

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

**THE MECHANISM OF REDUCTION OF AZOBENZENE BY ORGANOMAGNESIUM HALIDES<sup>1</sup>**

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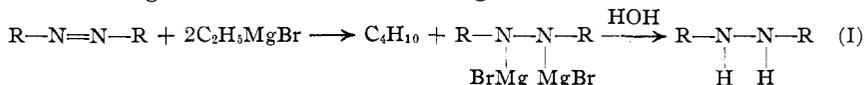
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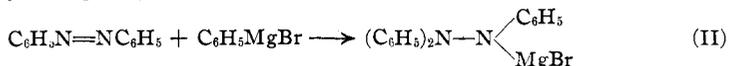
**Introduction**

In connection with studies concerning the constitution of types like aliphatic diazo compounds ( $R_2CN_2$ ) and diazo-imides ( $RN_3$ ) it was necessary to determine the mode of reaction of the Grignard reagent with a representative azo compound, namely, azobenzene. Azo compounds have been obtained in a number of reactions involving organomagnesium halides. In addition, the intermediate formation of azo compounds has been postulated in the interpretation of the mechanism of some reactions. Unfortunately, there appears to be some contradiction as well as considerable admitted uncertainty concerning the hypothetical intermediates.

Franzen and Deibel<sup>2a</sup> have shown that azobenzene and *p*-azotoluene react with ethylmagnesium bromide to give the corresponding hydrazo compounds. With no additional experimental evidence they proposed the following mechanism for the reducing action.



The reaction between azobenzene and  $RMgX$  compounds has been interpreted differently by others. First, Busch and Hobein<sup>3</sup> suggested tentatively that phenylmagnesium bromide added to azobenzene as follows.



This was proposed as a possible explanation for the formation of triphenylhydrazine from  $\beta$ -phenylhydroxylamine and phenylmagnesium bromide. Second, Hess and Rheinboldt,<sup>4</sup> in connection with studies concerning the reduction of the carbonyl group by some Grignard reagents, are inclined apparently to correlate the reduction of azobenzene with a compound such as benzaldehyde. According to this view the active reducing agent would be hydrogenmagnesium bromide ( $HMgBr$ ) formed from ethylmagnesium bromide with the accompanying evolution of ethylene. Franzen and Deibel<sup>2a</sup> did not report the nature of the evolved gas.

Long before the discovery of the Grignard reagent, Frankland and Louis<sup>5</sup>

<sup>1</sup> A preliminary report of this work was made at the Spring Meeting of the American Chemical Society held at Baltimore, Maryland, in April, 1925.

<sup>2</sup> (a) Franzen and Deibel, *Ber.*, **38**, 2716, (b) 2717 (1905).

<sup>3</sup> Busch and Hobein, *Ber.*, **40**, 2099 (1907).

<sup>4</sup> Hess and Rheinboldt, *Ber.*, **54**, 2043 (1921).

<sup>5</sup> Frankland and Louis, *J. Chem. Soc.*, **37**, 560 (1880).

studied the reaction between azobenzene and zinc diethyl. They obtained 70 g. of aniline from 80 g. of azobenzene and showed that the evolved gases consist of three volumes of ethylene to one of ethane. Because of the correspondence in many reactions involving zinc alkyls and RMgX compounds it might have been predicted that the course of reaction between azobenzene and these organometallic compounds would have some points of similarity. Some aniline is formed in the reaction of azobenzene with the Grignard reagent.

Certainly Reaction II suggested by Busch and Hobein is the one that would merit the greatest consideration if a forecast were to be made on the basis of current theories. There appears to be nothing in our present knowledge of the behavior of organomagnesium halides to warrant the interpretation proposed by Franzen and Deibel<sup>6</sup> (I). However, despite their limited experimental work they are correct.<sup>7</sup> By replacing the —MgX group by reliable reagents to get known compounds, it has been shown that reaction does take place according to Scheme I. *n*-Octane and other R-R compounds were obtained, generally in amounts that correspond with the hydrazo derivatives.

### Experimental Part

In general, 0.1 mole of azobenzene dissolved in ether<sup>8</sup> was added during stirring to an ether solution containing about 0.2 mole of the organomagnesium halide.<sup>9</sup> The mixture was then refluxed for eight hours, and early in this period a precipitate formed. With the lower RMgX compounds a gas was evolved, and although it was not collected it was tested for the presence of ethylenic hydrocarbons by bubbling through a solution of bromine in carbon tetrachloride.

