Summary

It has been shown that the two mononitro-acridine derivatives formed in the nitration of acridine are 1(9)- and 3(7)-nitro-acridine. The two mentioned acridine derivatives have been synthesized by condensing *o*-aminobenzaldehyde with *o*-bromonitrobenzene and with *p*-bromonitrobenzene, respectively, and closing the ring with concd. sulfuric acid. In a similar way 1(9)- and 3(7)-methylacridine have been synthesized.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE REACTION BETWEEN NITROSOBENZENE AND PHENYLMAGNESIUM BROMIDE

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Introduction

In connection with a study of the reaction between nitrobenzene and organomagnesium halides it was necessary to determine the mode of reaction between nitrosobenzene and phenylmagnesium bromide. Pickard and Kenyon[1] reported the formation of *p*-nitrosotoluene from *p*-nitrotoluene and an organomagnesium halide. The formation of a nitroso compound has not been confirmed in studies of the reaction of nitrobenzene, *p*- and *o*-nitrotoluene and *p*-nitrodimethylaniline with organomagnesium halides. Partly because the nitroso compounds may have been lost as a result of side reactions (no experimental details are given in the Note of Pickard and Kenyon), and particularly because both nitrobenzene and nitrosobenzene give diphenylamine when brought into reaction with phenylmagnesium bromide, it was thought that a study of the reaction with nitrosobenzene would help in an interpretation of the reaction between nitrobenzene and organomagnesium halides.

Historical Part

Many and varied compounds containing a nitrosyl (—N=O) group have been made to react with Grignard reagents. The most extensive studies have been carried out by Wieland and co-workers. Wieland[2] first studied the reaction with *p*-nitrosodimethylaniline and nitrogen dioxide. Later, with Roseeu, a more extensive study was made on nitrosobenzene;[3a] sub-

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

[2] Wieland, *Ber.*, **36,** 2315 (1903).

[3] (a) Wieland and Roseeu, *Ber.*, **45,** 494 (1912). (b) See also Wieland and Offenbächer, *Ber.*, **47,** 2111 (1914), for nitrosobenzene. (c) Wieland and Gambarjan, *Ber.*, **39,** 1499 (1906), for nitrosobenzene and nitrogen dioxide. (d) Wieland and Roth, *Ber.*, **53,** 210 (1920), for nitrosobenzene and *p*-nitrosotoluene. (e) Wieland and Kögl, *Ber.*, **55,** 1798 (1922), for *p*-nitrosotoluene, *p*-nitroso-anisole and *p*-nitrosodimethylaniline. (f) Wieland and Reverdy, *Ber.*, **48,** 1112 (1915), for nitroso-*p*-ditolylamine.

sequently[4] reactions were carried out with *p*-nitrosotoluene, nitroso-acetanilide, nitrosodiphenylamine and nitrosocarbazole. Tilden and Stokes[5] investigated the reaction between pinene nitrosochloride and methylmagnesium iodide, and Tilden and Shepheard[6] extended the reaction of limonene-α- and -β-nitrosochlorides. Rupe,[7] at an earlier time, reported the removal of hydrogen chloride from a reaction between bislimonene nitrosochloride and magnesium.

Oddo[8] has described the preparation of nitrosobenzene in 56% yield from the reaction between nitrosyl chloride and phenylmagnesium bromide.

Several oxides of nitrogen have been studied. Sand and Genssler[9] made a preliminary study of the reaction between nitric oxide and methylmagnesium iodide and phenylmagnesium bromide. Later, a more complete study of the reaction with methylmagnesium iodide was made by Sand and Singer.[10] Attention has already been called to Wieland's work on nitrogen dioxide.[2,3c] Zerner[11] first showed that no reaction takes place with nitrous oxide.

Wieland[12] studied the reaction between benzonitrile oxide and various RMgX compounds. Angeli[13a] and Cusmano[13b] have reported on nitrones; Angeli[13a] and Bigiavi[14] on glyoxime peroxides; Ponzio[15] on methylaminofurazan; Wieland and Semper[16] on anisylmethylfuroxan. A study is now in progress by Kohler and co-workers[17] on isoxazoline oxides and related compounds.

