[Contribution from the Chemical Laboratory of Iowa State College]

THE REACTION BETWEEN AROMATIC NITRO COMPOUNDS AND ORGANOMAGNESIUM HALIDES

By Henry Gilman and Roy McCracken

Received July 19, 1928 Published March 6, 1929

Introduction

The reaction between aromatic nitro compounds and organomagnesium halides is complex and confusing. Earlier work by several others shows wide differences in the nature of the final products. The present results indicate that the course or courses of the reaction vary considerably with such conditions as temperature, relative quantities of reagents, type of Grignard reagent (alkyl or aryl MgX) and on whether the RMgX compound is prepared prior to or during the reaction with the nitro compound.

Historical Part

Yocich[1] obtained an unidentified hydrocarbon of the formula $C_{16}H_{10}$, melting at 87–88.5°, from the reaction between nitrobenzene and phenylacetenylmagnesium bromide, $C_6H_5C{\equiv}CMgBr$. We have repeated this work and have shown that his hydrocarbon was diphenyl-di-acetylene, $C_6H_5C{\equiv}C{-}C{\equiv}CC_6H_5$. Oddo[2] isolated a yellow compound from the reaction between nitrobenzene and ethylmagnesium iodide. This compound, to which he ascribed the formula $C_6H_5N({=}O)C_2H_5(OMgI)$, gave, on hydrolysis, ethylaniline and a red uncrystallizable oil that was not identified.

Pickard and Kenyon[3] in a short note containing the results of some preliminary experiments of the action of RMgX compounds on aromatic nitro compounds state that *p*-nitrotoluene reacts very vigorously with organomagnesium halides in ether solution, forming an amorphous yellow compound. This compound when hydrolyzed with acids yielded principally *p*-nitrosotoluene, *p*-tolylhydroxylamine, *p,p'*-azoxytoluene and *p*-toluidine. It is unfortunate that further details were not published because the products obtained by them have not been reported by others, unless we except the small quantity of the corresponding aniline obtained in some of our studies.

Schmidlin and Hodgson[4] obtained triphenylcarbinol from the reaction between *m*-nitrobenzaldehyde and triphenylmethylmagnesium chloride. They are inclined to attribute the formation of the carbinol to a splitting reaction of diethyl ether by the Grignard reagent. Straus[5] used *p*-nitro-

---

[1] Yocich, *J. Russ. Phys.-Chem. Soc.*, **35**, 555 (1903).

[2] Oddo, *Atti. Accad. Lincei*, (V) **13**, ii, 220 (1904); (*J. Chem. Soc.*, **1904**, 1, 862).

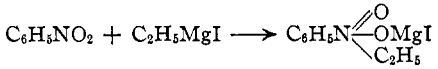
[3] Pickard and Kenyon, *Proc. Chem. Soc.*, **23**, 153 (1907).

[4] Schmidlin and Hodgson, *Ber.*, 41, 430 (1908).

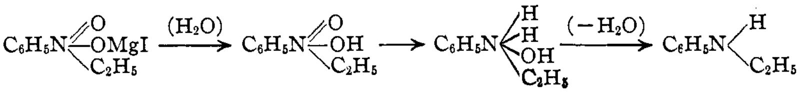
[5] Straus, *Ann.*, **393**, 235 (1912).

benzoyl chloride to characterize the -OMgX group in a substituted pentanol but instead of the expected *p*-nitrobenzoate he obtained a compound free of nitrogen and chlorine.

Hepworth[6] carried out a comprehensive investigation on the action of methylmagnesium iodide and ethylmagnesium bromide on nitrobenzene, *o*- and *p*-nitrotoluene and α-nitronaphthalene. In his experiments the Grignard reagent was prepared in the presence of the nitro compound by adding a mixture of the nitro compound and alkyl halide in ether to well-cooled ether containing powdered magnesium. By using about two moles of Grignard reagent per mole of nitro compound he obtained the respective alkylanilines and the azo compound corresponding with the nitro compound. Under the conditions of his experiments some unused nitro compound was generally recovered and he did not observe the formation of nitroso, hydroxylamine or azoxy compounds. He confirmed the formation of Oddo's[2] $C_6H_5N({=}O)C_2H_5(OMgI)$, but he disagrees with some of the following reactions proposed by Oddo.