After refluxing, the reaction mixture was hydrolyzed by an ammonium chloride solution. Several ether extractions were made, and the ether solution was washed with water, separated, and dried over sodium sulfate. The ether was distilled from a water-bath, and the residual crystal mass

<sup>6</sup> A somewhat comparable reaction is that between triphenylmethylmagnesium chloride and quinone. Three molecules of quinone and two of the Grignard reagent give quinhydrone and the triphenylmethyl ether of hydroquinone. [Schmidlin, Wohl and Thommen, *Ber.*, **43**, 1298 (1910).]

<sup>7</sup> Their explanation (Ref. 2) of the reduction of azines by RMgX compounds is probably incorrect, although their products (as well as others) were obtained in a later study by Busch and Fleischmann [*Ber.*, **43**, 740 (1910)]. The intermediate products formed from aldazines and ketazines are now under investigation.

<sup>8</sup> Because of the greater solubility of triphenylmethylmagnesium chloride and of phenylacetylmagnesium bromide in benzene, the azobenzene in benzene was added to an ether-benzene solution of the RMgX compound. The total volume of ether used in all other experiments was 250–300 cc.

<sup>9</sup> A slight excess over 0.2 mole of the RMgX compound was used. The excess was based on the yields of some Grignard reagents determined previously by Gilman and McCracken, *THIS JOURNAL*, **45**, 2462 (1923).

gave hydrazobenzene which was obtained quite pure by washing with small amounts of ether. A vacuum distillation of the mother liquors effected a further separation of the hydrazobenzene, azobenzene and R-R compound.

In experiments involving the replacement of the —MgX groups prior to hydrolysis, the special reagents, such as benzoyl chloride, were added to the mixture after the customary eight-hour period of refluxing. The quantity of such reagents used in a given experiment was equivalent to the RMgX compound. Subsequent to an additional four hours of refluxing during stirring, the mixture was hydrolyzed by ammonium chloride solution and then worked up in the customary manner.

All yields are based on the initial weight of azobenzene, even though considerable quantities of this compound were obtained in a few experiments.

Where solid compounds were obtained their identity was confirmed by a mixed-melting-point determination made with an authentic specimen when the true melting point was known.

TABLE I  
REACTION OF AZOBENZENE WITH ORGANOMETALLIC HALIDES

0.22 mole of organomagnesium halide used except as indicated in footnotes *b*, *c* and *h*, below.

Organometallic halide	Hydrazobenzene		R-R compound	Yield	
	G.	Yield, %		G.	%
CH <sub>3</sub> MgI <sup>a</sup>	6.0	32.6	....	...	..
<i>n</i> -C <sub>4</sub> H <sub>9</sub> MgBr <sup>b</sup>	9.7	52.7	<i>n</i> -octane	1	8.8
C <sub>6</sub> H <sub>11</sub> MgBr <sup>c</sup>	5.2	28.3	Di-cyclohexyl	5	30.1
C <sub>6</sub> H <sub>5</sub> MgBr <sup>d</sup>	7.5	41	Diphenyl	7.8	50.6
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> MgBr <sup>e</sup>	10.5	54.6	<i>p,p'</i> -ditolyl	5.6	30.8
MgBrC≡CMgBr <sup>f</sup>	0.9	4.9	....	...	..
C <sub>6</sub> H <sub>5</sub> C≡CMgBr <sup>g</sup>	...	..	....	...	..
C <sub>6</sub> H <sub>5</sub> CaI <sup>h</sup>	...	..	....	...	..
C <sub>2</sub> H <sub>5</sub> ZnI <sup>i</sup>	...	..	....	...	..
<i>n</i> -C <sub>4</sub> H <sub>9</sub> OMgI <sup>j</sup>	...	..	....	...	..
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NMgBr <sup>k</sup>	...	..	....	...	..
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SMgI <sup>l</sup>	...	..	....	...	..

<sup>a</sup> 10.5 G. or 57.7% of azobenzene was recovered.

<sup>b</sup> A large excess (0.44 mole) of RMgX compound was used because it was filtered through glass wool in order to remove the larger particles of magnesium which were thought to be responsible for the formation of 3.5 g. of aniline in another run. However, such reduction of hydrazobenzene to aniline by hydrogen from unused magnesium was not entirely excluded, for 1.8 g. of aniline was obtained in this run. (See "Discussion of Reactions.")

<sup>c</sup> 0.33 Mole of RMgX compound was used; 0.9 g. of aniline and 5 g. or a 27.5% yield of azobenzene were obtained. Formation of a troublesome emulsion that caused some of the ether layer to be lost explains, in part, the low yields.