Nitroparaffins which have an acid form may be considered to contain the nitrosyl group. Bewad[18] has studied the reaction of such nitro-

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[4] Wieland and Roseeu, *Ber.*, **48**, 1117 (1915).

[5] Tilden and Stokes, *J. Chem. Soc.*, **87**, 836 (1905).

[6] Tilden and Shepheard, *ibid.*, **89**, 920 (1906).

[7] Rupe and Altenburg, *Ber.*, **43**, 3471 (1910).

[8] Oddo, *Gazz. chim. ital.*, **39** [I], 659 (1909); *C. A.*, **5**, 686 (1911).

[9] Sand and Genssler, *Ber.*, **36**, 2083 (1903).

[10] Sand and Singer, *Ber.*, **35**, 3170 (1902); *Ann.*, **329**, 190 (1903).

[11] Zerner, *Monatsh.*, **34**, 1609, 1630 (1913). Several others tried this reaction subsequently. Lifschitz and Kalberer [*Z. physik. Chem.*, **102**, 393 (1922)] reported that nitrous oxide induced chemiluminescence when bubbled through phenylmagnesium bromide. This was not confirmed by subsequent work of others [Dufford, Calvert and Nightingale, THIS JOURNAL, **45**, 2058 (1923)]. The reaction with nitrogen pentoxide is being investigated.

[12] Wieland, *Ber.*, **40**, 1667 (1907).

[13] (a) Angeli, *Atti. accad. Lincei*, **20** [I], 546 (1911); *C. A.*, **5**, 3403 (1911). (b) Cusmano, *Gazz. chim. ital.*, **51** [II], 306 (1921); *C. A.*, **16**, 1401 (1922).

[14] Bigiavi, *Gazz. chim. ital.*, **51** [II], 324 (1921); *C. A.*, **16**, 1394 (1922).

[15] Ponzio, *Gazz. chim. ital.*, **53**, 507 (1923); *C. A.*, **17**, 3876 (1923).

[16] Wieland and Semper, *Ann.*, **358**, 36 (1908).

[17] A paper by Kohler and Barrett [THIS JOURNAL, **46**, 2105 (1924)] describes the reaction between triphenyl isoxazoline oxide and several Grignard reagents.

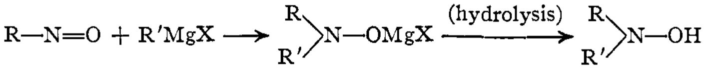
[18] Bewad, *Ber.*, **40**, 3065 (1907). Moureu [*Compt. rend.*, **132**, 837 (1901)] at an earlier time made a preliminary report on the reaction with both nitro-ethane and amyl nitrate.

paraffins with both alkyl zinc iodides and alkyl magnesium iodides. He has also reported, in the same paper, reactions with nitrous esters. Sudborough and Beard[19] describe the formation of additive compounds resulting from the reaction of nitrites with ethylene dibromide and magnesium.

Ingold[20] has used the electronic theory to interpret the mechanism of reaction between nitrosobenzene and RMgX compounds.

Interpretation of Reactions

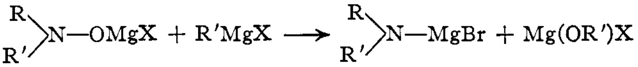
Wieland and Roseeu,[4] after directing attention to some chemical similarities of the nitrosyl and carbonyl groups, proposed the following as the first reaction between nitroso compounds and organomagnesium halides.



$$\mathrm{R{-}N{=}O} + \mathrm{R'MgX} \longrightarrow \begin{matrix}\mathrm{R}\\ \mathrm{R'}\end{matrix}\!\!>\mathrm{N{-}OMgX} \xrightarrow{\text{(hydrolysis)}} \begin{matrix}\mathrm{R}\\ \mathrm{R'}\end{matrix}\!\!>\mathrm{N{-}OH} \qquad (1)$$

This reaction is undoubtedly correct; however, it may not be the sole reaction, inasmuch as the by-products generally formed indicate concurrent or subsequent side reactions. Very probably the reaction between nitroso compounds and *alkyl* magnesium halides is more complex. It has long been known that many alkyl magnesium halides exercise a decided reducing action towards the carbonyl and other reactive groups.[21] Inasmuch as the work described here has been done with aryl magnesium halides, and because practically all other reported work on the mechanism of reaction of aromatic nitroso compounds has also been done with aryl magnesium halides, it will be understood that the R′ group in R′MgX is aryl.