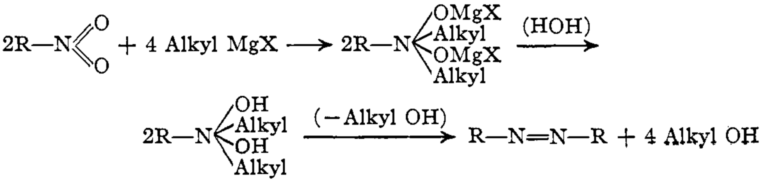
$$C_6H_5NO_2 + C_2H_5MgI \longrightarrow C_6H_5N\begin{array}{l}{=}O\\ {-}OMgI\\ {-}C_2H_5\end{array} \qquad (I)$$



$$C_6H_5N\begin{array}{l}{=}O\\ {-}OMgI\\ {-}C_2H_5\end{array} \xrightarrow{(H_2O)} C_6H_5N\begin{array}{l}{=}O\\ {-}OH\\ {-}C_2H_5\end{array} \longrightarrow C_6H_5N\begin{array}{l}{-}H\\ {-}H\\ {-}OH\\ {-}C_2H_5\end{array} \xrightarrow{(-H_2O)} C_6H_5N\begin{array}{l}{-}H\\ {-}C_2H_5\end{array} \qquad (II)$$

(A) (B)

Hepworth questions the intermediate formation of Compound (B), but sees no objection to postulating the direct loss of oxygen from Compound (A) to give ethylaniline. Admitting the difficulty of predicting the behavior of an unknown type like Compound (A), he suggests that "the loss of oxygen from such a compound is no more remarkable than the loss of carbon dioxide in the conversion of the simple monocarboxylic acid into the corresponding hydrocarbon, the more so if one accepts, what is probably the case, that Compound (A) is very unstable and just as likely to lose oxygen as Compound (B) is to lose water." He explains the formation of his azo compounds by the addition of two molecules of RMgX to his nitro compound to give an intermediate compound, two molecules of which, by the loss of four molecules of Alkyl OH compound, couple as follows



$$2R{-}N\begin{array}{l}{=}O\\ {=}O\end{array} + 4\ \text{Alkyl MgX} \longrightarrow 2R{-}N\begin{array}{l}{-}OMgX\\ {-}\text{Alkyl}\\ {-}OMgX\\ {-}\text{Alkyl}\end{array} \xrightarrow{(HOH)}$$

$$2R{-}N\begin{array}{l}{-}OH\\ {-}\text{Alkyl}\\ {-}OH\\ {-}\text{Alkyl}\end{array} \xrightarrow{(-\text{Alkyl OH})} R{-}N{=}N{-}R + 4\ \text{Alkyl OH} \qquad (III)$$

---

[6] Hepworth, *J. Chem. Soc.*, **117,** 1004 (1920).

Tanasescu[7] measured the volume of gas evolved in the Zerewitinoff analysis of *o*-nitrobenzaldehyde with methylmagnesium iodide. Gilman and Fothergill[8] then showed that Tanasescu was incorrect in attributing to *o*-nitrobenzaldehyde a cyclic hydroxy formula on the basis of gas evolved with methylmagnesium iodide, inasmuch as such gas evolution is an inherent property of aryl nitro compounds. Later, Gilman and Fothergill[9] extended their studies on the interference of nitro groups on the Zerewitinoff method for the quantitative estimation of active hydrogen.

Recent work by Mingoia[10] reports the formation of di-indyl-*m*-nitrobenzylidene from *m*-nitrobenzaldehyde and indylmagnesium bromide, and of di-α-methylindyl-*m*-nitrobenzylidene from the same aldehyde and α-methyl-indylmagnesium bromide. These results are somewhat surprising, for in view of the high reactivity of the aryl nitro group it might have been predicted that the nitro group would have been attacked at least concurrently with the action of the -CMgX compound on the aldehyde group.

Nitrosyl chloride (NO_2Cl) and nitrosyl bromide gave no nitrobenzene with phenylmagnesium bromide.[11] The products isolated were diphenyl and chlorobenzene or bromobenzene. References to reactions between the Grignard reagent and nitroparaffins, several oxides of nitrogen and a wide variety of compounds containing the nitroso group are to be found in a recent paper by Gilman and McCracken[12] on the reaction between nitrosobenzene and phenylmagnesium bromide.