<sup>d</sup> The characteristic precipitate did not form until the solution had been refluxed for nearly three hours; 8.2 g. or 45.5% of azobenzene was recovered.

<sup>e</sup> 1.0 G. of aniline and 4.5 g. or 24.7% of azobenzene were obtained.

<sup>f</sup> The gas evolved in the early part of the refluxing was not absorbed by a carbon tetrachloride solution of bromine. It was probably *n*-butane formed from unreacted ethylmagnesium bromide that was used to prepare the dibromomagnesium acetylene compound; 81.9% of azobenzene was recovered.

<sup>g</sup> All of the azobenzene was recovered in addition to 21 g. or 94% of the phenyl-acetylene. A repeat run in which the reaction mixture was refluxed for 16 hours gave similar results.

<sup>h</sup> 0.33 Mole of RMgX compound was used; 14 g. or 21% of unused iodobenzene was recovered, in addition to an almost quantitative amount of azobenzene.

<sup>i</sup> The reaction mixture was refluxed for 12 hours, and 17.1 g. or 94% of azobenzene was recovered.

<sup>j</sup> 93.4% of azobenzene and most of the *n*-butyl alcohol were recovered.

<sup>k</sup> 91.7% of diphenylamine and 94.5% of azobenzene were recovered.

<sup>l</sup> The azobenzene was recovered practically quantitatively in addition to 80% of *p*-thiocresol. Some *p,p'*-ditolyl disulfide was obtained from 4 g. of an oil. The disulfide was probably due to air oxidation of the thiocresol, for no hydrazobenzene was obtained.

TABLE II

## REACTION OF AZOBENZENE, RMgX COMPOUND AND ACYLATING AGENT

In these experiments 0.1 mole of azobenzene and 0.22 mole of RX compound were used.

RX	Acylating agent	Mole	Acylated hydrazobenzene	Yield G.	%
Ethyl bromide	Acetyl chloride	0.25	Mono-acetyl <sup>a</sup>	5.8	25.6
Ethyl bromide	Acetic anhydride	.25	Mono-acetyl <sup>b</sup>	5.0	22.1
Bromobenzene	Acetyl chloride	.33	Mono-acetyl <sup>c</sup>	4.5	20
Bromobenzene	Benzoyl chloride	.22	Dibenzoyl <sup>d</sup>	21.0	54
$\beta$ -Bromostyrene	Benzoyl chloride	.22	Dibenzoyl <sup>e</sup>	18.8	48
Phenyl-acetylene <sup>f</sup>	Benzoyl chloride	.22	....	..	..
Triphenylmethyl chloride <sup>g</sup>	Benzoyl chloride	.33	....	..	..
Ethyl bromide <sup>h</sup>	Benzoyl chloride	.22	....	..	..

<sup>a</sup> The oil from which the mono-acetyl-hydrazobenzene was obtained could not be induced to crystallize after standing for several months. A variety of solvents was tried and seeding with the known diacetyl-hydrazobenzene also gave no crystals. The oil distilled through the range 160–210° (3 mm.). The authentic specimen of mono-acetyl-hydrazobenzene used for the mixed melting point was prepared according to the method of Stern [*Ber.*, 17, 379 (1884)]. Temperatures recorded in this paper are uncorrected.

In another run 0.33 mole of freshly distilled acetyl chloride was used and 5.6 g. or 24.7% of mono-acetyl-hydrazobenzene was obtained.

<sup>b</sup> The heavy oil from which mono-acetyl-hydrazobenzene was obtained was extracted with hot water, the extract boiled with bone black for one hour, filtered and then set aside for slow evaporation. After ten days crystals were obtained melting at 104–105°. These were shown to be diacetyl-hydrazobenzene by comparison with the known compound prepared according to the method of Schmidt and Schultz [*Ann.*, 207, 320 (1881)].

This was the only experiment in which the heavy oil was extracted with hot water. The oil from the others also probably contained the diacetyl-hydrazobenzene.

<sup>c</sup> In addition to the same heavy oil, 12.3 g. or 80% of diphenyl and 1.0 g. or 5.5% of azobenzene were obtained.

<sup>d</sup> The formation of dibenzoyl-hydrazobenzene was confirmed by a mixed-melting-

point determination with the same compound prepared according to the method of Freundler [*Compt. rend.*, **136**, 1553 (1903)].