Almost invariably the reaction between nitroso and RMgX compounds extends, to a varying degree, beyond the formation of β,β-disubstituted hydroxylamines, Reaction 1, to secondary amines. Wieland and Roseeu[4] have proposed the following reaction to account for the formation of secondary amines from nitroso compounds.



$$\begin{matrix}\mathrm{R}\\ \mathrm{R'}\end{matrix}\!\!>\mathrm{N{-}OMgX} + \mathrm{R'MgX} \longrightarrow \begin{matrix}\mathrm{R}\\ \mathrm{R'}\end{matrix}\!\!>\mathrm{N{-}MgBr} + \mathrm{Mg(OR')X} \qquad (2)$$

On hydrolysis, the two magnesium products would give a secondary amine and a phenol or alcohol, depending on the R′ group.

Reaction 2 is only partly correct. We have shown that a β,β-disubstituted hydroxylamine, such as diphenylhydroxylamine, will react as postulated above with more Grignard reagent to give the secondary amine.

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[19] Sudborough and Beard, *Proc. Chem. Soc.*, **20**, 165 (1904). In continuation of studies on the alkylating reaction between some esters and the Grignard reagent, it has been shown in this Laboratory that alkyl esters of nitrous and nitric acids do not give the alkylating reaction characteristic of sulfonic esters.

[20] Ingold, *J. Chem. Soc.*, *127*, *513* (1925).

[21] Gilman and Pickens, THIS JOURNAL, **47**, 2406, 2414 (Ref. 19) (1925). Gilman and Adams, *ibid.*, **48**, 2004 (1926).

However, the mechanism (Reaction 2) proposed by Wieland and Roseeu is incorrect for several reasons.

First, phenol is not formed as a product of the reaction between nitrosobenzene or diphenylhydroxylamine and phenylmagnesium bromide. This statement requires the ordinary reservation that concerns all reactions involving phenylmagnesium bromide. That is, phenol is invariably a product (in limited amounts) whenever phenylmagnesium bromide is prepared or used in a reaction, unless extra precautions are taken to exclude atmospheric oxygen. Even when the preparation of phenylmagnesium bromide and its subsequent reaction with a compound is carried out in an atmosphere free from oxygen, it is still possible to have some phenol formed as the result of a reaction between phenylmagnesium bromide and the small amount of ether peroxide generally present in ether used for the preparation of Grignard reagents.[22] The quantity of phenol obtained from the reactions with nitrosobenzene and diphenylhydroxylamine was no larger than that present in the standard stock solution from which the phenylmagnesium bromide was taken. The reactions with nitrosobenzene and diphenylhydroxylamine were carried out in an atmosphere of pure, dry hydrogen.

Second, diphenyl is a chief product of reaction. Again, some diphenyl is invariably formed in the preparation of phenylmagnesium bromide. Here again check blank tests were made and it was shown that the quantity of diphenyl present in the stock solution was only the few per cent. that is present in the usual preparation of phenylmagnesium bromide. This quantity of diphenyl was, of course, deducted from the total yield of diphenyl in computing percentage yields.

Third, the number of molecules of Grignard reagent postulated by Wieland and Roseeu in Reaction 2 is incorrect.[23] According to their reactions, two equivalents of Grignard reagent are required to convert nitrosobenzene to diphenylamine or one equivalent to convert the intermediate magnesium halide addition product (Reaction 2) to diphenylamine. Experiment has

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[22] Gilman and Wood, This Journal, **48**, 806 (1926). Ivanoff, *Bull. soc. chim.*, **39**, 47 (1926).

