537 gm	40.1295 gm
Ether evolved	18.1395 "	14.4082 "
Percent of ether. Found	33.13	35.73
Percent of ether. Theoretical	34.76	34.76

From these results the empirical formula of magnesium ether iodide is $MgI_2 \cdot 2(C_2H_5)_2O$. From the similarity of its method of formation to that of the Grignard magnesium-alkyl-halide-ether compound one would infer that the two molecules of ether are held in combination with the magnesium and iodine by means of the ether oxygen atom which has become quadrivalent, thus:

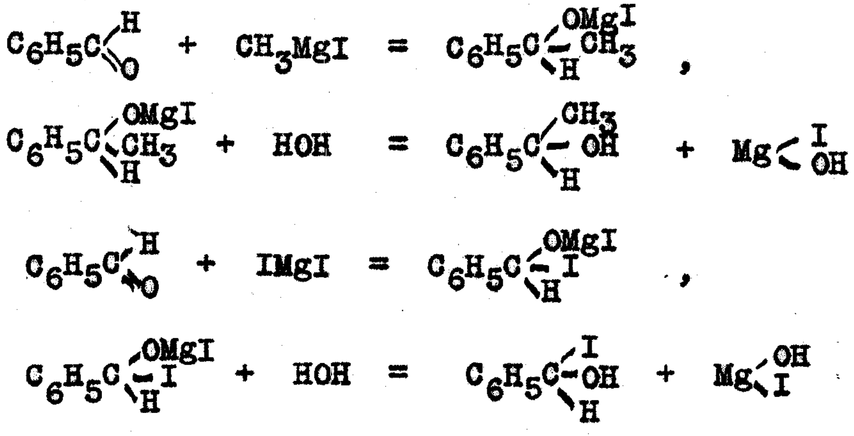


Grignard compound
according to Baeyer



Supposed formula of
magnesium-ether-iodide

Among the many reactions into which the Griguard compounds enter with various organic compounds, the most common are those with bodies containing the carbonyl group. Magnesium-ether-iodide has also been found to react with various compounds containing the carbonyl group but the resulting complexes upon decomposition with water have been so extremely unstable that their separation and identification so far has proved unsuccessful. Notwithstanding this, there is some evidence that magnesium-ether-iodide reacts with benzaldehyde to form a temporarily stable α-iodo alcohol, in accordance with the following reaction which is given in parallel with the Grignard reaction with benzaldehyde:



$$C_6H_5C\overset{H}{\underset{O}{<}} + CH_3MgI = C_6H_5C\overset{OMgI}{\underset{H}{\leftarrow}}CH_3 ,$$

$$C_6H_5C\overset{OMgI}{\underset{H}{\leftarrow}}CH_3 + HOH = C_6H_5C\overset{CH_3}{\underset{H}{\leftarrow}}OH + Mg\overset{I}{\underset{OH}{<}}$$

$$C_6H_5C\overset{H}{\underset{O}{<}} + IMgI = C_6H_5C\overset{OMgI}{\underset{H}{\leftarrow}}I ,$$

$$C_6H_5C\overset{OMgI}{\underset{H}{\leftarrow}}I + HOH = C_6H_5C\overset{I}{\underset{H}{\leftarrow}}OH + Mg\overset{OH}{\underset{I}{<}}$$

EXPERIMENTAL PART

According to theory, 50 grams of magnesium-ether-iodide would require 12.4 grams of benzaldehyde for the completion of the above reaction. Fifty grams of freshly prepared magnesium-ether-iodide was treated with 10 grams of benzaldehyde in a 1/4 litre round bottom flask. The magnesium-ether-iodide was dissolved upon the addition of the benzaldehyde and the thick syrupy solution which was of a yellow-brown color became very warm. The flask was attached to a return condensor and the mixture was gently heated to boiling. Ether was distilled off and the reaction mixture became reddish-brown in color.

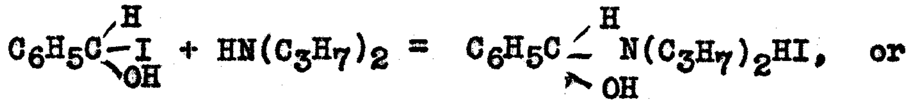
After heating for half an hour the contents of the flask were poured upon shaved ice and an energetic reaction followed. A yellow precipitate formed and was filtered off with the ice on a Buchner filter. The contents of the filter were extracted with ether and upon evaporation of the ether there was left a brown-red oil characterized by a peculiar odor and extremely irritating properties causing a copious flow of tears.