In addition, 12.4 g. or 80% of diphenyl, 2 g. or 11% of azobenzene, and 4.5 g. of benzanilide were obtained. The benzanilide resulted, no doubt, from the decomposition of dibenzoyl-hydrazobenzene during the vacuum distillation. Stern [*Ber.*, **17**, 379 (1884)] has reported a related reaction where azobenzene and acetanilide are obtained when mono-acetyl-hydrazobenzene is heated. It is possible that a small part of the benzanilide may have been due to a reaction between aniline and benzoyl chloride.

It was shown that dibenzoyl-hydrazobenzene is not formed in ether solution from hydrazobenzene and benzoyl chloride.

<sup>e</sup> In addition, 1,4-diphenylbutadiene was obtained in a 77.7% yield and 24.2% of azobenzene was recovered.

<sup>f</sup> Prior to the addition of benzoyl chloride, the mixture was refluxed for 16 hours, but there was no evidence of reaction. In order to make certain that phenylacetylmagnesium bromide was present before the addition of benzoyl chloride, a small amount was removed, treated with carbon dioxide, and phenylpropionic acid was obtained.

After hydrolysis with ammonium chloride, there were obtained 0.4 g. of benzamide, 17.7 g. or 94.2% of azobenzene, and a liquid that distilled between 150–210°. This liquid was not studied; it probably owes its formation to a reaction between benzoyl chloride and phenylacetylmagnesium bromide.

<sup>g</sup> In a first run, 69.3% of triphenylmethyl peroxide was obtained in addition to an apparently intractable red oil.

In a second run, the azobenzene and triphenylmethylmagnesium chloride were refluxed for 16 hours and then for an additional eight hours after benzoyl chloride had been added. After hydrolysis by ammonium chloride, air was bubbled in for four hours to expedite the formation of triphenylmethyl peroxide; 4 g. of benzamide and 44.9% of triphenylmethyl peroxide were obtained in addition to the red oil from which no dibenzoyl-hydrazobenzene was obtained.

<sup>h</sup> The reaction between azobenzene and ethylmagnesium bromide was carried out in an ice-salt mixture. A small amount of gas, possibly butane, was evolved. The quantity of precipitate formed was not as large as that observed in other experiments when the ether was refluxed. After the addition of benzoyl chloride, the reaction mixture was allowed to warm to room temperature where it stood for eight hours prior to hydrolysis. Again, only a small amount of precipitate was evident and not the comparatively large amount obtained in other runs that gave dibenzoyl-hydrazobenzene. After hydrolysis, 5 g. of a solid was obtained and this yielded some benzamide and a compound sparingly soluble in alcohol and benzene. This compound melted at 225–235° and was not further studied. Considerable azobenzene was obtained but no dibenzoyl-hydrazobenzene.

In another run the reaction mixture was cooled to 0° before the addition of benzoyl chloride. Again, some gas was evolved and after the mixture had been stirred for two hours the amount of precipitate was almost as large as that ordinarily observed when the reaction was carried out in boiling ether. After the addition of benzoyl chloride, the mixture was refluxed and, although a large amount of precipitate formed, no dibenzoyl-hydrazobenzene was obtained from the products of hydrolysis. About 7 g. of a compound melting at 232–235° was obtained.

*p,p'*-Azotoluene and Phenylmagnesium Bromide.—Ten and a half g. or 0.05 mole of *p,p'*-azotoluene in benzene was added to 0.11 mole of phenylmagnesium bromide. After the mixture had been refluxed for eight hours it was hydrolyzed and worked up in the customary manner. The only crystals that could be obtained from the residue were those of azotoluene. The apparent absence of *p,p'*-hydrazotoluene is due to its

greater solubility and to its ready oxidation to the azotoluene. Evidence of reduction was found in the formation of 5.7 g. or a 74% yield of diphenyl and 2.8 g. or a 26.1% yield of *p*-toluidine. *p,p'*-Hydrazotoluene when heated decomposes into *p,p'*-azotoluene and *p*-toluidine.<sup>10</sup>

***p*-Dimethylamino-azobenzene, Benzylmagnesium Chloride and Benzoyl Chloride.**—The reaction was carried out in the usual manner between 0.1 mole of *p*-dimethylamino-azobenzene in benzene, 0.22 mole of benzylmagnesium chloride and 0.22 mole of benzoyl chloride. After hydrolysis, 5 g. of a crystalline product was obtained and this yielded 2.0 g. of benzamide and 1.9 g. of a compound melting at 160–161° when crystallized from alcohol. This compound was fairly soluble in ether, formed a crystalline derivative when treated with dry hydrogen chloride and is, no doubt, the dibenzoyl-*p*-dimethylamino-hydrazobenzene.