Discussion of Reactions

Under the conditions of our experiments we have found that about four moles of Grignard reagent are necessary for each mole of nitro compound before obtaining the positive color test described by Gilman and Schulze[13] for reactive organometallic compounds. In addition to the secondary amine and ROH compounds, there also was obtained a very large quantity of R-R compound, essentially equivalent to the amount of ROH compound formed. Other compounds formed in very small quantities were *p*-phenyldiphenyl (when phenylmagnesium bromide was used), di-*p*-tolyl (when benzylmagnesium chloride was used) and aniline (when nitrobenzene was used). No azobenzene was obtained nor did we succeed (under our conditions) in isolating any nitroso, hydroxylamine or azoxy compounds. Special efforts were made in some experiments to isolate nitroso compounds that may have been formed at an intermediate stage.

[7] Tanasescu, *Bull. soc. chim.*, **39**, 1443 (1926).

[8] Gilman and Fothergill, This Journal, **49**, 2815 (1927).

[9] Gilman and Fothergill, *ibid.*, **50**, 867 (1928).

[10] Mingoia, *Gazz. chim. ital.*, **56**, 772 (1926); *C. A.*, **21**, 1117 (1927).

[11] Zuskine, *Bull. soc. chim.*, **37**, 187 (1925).

[12] Gilman and McCracken, This Journal, **49**, 1052 (1927).

[13] Gilman and Schulze, *ibid.*, **47**, 2002 (1925); *Bull. soc. chim.*, **41**, 1479 (1927).

With alkylmagnesium halides the course of reaction appears to differ markedly from that when arylmagnesium halides were treated with the same nitro compound. For example, nitrobenzene with benzylmagnesium chloride gave 1,2-diphenyl-1,2-dibenzylhydrazine, $(C_6H_5)(C_6H_5CH_2)NN(CH_2C_6H_5)(C_6H_5)$. A special search for tetraphenylhydrazine that might have resulted from nitrobenzene and phenylmagnesium bromide failed to reveal any of this compound. Furthermore, it was shown that tetraphenylhydrazine underwent no noticeable reaction with phenylmagnesium bromide under conditions that simulated those used in the nitro reactions.

The equations proposed by Oddo[2] and by Hepworth[6] (see Reactions I, II and III) do not present a complete picture of the reaction. First, four and not one nor two moles of Grignard reagent are required for each mole of nitro compound; and, under the conditions of our experiments, when an insufficient quantity of Grignard reagent to complete the Reaction was added, small amounts of all of our end-products were isolated, together with unattacked nitro compound. In one of Hepworth's reactions between *p*-nitrotoluene and alkylmagnesium halides the use of four equivalents of Grignard reagent merely increased the quantities of alkyl-*p*-toluidine, and even with this ratio there was some unaltered nitro compound. This illustrates in a striking manner the different reactions that take place when the RMgX compound is formed in the presence of nitro compound. Second, neither of their explanations takes into consideration the formation of R-R compound by a coupling reaction of the organomagnesium halide. Third, Oddo's reaction scheme makes no provision for the formation of ROH compound, and Hepworth's interpretation correlates the formation of ROH compound (the isolation of which, by the way, was not described in his experiments) with azo compound, whereas in our studies large quantities of ROH compound were obtained when no azo compound was isolated.

Some support of the intermediate acidic compound (A in Reaction II) and its direct loss of oxygen to give the secondary amine may be found in related reactions. For example, it has long been known that oxygen and chloropicrin induce marked luminescence with Grignard reagents, particularly with *p*-chlorophenylmagnesium bromide. Unpublished studies show that such luminescence is an inherent property of nitro compounds. Quite likely the nitro compounds behave as oxidizing agents toward RMgX compounds and such oxidation in general is known to induce chemiluminescence.[14] Also, *p*-phenyldiphenyl has been obtained in small quantities by the oxidation of phenylmagnesium bromide.[15]

The formation of R-R compound may go hand in hand with the apparent absence of azo compound in our experiments, inasmuch as azo compounds

---

[14] Gilman and Adams, This Journal, **47**, 2816 (1925).