Upon subjecting a few drops of this oil to distillation iodine fumes were copiously evolved and then benzaldehyde distilled off. On the other hand, when a solution of silver nitrate was added to a portion of the ether solution of the reaction product, silver iodide was precipitated. Upon separating the ether layer from this silver iodide precipitate and distilling off the ether, benzaldehyde was left and the former irritating properties of the original ether solution were gone. These facts indicated the existence of hydriodic acid and benzaldehyde in the compound, resulting from the decomposition of the reaction mixture. Whether or not benzaldehyde and hydriodic acid were in combination as α-iodo benzyl alcohol yet remains to be proved.

In order to determine this the ether solution was treated with mercuric oxide and the mixture was allowed to stand for 12 hours in order that the mercuric oxide might take up any free hydriodic acid. This ether solution of the red oil was perfectly colorless after the treatment with mercuric oxide thus showing that iodine had been removed by the oxide.

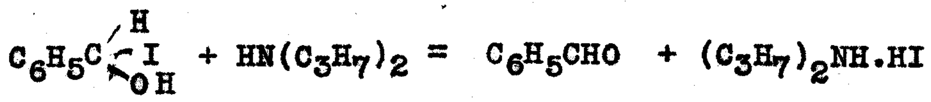
Upon distillation of a portion of this ether solution there remained a yellow oil which upon further heating was decomposed with an abundant evolution of iodine vapor. Another portion of the ether solution was treated with an excess of dipropyl amine. Now if the ether solution contained the α-iodo benzyl alcohol, then two possible reactions might occur, namely, (a) and (b).

(a)



$$C_6H_5C\begin{smallmatrix}H\\ I\\ OH\end{smallmatrix} + HN(C_3H_7)_2 = C_6H_5C\begin{smallmatrix}H\\ N(C_3H_7)_2HI\\ OH\end{smallmatrix}, \text{ or}$$

(b)



$$C_6H_5C\begin{smallmatrix}H\\ I\\ OH\end{smallmatrix} + HN(C_3H_7)_2 = C_6H_5CHO + (C_3H_7)_2NH.HI$$

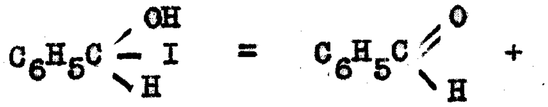
Upon the addition of the dipropyl amine there was no apparent reaction at first, but soon there was noticed a slight turbidity. In the course of half an hour a sediment had formed and later fine crystals were deposited. These needle shaped short fine crystals continued to deposit on the sides of the test tube for about three hours, when they were filtered off, washed with ether and dried. They had neither the odor of benzaldehyde nor the characteristic odor of dipropyl amine. However upon treating the crystals with dilute sodium hydroxide solution, dipropyl amine was found, and no traces of benzaldehyde could be detected. Hence the crystalline precipitate was dipropylamine hydriodide: $(C_3H_7)_2NH.HI$.

The filtrate from the dipropyl amine hydroiodide was found to contain the benzaldehyde. These facts are in complete accord with the supposed reaction (b) indicated on the preceding page, from which the conclusion is drawn that magnesium-ether-iodide and benzaldehyde react to form a complex which is decomposed by water with the formation of a compound of benzaldehyde and hydriodic acid which is probably the hitherto unprepared α- iodo benzylalcohol.

Various attempts have been made to prepare α- halide alcohols but have been unsuccessful from the fact that they are readily dissociated into an aldehyde and the halide acid in accordance with the reaction:

$$R\text{-}C{<}^{OH}_{H}{-}X \quad R\text{-}C{\lessdot}^{O}_{H} + HX$$

. This reaction explains the result of heating the compound of benzaldehyde and hydriodic acid,



$$C_6H_5C{<}^{OH}_{H}{-}I = C_6H_5C{\lessdot}^{O}_{H} + HI$$

, whereupon iodide vapor and benzaldehyde were obtained.

There are other indications that magnesium-ether-iodide is analagous in composition to the Grignard compounds. Evans and Lowenstein found that when an ether solution of an alkyl magnesium halide was added to an ether solution of quinone a dirty greenish blue precipitate was formed which when decomposed with water gave hydroquinone. Magnesium-ether-iodide in ether solution, when added to an ether solution of quinone, also gives a similiar dirty greenish blue precipitate, the composition of which yet remains to be determined.