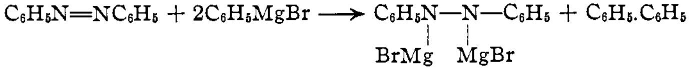
[23] Actually, however, Wieland and Roseeu[3a] used more than one equivalent of phenylmagnesium bromide in the preparation of diphenylhydroxylamine from nitrosobenzene. They used 2.5 equivalents and found that if a greater excess were used it resulted in the formation of sufficient diphenylamine to interfere seriously with the subsequent isolation of the diphenylhydroxylamine. On the other hand, if they used but 1.5 equivalents they obtained dark, apparently intractable resins. They believed that an excess of the Grignard reagent is necessary to change the loose molecular complex that is first formed, to a true addition compound which will not give unchanged nitrosobenzene on hydrolysis. See p. 1057 of this paper, where Reaction 5 is discussed.

It must be remembered that the quantities of Grignard reagent mentioned above were very probably larger than those actually used by them. See Gilman and McCracken, This Journal, **45**, 2462 (1923), for the yields of some Grignard reagents.

shown that the quantity of phenylmagnesium bromide required is more than that postulated in Reaction 2. Three equivalents and not two are required with nitrosobenzene, and two equivalents and not one are required with the O-bromomagnesium diphenylhydroxylamine (Reaction 2) to complete the reaction resulting in the formation of diphenylamine. Of course, three equivalents are required when one starts with diphenylhydroxylamine inasmuch as one equivalent is necessary to replace the hydrogen of the hydroxyl group by an —MgX group. The amounts of Grignard reagent required for these reactions were very readily determined. First the stock solution was titrated with standard acid according to the method of Gilman, Wilkinson, Fishel and Meyers[24] for the quantitative estimation of Grignard reagent. Aliquots of this standard solution were then added to the nitrosobenzene or diphenylhydroxylamine until an excess of Grignard reagent was shown to be present according to the color test of Gilman and Schulze.[25]

We also observed the formation of azobenzene in small quantities as reported by Wieland and Roseeu.[4] However, a small amount of *p*-diphenylbenzene was isolated and identified, and this compound has apparently not been reported in earlier work with nitroso compounds. An explanation for the formation of these compounds will be reported later.

The presence of both azobenzene and diphenyl in the reaction products naturally suggests that the diphenyl may have come in part, at least, from a secondary reaction between azobenzene and phenylmagnesium bromide. Gilman and Pickens[21] have shown that the following reaction takes place between azobenzene and practically all Grignard reagents, particularly phenylmagnesium bromide.



$$C_6H_5N{=}NC_6H_5 + 2C_6H_5MgBr \longrightarrow \underset{BrMg}{C_6H_5N}{-}\underset{MgBr}{N}{-}C_6H_5 + C_6H_5.C_6H_5 \qquad (3)$$

That is, equivalent amounts of hydrazobenzene and diphenyl are formed subsequent to the hydrolysis of the reaction between azobenzene and phenylmagnesium bromide. Admittedly, the hydrazobenzene formed in this reaction could undergo ready oxidation to azobenzene. However, the quantity of azobenzene obtained was very small and the quantity of diphenyl was quite large. We cannot be dealing here, either, with a kind of catalytic reaction where a small amount of hydrazobenzene is formed by hydrolysis of the corresponding dibromodimagnesium azobenzene (Reaction 3) and then oxidized to azobenzene to give more diphenyl and dibromodimagnesium azobenzene, because the reactions were carried out in an atmosphere of pure, dry hydrogen.

Accordingly the chief reaction between nitrosobenzene and phenyl-

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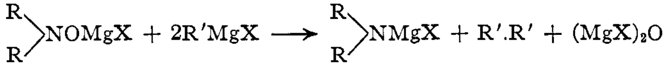
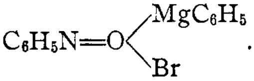
[24] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923). Gilman and Meyers, *Rec. trav. chim.*, **45**, 314 (1926).

