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I. The correlation of some aromatic types with physiological action, Local anesthetics containing the furan, thiophene and pyrrole nuclei; II. Studies in reduction: A. The existence of hydrogenmagnesium halides, B. The reduction of azo compounds

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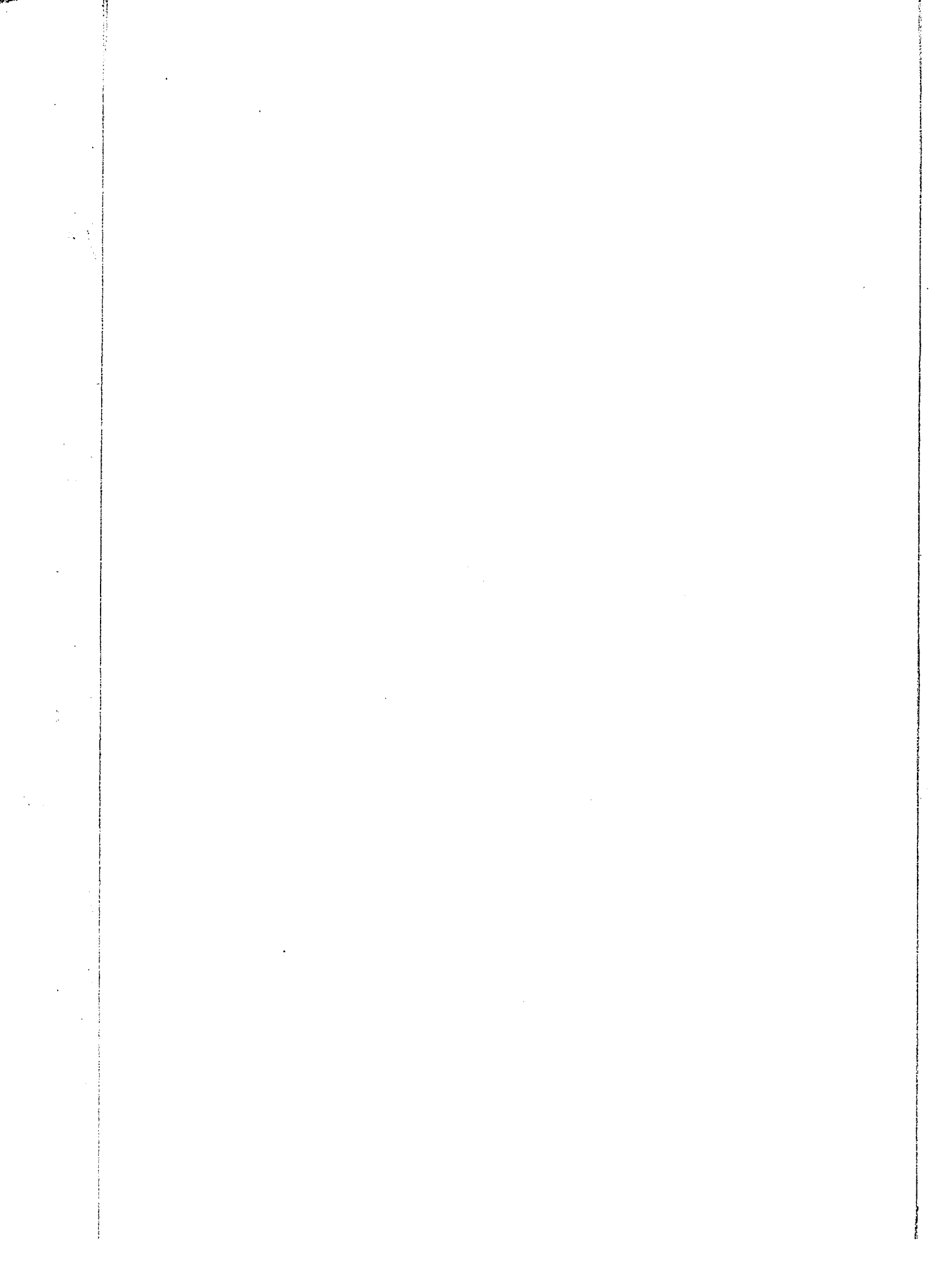
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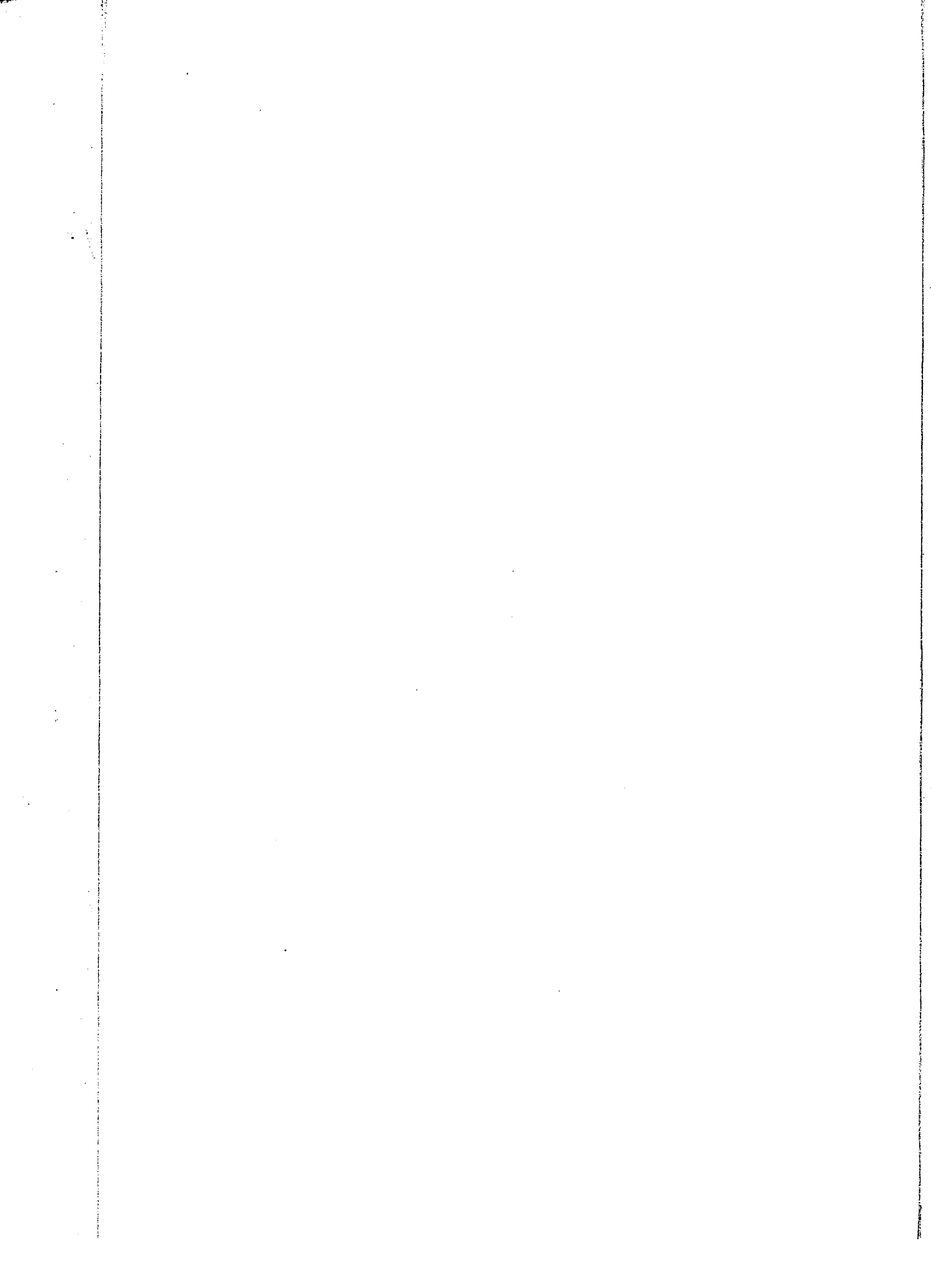
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I. THE CORRELATION OF SOME AROMATIC  
TYPES WITH PHYSIOLOGICAL ACTION.  
LOCAL ANESTHETICS CONTAINING THE  
FURAN, THIOPHENE AND PYRROLE  
NUCLEI.