[15] Wuyts, *Compt. rend.*, **148**, 930 (1909).

are known to react with Grignard reagents to give hydrazobenzene and R-groups which may couple to give R-R compounds or disproportionate to the corresponding olefinic and saturated hydrocarbons.[16] However, the R-R compound may also owe its formation to some other reaction or reactions, inasmuch as the reduction of azo compound should have yielded corresponding quantities of hydrazo compound. Hydrazo compounds have not as yet been identified and if such compounds were formed in appreciable quantities the method of working up the reaction products should have yielded large quantities of the corresponding azo compound as a consequence of the ready oxidation of hydrazo compounds.

For the present it may suffice to represent the reaction between nitrobenzene and phenylmagnesium bromide (a typical *aryl*magnesium halide) as follows

$$C_6H_5NO_2 + 4C_6H_5MgBr \xrightarrow{(H_2O)} (C_6H_5)_2NH + C_6H_5OH + C_6H_5C_6H_5 \qquad (IV)$$

At best such a representation is somewhat superficial and does not take into consideration the several concurrent and successive reactions that undoubtedly occur, the explanation of which must wait on an examination now in progress of the apparently intractable oils formed in these reactions. We have no experimental proof, at this time, for the mode of formation of the tetra-substituted hydrazines when *alkyl*magnesium halides are used. Alkylmagnesium halides are known to act in some cases as strong reducing agents, liberating olefinic hydrocarbons,[17] and we may be dealing here with addition of and reduction by the alkylmagnesium halide to give divalent nitrogen residues which then associate to tetra-substituted hydrazines.

Experimental Part

Details will be given here for a typical run between nitrobenzene and phenylmagnesium bromide. Table I contains an account of the several products obtained and their quantities. From the yields of phenol and diphenyl given in Table I there have already been deducted the quantities of these compounds present in the stock solution of phenylmagnesium bromide prior to reaction with nitro compound. In each 0.1 mole of this stock solution there were about 0.15 g. of phenol and 0.6 g. of diphenyl

The nitrobenzene (24.6 g. or 0.2 mole) was dissolved in 200 cc. of dry ether in a one-liter three-necked flask provided with a mechanical stirrer, reflux condenser and a separatory funnel. Phenylmagnesium bromide was added dropwise with stirring and the reaction mixture was cooled with running water. After the addition of 0.4 mole of the Grignard reagent during one hour, a test[13] portion showed no RMgX compound; 0.2 mole more of phenylmagnesium bromide was added and the mixture gave no color

---

[16] Gilman and Pickens, THIS JOURNAL, **47**, 2406 (1925); Gilman and Adams, *ibid.*, **48**, 2004 (1926); Gilman and Fothergill, *ibid.*, **50**, 867 (1928) (see footnote 5 on p. 868); Rheinboldt and Kirberg, *J. prakt. Chem.*, **118**, 1 (1928).

[17] See refs. 8 and 9 of this paper, in which attention is directed to the evolution of such unsaturated hydrocarbons when nitro compounds are treated with alkylmagnesium halides.

TABLE IA

REAGENTS

	Nitro compound	G.	Moles	RMgX	Moles
1	$C_6H_5NO_2$	24.6	0.2	C_6H_5MgBr	0.8
2	$C_6H_5NO_2$	24.6	.2	C_6H_5MgBr[a]	.8
3	α-$C_{10}H_7NO_2$	17.3	.1	C_6H_5MgBr	.7
4	$C_6H_5NO_2$	12.3	.1	$C_6H_5C{\equiv}CMgI$[b]	.1
5	*o*-$CH_3C_6H_4NO_2$	13.7	.1	C_6H_5MgBr	.6
6	*o*-$CH_3C_6H_4NO_2$	13.7	.1	C_6H_5MgBr	.3
7	*o*-$CH_3C_6H_4NO_2$	13.7	.1	C_6H_5MgBr	.2
8	*o*-$CH_3C_6H_4NO_2$	13.7	.1	C_6H_5MgBr	.1
9	*p*-$CH_3C_6H_4NO_2$	13.7	.1	C_6H_5MgBr	.6

[a] In this experiment the phenylmagnesium bromide was prepared in the presence of nitrobenzene to simulate the conditions of Hepworth[6] in order to obtain, if possible, something like the relatively large amounts of azobenzene he secured. However, because it was impossible to make bromobenzene react with magnesium in the presence of nitrobenzene at low temperatures (−15°), the reaction was carried out without cooling, under which condition it proceeded smoothly. The mixture of bromobenzene and nitrobenzene in ether was added during three hours and after refluxing for two hours the mixture was hydrolyzed with 400 cc. of a saturated ammonium chloride solution. About 0.5 g. of aniline was obtained in this experiment but no azobenzene nor unaltered nitrobenzene. There was a large quantity of unidentified tarry product in this experiment.