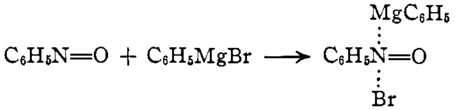
[25] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

magnesium bromide takes place in at least two stages. The first is represented by Reaction 1 and the second may be represented by the reaction



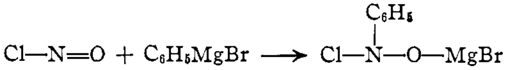
$$\mathrm{R_2NOMgX} + \mathrm{2R'MgX} \longrightarrow \mathrm{R_2NMgX} + \mathrm{R'.R'} + \mathrm{(MgX)_2O} \qquad (4)$$

It is highly probable that Reaction 1 is preceded by an addition reaction leading to the formation of a more or less loosely bound complex molecule. Omitting, for the sake of convenience, the part that ether may play in such a loosely held complex molecule, the preliminary addition may involve an increase in valence of the oxygen or nitrogen or magnesium. It is extremely unlikely that Reaction 1 is reversible, and yet Wieland and Gambarjan[3c] obtained a bright yellow, crystalline compound from nitrosobenzene and phenylmagnesium bromide which gives up the nitrosobenzene on hydrolysis.[23] Wieland and Kögl[3e] have also described an addition compound of *p*-nitrosodimethylaniline and phenylmagnesium bromide from which the original nitroso compound is obtained on hydrolysis. Wieland and Gambarjan[3c] have suggested that the addition compound may have the following oxonium structure:  $C_6H_5N{=}O\langle^{MgC_6H_5}_{Br}$. A second possible formula for such addition compounds might involve the higher coördination valences of magnesium, and a third possible formula would be that involving the higher valences of nitrogen as in the following reaction, if we split the phenylmagnesium bromide as Wieland has done in his oxonium formula.



$$C_6H_5N{=}O + C_6H_5MgBr \longrightarrow C_6H_5\overset{\overset{MgC_6H_5}{\vdots}}{\underset{\underset{Br}{\vdots}}{N}}{=}O \qquad (5)$$

Not enough is known with reasonable certainty concerning such loosely held complexes to warrant further consideration at the present time of the relative merits of these and other possible structures. A structure of this general type would be helpful in interpreting Oddo's[8] reaction for the preparation of nitrosobenzene in 56% yield by passing the vapors of nitrosyl chloride into phenylmagnesium bromide. Under the conditions of his experiment there was present an excess of Grignard reagent which might be expected to react with the nitrosobenzene if it were present as such.[23] However, a loose molecular complex is not required to explain the nitrosyl chloride reaction. The following reaction might be sufficient.



$$Cl{-}N{=}O + C_6H_5MgBr \longrightarrow Cl{-}\overset{\overset{C_6H_5}{|}}{N}{-}O{-}MgBr \qquad (6)$$

Opposed to the acceptance of this reaction mechanism (Reaction 6) is the ready reaction of Grignard reagents with halogen attached to nitrogen, as well as the ready reaction of Grignard reagent compounds towards simple bromomagnesium hydroxylamines.[26]

It would be quite unwarranted, on the basis of known experiments, to extend the reaction mechanisms proposed here to all nitrosyl groups. Very probably such mechanisms do apply to compounds having a nitrosyl group attached to a carbon atom,[27] but even with such compounds distinctions will probably have to be made between aryl and alkyl magnesium halides. Furthermore, the course of reaction may be affected by the experimental conditions. The work described here was done under conditions followed rather generally in the unpublished studies on nitrobenzene, and in some experiments they may be said to duplicate essentially the conditions used by Wieland and co-workers. Deviations in temperature are without essential effect on the course of reaction between nitrobenzene and phenylmagnesium bromide.