The oil on vacuum distillation gave 12 g. or a 66% yield of dibenzyl, a little benzamide and a small amount of a compound melting at 223–225°. This last compound is very likely benzoyl-*p*-amino-dimethylaniline  $[(\text{C}_6\text{H}_5)_2\text{NC}_6\text{H}_4\text{NHCOC}_6\text{H}_5]$  which melts<sup>11</sup> at 228°.

**Diazo-aminobenzene, Ethylmagnesium Bromide and Benzoyl Chloride.**—A gas was evolved when 0.1 mole of diazo-aminobenzene was added to 0.33 mole of ethylmagnesium bromide. After the mixture had been refluxed for 16 hours, 0.33 mole of benzoyl chloride was added whereupon a vigorous reaction took place. The products obtained were 2.5 g. of benzamide, 8.0 g. of benzamide and 16 g. or a 31.3% yield of *sym.*-diphenyl-tribenzoyl-triazane  $[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{CO})\text{NN}(\text{COC}_6\text{H}_5)\text{N}(\text{COC}_6\text{H}_5)(\text{C}_6\text{H}_5)]$ , m. p. 160–161°, that crystallized in needles from alcohol. When 2.0 g. of this compound was hydrolyzed by boiling with concd. hydrochloric acid, 1.6 g. of benzoic acid, 0.6 g. of aniline hydrochloride and some ammonium chloride were obtained.

**Azobenzene, Ethylmagnesium Bromide and Phenylisocyanate.**—Phenylisocyanate (0.22 mole) was added to the reaction mixture obtained from 0.1 mole of azobenzene and 0.22 mole of ethylmagnesium bromide; 11 g. of an ether-insoluble mixture was obtained after hydrolysis, and from this there were isolated a small amount of tri(phenylisocyanurate)  $[(\text{C}_6\text{H}_5\text{NCO})_3]$ , m. p. 275–276°, and two unidentified solids that when crystallized from alcohol melted at 178–179° and 185–186°, respectively. The ether extract of the hydrolysis mixture gave a heavy oil from which the only product obtained was azobenzene.

**Hydrazobenzene, Ethylmagnesium Bromide and Phenylisocyanate.**—Phenylisocyanate (0.22 mole) was added to the reaction product of 0.1 mole of hydrazobenzene and 0.22 mole of ethylmagnesium bromide; 14 g. of an ether-insoluble mixture was obtained after hydrolysis. Several recrystallizations from benzene and from alcohol gave a little carbanilide, formed probably by the hydrolysis of phenylisocyanate, and a compound that melted sharply at 212°. This compound does not have the properties of the expected dicarbanilido-hydrazobenzene, which is described<sup>12</sup> as a gray, amorphous substance, insoluble in benzene and melting at 218–220°.

**Azobenzene, Phenylmagnesium Bromide and Phenylisocyanate.**—The same equivalent quantities were used as in the experiment with ethylmagnesium bromide; 14 g. of an ether-insoluble compound was obtained after hydrolysis. When recrystallized from either alcohol or benzene it melted sharply at 175°. When this compound was heated, the odor of phenylisocyanate was evident, but the compound which melts at the same temperature as diphenyl-di-isocyanate  $[(\text{C}_6\text{H}_5\text{NCO})_2]$  does not give the reactions described for this polymer.

<sup>10</sup> Melms, *Ber.*, 3, 549 (1870).

<sup>11</sup> Börnstein, *Ber.*, 29, 1479 (1896).

<sup>12</sup> Goldschmidt and Rosell, *Ber.*, 23, 487 (1890).

The ether solution gave 12 g. of a mixture from which azobenzene was removed by washing with petroleum ether. The residue after recrystallization from alcohol gave 5 g. of diphenyl, some carbanilide, and 3.5 g. of benzanilide, probably formed as a result of the reaction between phenylisocyanate and phenylmagnesium bromide.

**Azobenzene, Phenylmagnesium Bromide and Diethyl Sulfate.**—Diethyl sulfate (0.33 mole) was added to the reaction product of 0.1 mole of azobenzene and 0.22 mole of phenylmagnesium bromide. After the mixture had been refluxed for eight hours, it was hydrolyzed and the residue obtained from the ether extractions was vacuum-distilled. Diphenyl was obtained in a yield of 12.5 g. or 81.1%.