[b] This experiment was carried out with the sole purpose of identifying Yocich's[1] hydrocarbon ($C_{16}H_{10}$) melting at 87–88.5°. Among the reaction products was 2 g. of diphenyl-di-acetylene melting at 88°. Its identity was confirmed by a mixed melting point determination and by the preparation of the picrate, which melted at 108°. In addition to 8.8 g. of recovered nitrobenzene, there was obtained one g. of phenylacetylene iodide ($C_6H_5CI{=}CHI$) melting at 76° and showing no depression in a mixed melting point determination with an authentic specimen. This di-iodo compound may owe its formation to a reaction between the small excess of phenylacetylene and some iodine resulting from the ethylmagnesium iodide used in the preparation of the phenylacetenylmagnesium iodide.

TABLE IB

PRODUCTS

	Amine	G.	Phenol, g.	Diphenyl, g.	*p*-$C_6H_5C_6H_4C_6H_5$, g.
1	$(C_6H_5)_2NH$	19.5	15.5	24.5	1.0
2	$(C_6H_5)_2NH$	9.5	8.8	19.7	0.5
3	(α-$C_{10}H_7$)$(C_6H_5)NH$[a]	7.8	...	..	...
4	....	..	..	..	...
5	(*o*-C_7H_8)$(C_6H_5)NH$	10.8[b]	7.9	14.8	0.5
6	(*o*-C_7H_8)$(C_6H_5)NH$	9.7[b]	7.8	4.7	0.1
7	(*o*-C_7H_8)$(C_6H_5)NH$	4.4[b]	4.97	3.7	...
8	(*o*-C_7H_8)$(C_6H_5)NH$	2.2[b]	3.52	..	...
9	(*p*-C_7H_8)$(C_6H_5)NH$	8.7	7.9	14.0	1.0

[a] The only product looked for here was the phenyl-α-naphthylamine in order to ascertain the value of this reaction for the preparation of some secondary aromatic amines.

[b] Expts. 5, 6, 7 and 8 are illustrative of the effects of varying quantities of Grignard reagent with a given quantity of nitro compound. No *o*-nitrotoluene was recovered in Expts. 5 and 6 but the quantities recovered in Expts. 7 and 8 were 2.7 g. (19.7%) and 7.5 g. (54.7%), respectively.

test[13] at the end of five hours; 0.1 mole more gave no test after twelve hours, and an additional 0.1 mole reacted within twenty-four hours. The total quantity of phenylmagnesium bromide added was about 0.8 mole or four equivalents per equivalent of nitrobenzene; the total time of reaction was forty-two hours. Several experiments showed that the addition of phenylmagnesium bromide in excess of four equivalents gave a color test that persisted. In some other studies on the rates of reaction of various compounds with the Grignard reagent, it has been shown that two equivalents of *n*-butyl- and of phenylmagnesium bromide are used up almost at once (within five minutes) when added to 0.1 mole of nitrobenzene in an ether solution that is refluxed.

The reaction mixture was then decomposed in a few cases with cold, dilute hydrochloric acid or more generally by a saturated ammonium chloride solution. The ether layer was separated and extracted with two 100-cc. portions of 10% sodium hydroxide. The phenol obtained by acidification of this extract followed by ether extraction and distillation weighed 15.5 g. and boiled at 180–182°. In many experiments the phenol was recovered and weighed as tribromophenol. The reaction was carried out in an atmosphere of hydrogen because the extended time of reaction would have resulted in most of the Grignard reagent being oxidized to phenol by atmospheric oxygen.

The ether layer was dried with sodium sulfate, filtered and treated with hydrogen chloride to precipitate the hydrochlorides of the amines. The crude hydrochloride was filtered and treated with sodium hydroxide to liberate the amine, which was extracted with ether and purified by vacuum distillation. In this manner 19.5 g. of diphenylamine was obtained boiling at 176–178° (20 mm.) and melting at 50°. A mixed melting point determination with an authentic specimen of diphenylamine melted at 52°.