Experimental Part

In general, 10.7 g., or 0.1 mole, of nitrosobenzene, purified by vacuum sublimation, was used in each run. The solution of nitrosobenzene in about 300 cc. of ether was made up and used in a three-necked flask provided with a reflux condenser, stirrer, dropping funnel and a tube for admitting pure, dry hydrogen. The heat of reaction produced by the slow addition of the first equivalent (0.1 mole) of phenylmagnesium bromide solution in ether caused a gentle refluxing. Early in the reaction, a brown precipitate formed and later this darkened and then disappeared. There was only a moderate reaction during the addition of the second equivalent of Grignard reagent, and after stirring for six hours the qualitative color test[25] for Grignard reagent was negative. More of the phenylmagnesium bromide (0.05 mole) was added, and after being allowed to stand overnight the solution again gave a negative test. A positive test, showing an excess of Grignard reagent, was obtained only when a total of three equivalents (in this case 0.3 mole) of phenylmagnesium bromide had been added. This test persisted even after stirring for one day.

The reaction mixture was decomposed by ice; then the ether layer was separated and dried with calcium chloride, filtered, and evaporated in a vacuum while a stream of hydrogen was passed over the ether. The residual solid yielded no crystalline diphenylhydroxylamine when treated with petroleum ether, although qualitative tests showed that some diphenylhydroxylamine was present.

The petroleum ether layer (and in other experiments, the ether layer) was extracted with dil. sodium hydroxide solution to remove phenol. Phenol was estimated gravimetrically by conversion to tribromophenol. Blank runs, made with equal volumes of the phenylmagnesium bromide solution which were stirred with 300 cc. of ether under conditions corresponding with those of the actual nitrosobenzene run, showed that practically identical amounts of phenol were present in each case.

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[26] Bromomagnesium derivatives of aldoximes and particularly ketoximes are quite resistant to Grignard reagents, as is known by the work of others, and studies now in progress in this Laboratory.

[27] It may be questioned whether amine oxides are to be classed with nitroso compounds. Studies with dimethylaniline oxide, as a type, show the formation of phenol and diphenyl, but in smaller amounts than are obtainable from nitrobenzene and nitrosobenzene.

TABLE I

NITROSOBENZENE AND PHENYLMAGNESIUM BROMIDE

Expt.[a]	Nitrosobenzene		C_6H_5MgBr,	Diphenylamine		Diphenyl,		Phenol,
	G.	Moles	moles	G.	Yield, %[b]	g.	Yield, %[c]	g.
A	10.7	0.1	0.3	5.6	33.1	11	60[d]	1.53
B	10.7	.1	.3	3.5	20.7[e]	7.1	32.7[f]	0.35
C	4.6	.043	.15	2.2	36.4	6.1	77.0	.6
D	10.7	.1	.3	7.2	42.6	10.4	54.5	.85
E	10.7	.1	.4	2.0	11.8	7.4	32.7	3.4[g]

[a] Expts. A, B and C were carried out at room temperature, D in boiling ether and E in a mixture of ether and benzene which was also refluxed. The purpose of Expt. D was to see if it were possible to increase the quantities of diphenylamine and of phenol. Because the yield of diphenylamine was increased when the ether solution was refluxed after the addition of the Grignard reagent, Expt. E was carried out at the higher temperature of the ether-benzene mixture to determine whether more diphenylamine would form. This time the phenylmagnesium bromide was added to the boiling solution of nitrosobenzene in 200 cc. of benzene. Refluxing was continued for four hours and a positive test was obtained only after the addition of the fourth equivalent of Grignard reagent. Considerable tarry material was formed in this high-temperature run.

[b] The yields of diphenylamine are undoubtedly somewhat lower than those actually obtained, because an investigation of the small fractions distilling above the boiling point of diphenylamine showed them to contain varying amounts of this base.

[c] The listed yields of diphenyl are those calculated after deducting the quantity of diphenyl determined in a number of blank runs. In this connection it is interesting to note that when a stock solution of phenylmagnesium bromide is kept in a bottle provided with an apparently tight-fitting rubber stopper, the quantity of diphenyl gradually increases with time. Experiments made to correct some conclusions of Meyer and Tögel [*Ann.*, **347**, 55 (1906)] indicate that this gradual increase in diphenyl is due not to moisture alone, but to moist air (or oxygen) which gets into the solution even during the ordinarily careful handling of the reagent.