Two and a half g. of a liquid distilled between 140° and 155° (1.5 mm.). On redistillation, 1.5 g. was obtained between 140° and 145° (1.5 mm.). *sym.*-Diphenyl-diethyl-hydrazine boils at 141° (1 mm.). However, the liquid obtained did not give the characteristic color reaction with acetic acid.<sup>13</sup>

### Discussion of Reactions

The mechanism of reaction suggested by Franzen and Deibel (Scheme I) is undoubtedly correct. The presence of an —MgX group on each of the nitrogen atoms is established by replacing these groups by the acetyl and benzoyl groups. Furthermore, the yield of R-R compound corresponds with that of hydrazobenzene or its derivatives.

**The HMgX Theory of Reduction.**—Admittedly some facts exist which can be used to lend support to the suggestion of Hess and Rheinboldt<sup>4</sup> that reduction may be due to addition of the hypothetical<sup>14</sup> hydrogenmagnesium halide. The HMgX compounds are supposed to be formed with an olefinic compound from Grignard reagents having a hydrogen and the —MgX group on adjacent carbon atoms. First, significant quantities of *mono*-acetyl-hydrazobenzene were formed in several experiments where acetyl chloride and acetic anhydride were used to "anchor" the —MgX groups. Second, no apparent reduction occurred with dibromomagnesium acetylene, phenylacetylenylmagnesium bromide and triphenylmethylmagnesium chloride. These are exactly the types that should not be capable of forming HMgX compounds and, accordingly, they would not be expected to cause reduction on the basis of HMgX addition to the azo linkage. Third, the absence of reducing action with ethylmagnesium bromide at low temperatures also fits in correctly with the HMgX theory which postulates, in general, an elevated temperature in order to have the RMgX compound break down into HMgX and an olefinic compound. This dissociation is assumed to follow a preliminary addition of the entire RMgX compound.

There is no ready explanation for the formation of *mono*-acetyl-hydrazobenzene. However, some *diacetyl*-hydrazobenzene accompanies the formation of the *mono*-acetyl derivative. Furthermore, with benzoyl chloride no *monobenzoyl*-hydrazobenzene was obtained. The experiment with

<sup>13</sup> Wieland and Fressel, *Ann.*, **392**, 133 (1912).

<sup>14</sup> A later paper will contain an account of some new attempts to prepare hydrogenmagnesium halides, particularly by catalytic reduction of RMgX compounds.

diethyl sulfate is an indication of the presence of two  $\text{—MgX}$  groups. This reagent which has been so useful in the characterization of the  $\text{—MgX}$  group in other studies<sup>15</sup> suffers the inherent disadvantage of giving here a highly reactive tetra-substituted hydrazine.<sup>13</sup> Little can be said concerning the reactions with phenylisocyanate, because of the obvious formation of by-products (probably cyclic in nature) with the reactive hydrazo derivatives.

It is true that those Grignard reagents which do not have a hydrogen and an  $\text{—MgX}$  group on adjacent carbon atoms do not effect reduction of the azo group. However, it is equally true that compounds which generally are not expected to give  $\text{HMgX}$  do effect reduction of the azo group. Such compounds are methylmagnesium iodide, benzylmagnesium chloride and the arylmagnesium halides. It is possible that the reported failure of triphenylmethylmagnesium chloride to reduce azobenzene may be due to steric influences. This is doubtful in view of the reactions this  $\text{RMgX}$  compound undergoes wherein steric hindrance is apparently of a greater order. The failure of the acetenylmagnesium halides to reduce may be due in part to their lesser activity. Several unpublished reactions show that these compounds are less active than other Grignard reagents.

The objection concerning the absence of reduction with ethylmagnesium bromide at a low temperature is not a serious one. Everything points to the formation of an intermediate molecular addition compound. Obviously the application of heat may be just as necessary to cause dissociation of the  $\text{RMgX}$  complex into  $\text{—MgX}$  and  $\text{R}$  as into  $\text{HMgX}$  and an olefinic compound. The failure of ethylmagnesium bromide to reduce at low temperatures may be cited by some as another example of the general inertness of the azo group.<sup>16</sup>

Above all, it cannot be too strongly emphasized that no olefinic compound was found in the products of reaction. Such a compound is an invariable concomitant of reductions according to the  $\text{HMgX}$  theory.