The ether filtrate from the hydrochloride precipitate was fractionally distilled. Redistillation of a first fraction (25.5 g. distilling between 240–275° and melting at 63–67°) gave 21 g. of diphenyl that distilled at 252–256° and melted at 69–70°. The residue of this first fraction was added to a second fraction (boiling between 275° (740 mm.) and 250° (30 mm.) and weighing 9.2 g.) and the combined portions were dissolved in benzene and treated with hydrogen chloride to assure complete removal of the amine. No amine hydrochloride precipitated on this treatment. This benzene solution, when distilled in a vacuum, gave an additional 3.5 g. of diphenyl (making a total of 24.5 g. of diphenyl), and one g. of *p*-phenyldiphenyl that melted at 203° after crystallization from alcohol. In every case, where possible, the identity of solids was confirmed by mixed melting point determinations made with authentic specimens.

Reaction between Nitrobenzene and Benzylmagnesium Chloride.—In view of the products obtained from the reaction between nitrobenzene and phenylmagnesium bromide, we expected the reaction between nitrobenzene and benzylmagnesium chloride to proceed after the general scheme represented in Reaction IV and to give, accordingly, benzylaniline, benzyl alcohol and dibenzyl. However, unusual difficulty was experienced in working up the basic fractions and the isolation of benzaldehyde prompted a number of experiments the object of which was to throw some light on the formation of the aldehyde and the difficulty of obtaining the expected benzylaniline. In view of the final identification of the 1,2-diphenyl-1,2-dibenzylhydrazine, it is unnecessary at this time to give an account of these several orienting experiments.

Thirty and eight-tenths g. (0.25 mole) of nitrobenzene was added slowly with stirring to one mole of benzylmagnesium chloride kept cool by running water. After allowing the reaction mixture to stand overnight, it was hydrolyzed by 100 cc. of water. The dark-colored oil obtained from the ether layer when fractionally distilled in a vacuum yielded 2.5 g. of aniline (identified by the formation of benzanilide and *p*-nitrobenzanilide), 22.6 g. of dibenzyl (after deducting the quantity of dibenzyl formed in the preparation of benzylmagnesium chloride), 3 g. of *p*-ditolyl and a basic fraction which when treated in ether solution with hydrogen chloride gave 4.5 g. of a hydrochloride.

This hydrochloride was formed from 12.2 g. of a basic fraction that distilled over a wide temperature range, 150° (10 mm.) to 200° (5 mm.). After crystallization from an alcoholic hydrogen chloride solution, the salt melted at 213°. When refluxed with dilute hydrochloric acid it yielded benzaldehyde (identified by the phenylhydrazone), aniline (identified as tribromoaniline) and benzylaniline (identified as the hydrochloride). The derivatives of all three products of hydrolysis were identified in turn by mixed melting point determinations made with authentic specimens of the corresponding compounds.

Franzen and Zimmermann[18] first prepared 1,2-diphenyl-1,2-dibenzylhydrazine hydrochloride and found it to melt at 215.5°. On acid hydrolysis they obtained from it benzaldehyde, aniline and benzylaniline. Later, Wieland and Fressel[19] attempted to prepare the tetra-substituted hydrazine by the method used by Franzen and Zimmermann, by heating the corresponding tetrazene. However, they observed that the high temperature necessary to distil the hydrazine is sufficient to decompose this compound; and the distillation of the tetrazene yielded benzylaniline and benzalaniline. Acid hydrolysis would accordingly break down the benzalaniline to give benzaldehyde and aniline, so that the three products obtained by Franzen and Zimmermann from the hydrolysis of their supposed 1,2-diphenyl-1,2-dibenzylhydrazine would come, in reality, from the two decomposition products of their hydrazine, benzylaniline and benzalaniline. The high melting point (215.5°) observed by Franzen and Zimmermann is explained by Wieland and Fressel as being due to rapid heating. However, it should be recalled that we identified our benzylaniline by the melting point of the corresponding hydrochloride and under our conditions of determining melting points it agreed with the correct point as given in the literature.

For our present purposes it does not make any difference whether we had in hand the hydrazine or its decomposition products (benzylaniline and benzalaniline), inasmuch as the compounds obtained by Franzen and Zimmermann and by Wieland and Fressel were prepared by a standard procedure for the preparation of such hydrazines and because Wieland and Fressel admit that their decomposition products (benzylaniline and benzalaniline) came from the tetra-substituted hydrazine.