[d] One g. of hydrazobenzene hydrochloride was obtained by the reduction of the azobenzene that distilled prior to the diphenyl. In other experiments the azobenzene was not determined, but was unquestionably present, as evidenced by the highly characteristic red color which was discharged on reduction by zinc dust and acetic acid.

[e] The low yield of diphenylamine in this experiment is due to the removal of some of the basic material in an effort to get crystalline diphenylhydroxylamine.

[f] The quantity of *p*-phenyldiphenyl obtained in this experiment was 0.3 g.

[g] It is difficult to account for this high yield of phenol. Possibly the high temperature used in this experiment causes the reaction to take a different course than is the case with the other experiments. It is to be noted that about four and not the usual three equivalents of phenylmagnesium bromide were required here. No blank run was made to determine whether the quantity of phenol increases when phenylmagnesium bromide is refluxed in an ether-benzene solution in an atmosphere of pure, dry hydrogen. In this connection it is interesting to observe that some experiments on chemiluminescence now in progress show that supposedly pure and dry hydrogen will cause *p*-chlorophenylmagnesium bromide to luminesce. Such luminescence disappears when the hydrogen, after the usual treatment for purification and drying, is bubbled through phenylmagnesium bromide. Probably the Grignard reagent will remove very small amounts of oxygen not taken up by pyrogallate solutions. If so, then it is possible that the traces of oxygen in "pure" hydrogen oxidize phenylmagnesium bromide (or ether[22]) more rapidly at higher temperatures.

After removing phenol by the alkaline extraction, the ether solution was dried with calcium chloride and treated with hydrogen chloride to precipitate the diphenylamine hydrochloride and other salts of basic materials. The crude amine hydrochloride was treated with sodium hydroxide solution, which in turn was extracted with ether. This ether solution was then dried, and after removing the ether, the amine was distilled in a vacuum. Most of the distillate was pure diphenylamine, according to the boiling point, melting point and mixed melting point made with an authentic specimen.

Vacuum distillation of the ether solution, after filtering the diphenylamine hydrochloride, gave first the small amounts of azobenzene, then the pure diphenyl and finally the small amounts of *p*-phenyldiphenyl.

The Reaction Between β,β-Diphenylhydroxylamine and Phenylmagnesium Bromide.—The directions of Wieland and Roseeu[3a] and Roth [3d] must be followed explicitly in order to obtain the crystalline diphenylhydroxylamine. Qualitative tests show that this hydroxylamine is present when slight departures are made in the experimental conditions (such as insufficient cooling), but it is almost impossible to crystallize it from the diphenylamine which accompanies it. In one experiment where this difficulty was met, the entire reaction mixture was worked up after the manner used in the experiments given in Table I, and there was obtained 36.1% of diphenylamine, 27.6% of diphenyl, 0.2 g. of *p*-phenyldiphenyl (starting with 0.1 mole of nitrosobenzene) and no phenol other than that originally present. The diphenylhydroxylamine when kept in a desiccator darkens somewhat after one day; it then undergoes considerable decomposition and takes on a liquid consistency after two days; finally, after several days, it solidifies and takes on the appearance of diphenylamine.

Phenylmagnesium bromide was added to 9.25 g. (0.05 mole) of diphenylhydroxylamine dissolved in 200 cc. of ether. The first equivalent (0.05 mole) of Grignard reagent reacted at once, quite probably replacing the hydrogen by the —MgBr group. Altogether three equivalents (0.15 mole) of phenylmagnesium bromide were required before a faint positive color test showed an excess of Grignard reagent. The reaction mixture was allowed to stand for 24 hours prior to hydrolysis. During the first five hours the mixture was cooled with ice and salt, and for the remaining time was allowed to stand at room temperature, stirring being used throughout. On working up as in the other experiments there was obtained 3.4 g. or 40.2% of diphenyl-amine, 5.4 g. or 70.1% of diphenyl and 1.08 g. of phenol. A blank run showed the same quantity of phenol in a corresponding aliquot of the Grignard reagent.