**Reduction Beyond the Hydrazobenzene Stage.**—Aniline was found among the products in several experiments where azobenzene was used, and *p*-toluidine was obtained in the *p,p'*-azotoluene run. It was first thought that the aniline owed its formation to reduction of hydrazobenzene by hydrogen formed during hydrolysis from the unused magnesium. In a check experiment the Grignard reagent was filtered from large particles of unused magnesium, and although the yield of aniline decreased, the amount obtained was appreciable.

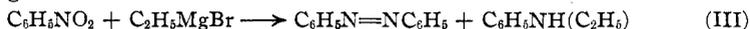
Two other explanations suggest themselves for the formation of aniline (and *p*-toluidine). First, the hydrazobenzene may have been transformed

<sup>15</sup> Gilman and Hoyle, *THIS JOURNAL*, **44**, 2621 (1922). Also, Gilman and Kinney, *ibid.*, **46**, 493 (1924).

<sup>16</sup> Hurd, *Science*, **61**, 495 (1925).

partly, during the vacuum distillation, into aniline and azobenzene. This reaction has been observed by others but generally at higher temperatures than those used in this study. Second, the Grignard reagent may have reacted with the intermediate hydrazo derivative, reducing it to aniline. This splitting between the two nitrogen atoms has already been suggested by Wieland and Roseeu<sup>17</sup> to account for the formation of diphenylamine from the Grignard reagent and trisubstituted hydrazines having two phenyl groups on a nitrogen. Also, it will be recalled that azobenzene and zinc diethyl give an excellent yield of aniline.<sup>5</sup>

**Effect of Temperature.**—Attention has already been directed to the fact that the reduction of azobenzene to hydrazobenzene requires that the reaction be carried out at the boiling point of ether. Hepworth<sup>18</sup> in a study of the reaction between aromatic nitro compounds and alkylmagnesium halides obtained azo compounds and secondary amines, by the following reaction.



The reactions were carried out in an ice-salt mixture, and the RX compound was added with the nitro compound to magnesium so that the Grignard reagent was used up at the moment of its formation. Unpublished results of work now in progress show that when the reaction mixture from prepared RMgX compound and aromatic nitro compound is allowed to reflux during the addition of one or the other of these compounds in ether solution, no azo or hydrazo compound is obtained. For the present it is hazardous to interpret the different course of reaction, for no experiments have yet been made at the boiling point of ether and with the RMgX compound prepared *in the presence* of nitro compound.

Busch and Hobein<sup>3</sup> obtained *p,p'*-dichloro-azobenzene when the mixture formed in the reaction between *p*-chlorophenylhydroxylamine and phenylmagnesium bromide was cooled. As was previously mentioned<sup>3</sup> they obtained triphenylhydrazine from  $\beta$ -phenylhydroxylamine and phenylmagnesium bromide when the mixture was not cooled. If the azo compound is treated with the Grignard reagent in ether solution with no external cooling then reduction to the corresponding hydrazo compound should take place.

One conclusion to be drawn, therefore, from the present work as it concerns the studies of Hepworth and of Busch and Hobein is that no azo compound is formed as an intermediate product when their reactions are carried out without external cooling.

**Mechanism of Other Reductions.**—Many varied types of compounds undergo reduction by means of the Grignard reagent.<sup>19</sup> Current theories

<sup>17</sup> Wieland and Roseeu, *Ber.*, **48**, 1117 (1915).

<sup>18</sup> Hepworth, *J. Chem. Soc.*, **117**, 1004 (1920).

<sup>19</sup> Meisenheimer, *Ann.*, **442**, 180 (1925). This is the most recent reference to the reducing action of RMgX compounds. Earlier references are obtainable from this article and Ref. 4.

to account for such reduction are based on the intermediate formation of  $\text{HMgX}$ . Satisfactory proof of such a mechanism has been offered for the reduction of some carbonyl compounds. However, R-R compounds have been obtained in a number of reactions where reduction takes place. Aromatic nitro compounds are reduced to secondary amines, and unusual amounts of R-R compounds accompany such reduction.<sup>20</sup> Even with a carbonyl compound such as furfural, large amounts of R-R compounds are reported.<sup>21</sup> Some peroxides, diethyl peroxide in particular, give considerable quantities of biphenyl when treated with phenylmagnesium bromide.<sup>20</sup>

It is probable that reductions other than those of azo compounds may involve the addition of two or more  $\text{—MgX}$  groups and the formation of R-R compounds.

**Reaction with Other Azo Groups.**—The four azo compounds studied in this work are aromatic in nature. It is probably safe to predict that a like reaction will occur with azo compounds having one or both of the R groups attached to the nitrogens aliphatic in nature.