Reaction between Nitrobenzene and Ethylmagnesium Bromide.—By analogy with the benzylmagnesium chloride reaction, one would expect to get 1,2-diphenyl-1,2-diethylhydrazine from the reaction between nitrobenzene and ethylmagnesium bromide. Experiment verified this. Wieland and Fressel[19] found this hydrazine to be unstable and to undergo considerable decomposition even when distilled in a high vacuum. The boiling point of their compound was 141° (1 mm.). Our hydrazine boiled at 118–123° (0.5 mm. (or less)). Hydrolysis by heating with dilute hydrochloric acid gave the products described by Wieland and Fressel,[19] namely acetaldehyde, aniline and ethylaniline. However, our compound did not give the characteristic color reaction with acetic acid that they described. This was not wholly unexpected, inasmuch as Gilman and Pickens[20] prepared this hydrazine from azobenzene, phenylmagnesium bromide and diethyl sulfate, and found it to distil at 140–145° (1.5 mm.), but not to give the color test. The reason for this discrepancy is to be found in the observation of Wieland and Fressel[19] that the tetrazene from which their hydrazine was prepared also gives the color test. Very probably their hydrazine was contaminated with some tetrazene.

---

[18] Franzen and Zimmermann, *Ber.*, **39**, 2566 (1906).

[19] Wieland and Fressel, *Ann.*, **392**, 150 (1912).

[20] Gilman and Pickens, THIS JOURNAL, **47**, 2406, 2412 (1925)

The formation of the hydrazine prompted a repetition of Hepworth's[6] experiment in which nitrobenzene and ethyl bromide were added to magnesium in ether to give ethylaniline and azobenzene. We found that the ethylaniline fraction boiled over a wide range (200–270°) when first distilled at atmospheric pressure. The fraction containing ethylaniline also gave qualitative tests for the hydrazine (acetaldehyde on acid hydrolysis) and for aniline. From this one may conclude that the hydrazine is one of the products of reaction and that a part, at least, of their and our ethylaniline may have resulted from the known course of thermal decomposition of the hydrazine to give ethylaniline.

Attempted Isolation of Tetraphenylhydrazine and its Treatment with Phenyl- and *n*-Butylmagnesium Bromides.—Several reactions were carried out between nitrobenzene and phenylmagnesium bromide with the express purpose of either identifying or isolating tetraphenylhydrazine or its rearrangement products. All of these unsuccessful experiments were made after it was shown that alkylmagnesium halides with nitrobenzene gave tetra-substituted hydrazines. The respective fractions that might have contained the tetraphenylhydrazine neither gave the characteristic color test[21] for the hydrazine nor did they yield the sparingly soluble diphenylbenzidine[21] that results from the rearrangement of tetraphenylhydrazine by concd. sulfuric acid.

Also, no reaction appeared to take place when 25.4 g. (0.08 mole) of tetraphenylhydrazine in 500 cc. of ether and 200 cc. of benzene was treated with 0.1 mole of phenylmagnesium bromide for fifteen hours at room temperature. On working up the reaction product in the customary manner, there was recovered 22.5 g. (85.2%) of the tetraphenylhydrazine. A less exact experiment with tetraphenylhydrazine (5 g.) and *n*-butylmagnesium bromide (0.05 mole) showed no evidence of reaction and most of the hydrazine was recovered.

Attempts to Isolate an Intermediate Nitroso Compound.—From 61.5 g. (0.5 mole) of nitrobenzene and 1.0 mole of phenylmagnesium bromide there was obtained 17.7 g. of phenol and 18 g. of unaltered nitrobenzene, but no nitrosobenzene. The high yield of phenol obtained here and the yields of phenol described in Expts. 6, 7 and 8 (Table I) indicate that the successive reactions leading to the formation of phenol proceed more rapidly than the initial reaction with nitro compound.

Equally unsuccessful attempts were made to isolate nitrosobenzene in several experiments in which the temperature and the ratio of nitrobenzene to RMgX were varied. In only one experiment was there a faint green color during the steam distillation procedure employed to remove any nitrosobenzene.