ACTION OF AMMONIA AND ANILINE UPON MAGNESIUM-ETHER-IODIDE

When dry gaseous ammonia is passed into an ether solution of magnesium-ether-iodide, heat is evolved and a heavy white precipitate is instantly formed. If an excess of ammonia is passed thru the solution and the precipitate filtered off, the filtrate is found to contain no traces of magnesium-ether-iodide.

The filtrate when dried was an amorphous white powder smelling strongly of ammonia. When a small portion is added to water there is a slight evolution of heat and a more pronounced odor of ammonia. Upon boiling magnesium hydroxide is precipitated and ammonia is evolved. After neutralizing with dilute acid, silver iodide is precipitated upon the addition of silver nitrate.

When the dry compound is heated in a test tube, ammonia is given off and a yellowish powder is left which upon further heating is decomposed with the evolution of iodine fumes and ammonia. No combustible gases were evolved.

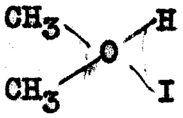
Several analyses of this ammonia-magnesium-iodide compound were made and it was impossible to secure uniform results. When freshly prepared, the compound analysed gave results approximating to the formula $MgI_2 6NH_3$. After allowing the compound to remain in a sulphuric acid dessicator for several days the analyses were repeated and varying results were obtained approximating to the formulae $MgI_2.5NH_3$ and $MgI_2.4NH_3$. These varying results are due to the instability of the compound.

Compounds of magnesium iodide with various aliphatic and aromatic amines were obtained by simply adding an ether solution of an amine to an ether solution of magnesium-ether-iodide whereupon the complex compounds were immediately precipitated. The compound of magnesium iodide and aniline upon analysis gave results approximating to the formula $MgI_2.4C_6H_5NH_2$. The results of this analysis were as follows:

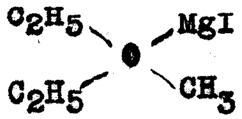
Weight of substance	0.1138 gm	0.1346 gm.
Weight of MgO	0.0078 gm	0.0091 gm
Percent Mg	4.11	4.05
Iodine determined volumetrically	1cc$AgNO_3$ =	.0697 gm iodine
Weight of substance	0.1701 gm	0.1626
No.cc $AgNO_3$ solution	9.976 cc	9.485 cc
Percent Iodine	40.87	40.65
Theory for $MgI_2.4C_6H_5NH_2$,	Mg. 3.73 percent	I = 39.00 percent

Various compounds of inorganic salts with ether have been known for many years but structural formulae have not been assigned to them since the ether has been regarded simply as "ether of crystallization". However since the oxygen atom in such ether compounds as $(CH_3)_2O.HI$ and the Griguard complexes are now commonly regarded as quadrivalent, structural formulae containing quadrivalent oxygen atoms might be suggested for the inorganic salts containing ether. Thus for instance:

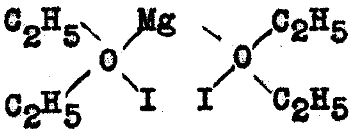
$(CH_3)_2).HI$



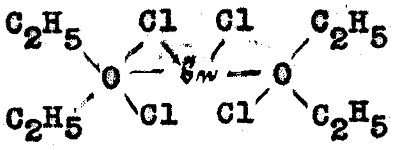
$(C_2H_5)_2O\cdot CH_3MgI$



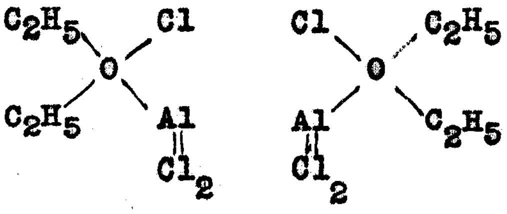
$(C_2H_5)_2O\ 2\cdot MgI_2$



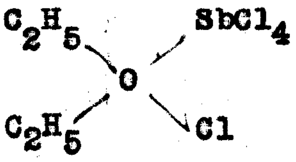
$[(C_2H_5)_2O]_2\ SnCl_4$*



$[(C_2H_5)_2O]_2\ Al_2Cl_6$



$(C_2H_5)_2O\cdot\ SbCl_5$**



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* Comptes Rendus XXI. 371: LII, 396: LVII, 537. LX,300

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