The Reaction Between *p*-Nitrosodimethylaniline and Phenylmagnesium Bromide.—This reaction was previously studied by Wieland[2] and Wieland and Kögl.[3e] They obtained *p,p′*-azo-N-dimethylaniline from the reaction between *p*-nitrosodimethylaniline and phenylmagnesium bromide, *p*-tolylmagnesium bromide and ethylmagnesium bromide. However, the reaction did not proceed as regularly as with nitrosobenzene and the expected hydroxylamine and secondary amine derivatives were not obtained.

The same difficulties were encountered in this work, and although the expected *p*-dimethylaminodiphenylamine was not obtained in crystalline form, the oil gave the highly characteristic color reactions of this compound with ferric chloride[28] and with hydrochloric acid.[29] Seeding with an authentic specimen of the desired base was without effect.

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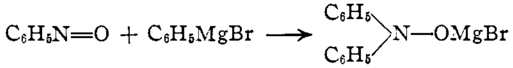
[28] Fischer and Wacker, *Ber.*, **21**, 2612 (1888).

[29] Piccard, *Ber.*, **46**, 1843 (1913).

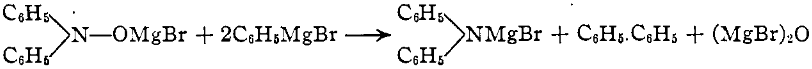
The procedures followed were those previously given in this paper. Again it was shown that about three equivalents of Grignard reagent are required. The quantity of phenol obtained is equal to that present in the original Grignard solution. Several runs were made under varying conditions of temperature. In one of the runs, at room temperature, there was obtained 24.7% of diphenyl and 26.4% of an oil that very probably consisted largely of *p*-dimethylaminodiphenylamine. In two other runs at higher temperatures the yield of diphenyl was 27.3 and 22.1%.

Summary

The following reactions are probably the chief ones that take place when phenylmagnesium bromide is added to nitrosobenzene.



$$C_6H_5N{=}O + C_6H_5MgBr \longrightarrow \begin{matrix}C_6H_5\\C_6H_5\end{matrix}{>}N{-}OMgBr \qquad (I)$$



$$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}{>}N{-}OMgBr + 2C_6H_5MgBr \longrightarrow \begin{matrix}C_6H_5\\C_6H_5\end{matrix}{>}NMgBr + C_6H_5.C_6H_5 + (MgBr)_2O \qquad (II)$$

Reaction II corrects the mechanism reported previously by others.

AMES, IOWA

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, COLUMBIA UNIVERSITY, No. 536]

ALPHA FURFURYL IODIDE (2-IODOMETHYL FURAN)

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In this paper the name α-furfuryl chloride, bromide, etc., will be used to denote the 2-methyl furan derivatives. Two furfuryl derivatives, C_4H_3-OCH_2–, are possible, those where the CH_2 group occurs in the 2 and in the 3 position.

In order to avoid the much longer notation which would be necessary to describe these derivatives if the 2-methyl furan notation were used, it seems justifiable to employ the shorter one which has the further advantage of longer usage.

The α-furfuryl halides have been but little investigated owing to their instability. Von Braun and Köhler[1] obtained the bromo derivative by treating α-furfurylmethylamine with cyanogen bromide, and Gilman and Vernon[2] prepared a solution of the chloro derivative by acting on α-furfuryl alcohol with thionyl chloride and with hydrogen chloride in the presence of a drying agent. Von Braun and Köhler were not able to isolate the bromide in a pure state for as soon as the ether in which it had been prepared was evaporated, the residue turned black. Neither could Gilman and Vernon isolate the corresponding chloride which they identified

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[1] Von Braun and Köhler, *Ber.*, **51**, 87 (1918).

[2] Gilman and Vernon, THIS JOURNAL, **46**, 2576 (1924).