Attention was then directed to the possibility of isolating a more stable nitroso compound, *p*-nitrosodimethylaniline, when *p*-nitrodimethylaniline was used as the initial compound. However from 16.6 g. (0.1 mole) of *p*-nitrodimethylaniline and 0.1 mole of phenylmagnesium bromide there was recovered 7.8 g. (47%) of the nitro compound, but no *p*-nitrosodimethylaniline. From another experiment starting with 0.1 mole of *p*-nitrodimethylaniline and 0.4 mole of phenylmagnesium bromide there were isolated 4.4 g. of phenol, 5 g. of diphenyl and 5.6 g. of an intractable amino compound that may have been *p*-dimethylaminodiphenylamine.[22]

Reaction between Dimethylaniline Oxide and Phenylmagnesium Bromide.—The $R(Alkyl)_2N(OH)_2$ intermediate postulated by Hepworth[6] (see Reaction III) might be expected to lose water and form a dialkylaniline oxide. For this reason, 27.4 g. (0.2 mole) of dimethylaniline oxide partially dissolved in 600 cc. of warm (40°) benzene was treated with 0.4 mole of phenylmagnesium bromide. The following products were isolated: phenol (3.56 g.), diphenyl (8.6 g.) and dimethylaniline (2.5 g.). The am-

---

[21] Wieland and Gambarjan, *Ber.*, **39**, 1499 (1906).

[22] Ref. 12, pp. 1060–1061.

moniacal solution obtained on hydrolysis yielded a very small quantity of a solid that dissolved readily in hydrochloric acid giving a purple color.

Reaction between Ethyl Nitrate and Phenylmagnesium Bromide.—This reaction was carried out at a very low temperature (about −80°) to determine whether nitrobenzene might be formed in accordance with the following reaction

$$C_6H_5MgBr + C_2H_5ONO_2 \longrightarrow C_6H_5NO_2 + C_2H_5O(MgBr) \qquad (V)$$

Kinkead[23] previously studied this reaction at about 0° and reported the production of a blue solution on extraction with chloroform, which had the properties of an indicator. Hepworth,[24] at −15°, obtained dimethylhydroxylamine, $(CH_3)_2NOH$, and diethylhydroxylamine from methyl- and ethylmagnesium halides, respectively.

When 0.2 mole of phenylmagnesium bromide was added dropwise and with stirring to 0.3 mole of ethyl nitrate cooled by a slush of carbon dioxide and acetone, diphenyl and phenol were obtained but no nitrobenzene.

Summary

The products obtained in the reaction between aryl nitro compounds and organomagnesium halides vary markedly with experimental conditions. Under the conditions of the experiments described here, the following general reaction takes place

$$C_6H_5NO_2 + 4C_6H_5MgBr \longrightarrow (C_6H_5)_2NH + C_6H_5OH + C_6H_5{\cdot}C_6H_5$$

With *alkyl*magnesium halides, tetra-substituted hydrazines are among the reaction products. Ethylmagnesium bromide and nitrobenzene, for example, give 1,2-diphenyl-1,2-diethylhydrazine, $(C_6H_5)(C_2H_5)NN(C_2H_5)(C_6H_5)$. The formation of alkylanilines in this reaction is due in part to the decomposition of such hydrazines.

AMES, IOWA

[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE PROPERTIES AND CHEMICAL CONSTITUTION OF GLUCIC ACID

BY E. K. NELSON AND C. A. BROWNE

RECEIVED SEPTEMBER 21, 1928 PUBLISHED MARCH 6, 1929

H. Winter,[1] while working in the laboratory of Fraser Eaton and Company, Soerabaya, Java, announced in 1894 that upon warming an aqueous solution of 1% invert sugar with 0.5% of calcium oxide in the form of calcium hydroxide at 66.5°, he obtained a voluminous, white flocky precipitate which redissolved on further heating. This precipitate turned brown on exposure to the air and because of its slimy character could not be filtered readily. Winter purified the precipitate, which he supposed to be a basic calcium salt, by decanting and washing five times with lime water, the settling of the precipitate being performed in a well-closed flask, filled

[23] Kinkead, *Chem. News*, **122**, 4 (1921).

[24] Hepworth, *J. Chem. Soc.*, 119, 251 (1921).

[1] Winter, *Z. Ver. Rübenzucker Ind.*, **44** (old series), 1049 (1894).