However, there are other types that have two nitrogen atoms joined by a double or triple bond, and they do not show the reaction of  $\text{RN=NR}$  compounds towards the Grignard reagent. Among these are aliphatic diazo compounds ( $\text{R}_2\text{CN}_2$ ),<sup>22</sup> diazo-imides ( $\text{RN}_3$ )<sup>22</sup> and diazonium salts.<sup>20</sup>

Rosset<sup>23</sup> recently published an account of the reaction between phenylmagnesium bromide and phosphorus chloronitride,  $(\text{PNCl}_2)_3$ . A trimer was obtained in which all of the chlorine atoms were replaced by phenyl groups. Although the structure of these compounds is not known, one of the suggested formulas is a 6-membered ring with double bonds between alternate phosphorus and nitrogen atoms. If this structure is correct, one might expect reduction of the  $\text{—P=N—}$  linkage after the manner of reaction of the  $\text{—N=N—}$  linkage. A more satisfactory  $\text{—P=N—}$  linkage for a study of this kind is to be found in the phosphazines of Staudinger.<sup>24</sup>

**Applications.**—The good yields of some R-R compounds suggest the possibility of using azobenzene and  $\text{RMgX}$  compounds in synthetic work. This is strikingly illustrated by the high yield of pure 1,4-diphenylbutadiene from styrylmagnesium bromide. Although the azobenzene can be readily recovered from the hydrazobenzene, it remains to be determined whether

<sup>20</sup> Unpublished results.

<sup>21</sup> Hale, McNally and Pater, *Am. Chem. J.*, **35**, 68 (1906).

<sup>22</sup> A report of this work was made at the Spring Meeting of the American Chemical Society at Baltimore, Maryland, in April, 1925. See *Science*, **61**, 495 (1925). Detailed results will be published later.

<sup>23</sup> Rosset, *Compt. rend.*, **180**, 750 (1925).

<sup>24</sup> Staudinger and Mayer, *Helvetica Chim. Acta*, **2**, 619 (1919). Studies of this type as well as of arseno- and stibinobenzene are in progress.

the reaction has sufficient advantages over other methods, one of which involves the Grignard reagent.<sup>25</sup>

The reaction may find some application in the preparation of substituted hydrazo compounds, where the corresponding hydrazo compounds are very unstable. The —MgX groups on the two nitrogens are undoubtedly capable of undergoing many of the reactions of Grignard reagents. These salts are more accessible than the alkali metal salts of Schlenk.<sup>26</sup>

Because of the apparently different rates of reaction between RMgX compounds and azobenzene it may be possible to determine the relative reactivities of Grignard reagents, inasmuch as all RMgX reactions involve at some stage a dissociation into R and —MgX.<sup>27</sup>

### Summary

It has been proved that the following reaction takes place between azobenzene and the Grignard reagent.  $C_6H_5N=NC_6H_5 + 2RMgX \longrightarrow C_6H_5N(MgX)N(MgX)C_6H_5 + R-R.$

AMES, IOWA

## COMPOUNDS FORMED BETWEEN TRIMETHYLTIN HYDROXIDE AND TRIMETHYLTIN HALIDES

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Callis<sup>1</sup> has observed that under the action of sunlight, trimethyltin iodide acquires a brown color which slowly disappears in the dark. After some time, crystals are formed which at times are contaminated by other products. Callis showed that oxygen is absorbed in the course of the reaction. The brown color is apparently due to iodine which is displaced from the compound by oxygen under the action of sunlight.

It was thought worth while to study the crystalline product formed in this photochemical reaction. It was found that the disappearance of color, when the iodide is removed from the action of light, is due to the presence of tetramethyltin as impurity. In the absence of sunlight, the iodine, previously formed, slowly reacts with the tetramethyltin to form trimethyltin iodide and methyl iodide, according to a well-known reaction. The compound formed, which crystallizes in the form of needles, is readily soluble in water and absolute alcohol and only slightly soluble in such organic solvents as benzene and ether. Its aqueous solutions are strongly acidic, indicating a relatively high degree of hydrolysis.

<sup>25</sup> Gilman and Parker, *THIS JOURNAL*, **46**, 2823 (1924).

<sup>26</sup> Schlenk, Appenrodt, Michael and Thal, *Ber.*, **47**, 473 (1914).

<sup>27</sup> Kondyrew [*Ber.*, **58**, 459 (1925)] is now studying the conductivities of RMgX compounds.

<sup>1</sup> Callis, *Dissertation*, Clark University, 1922.