II. STUDIES IN REDUCTION.

- A. THE EXISTENCE OF HYDROGENMAGNESIUM  
HALIDES.  
B. THE REDUCTION OF AZO COMPOUNDS.

By

Russell Marion Pickens.

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## STUDIES IN REDUCTION.

A. The Existence of Hydrogenmagnesium Halides.

B. The Reduction of Azo Compounds.

### INTRODUCTION.

It was only a short time after the introduction of the Grignard reagent that its reducing properties became evident. Grignard<sup>1</sup>, in treating benzaldehyde with isoamylmagnesium bromide obtained some benzyl alcohol and diisoamyl besides the phenylisoamyl carbinol that resulted from the normal reaction.

Yocich found that arylmagnesium halides<sup>2</sup> and phenylacetylenemagnesium bromide<sup>3</sup> add to the carbonyl group of chloral to form the corresponding tertiary alcohols. However when ethylmagnesium bromide and isoamylmagnesium bromide react with chloral he<sup>4</sup> found that a reducing action took place to form trichloroethyl alcohol, and with isoamylmagnesium bromide, some isoamylene was obtained as a byproduct.

When phenylacetylenemagnesium bromide was allowed

1. Grignard, Ann. chim., (7) 24, 433 (1901).
2. Yocich, J. Russ. Phys. Chem. Soc., 34, 96 (1902).  
J.C.S., 106, 402 (1914).
3. Yocich, *ibid.*, 34, 241 (1902).  
J.C.S., 106, 403 (1914).
4. Yocich, *ibid.*, 36, 443 (1904).  
J.C.S., 106, 375 (1914).

to react with nitrobenzene Yocich<sup>5</sup> obtained a hydrocarbon having the composition  $C_{18}H_{10}$  which is a product of the reducing action of this Grignard reagent on nitrobenzene. The hydrocarbon has since been identified as diphenyl diacetylene<sup>6</sup>.

By the action of alkylmagnesium halides on nitrogen dioxide Wieland<sup>7</sup> has shown that the analogy to carbon dioxide does not hold. For example, nitrogen dioxide and ethylmagnesium iodide yields  $\beta, \beta'$ -diethyl hydroxylamine.

Göttermann and Maffezzoli<sup>8</sup> found that while arylmagnesium halides reacted with ethyl formate to give satisfactory yields of aldehydes the use of isobutylmagnesium bromide resulted in a low yield. The difficulty was probably due to a reducing action.

In attempting to prepare cyclohexyl cyclohexanol from cyclohexanone and cyclohexylmagnesium chloride Sabatier and Mailhe<sup>9</sup> found that cyclohexene and cyclohexanol were formed. They<sup>10</sup> report an analogous reaction when benzophenone was treated with cyclohexy-

5. Yocich, J. Russ. Phys. Chem. Soc., 35, 555 (1903).  
J. C. S., 106, 396 (1914).

6. Unpublished work of Gilman and McCracken.

7. Wieland, Ber., 36, 2315 (1903).

8. Göttermann and Maffezzoli, Ber., 36, 4152 (1903).

9. Sabatier and Mailhe, Compt. rend., 138, 1321 (1904).

10. Sabatier and Mailhe, ibid., 139, 343 (1904).

magnesium chloride. In this case benzhydrol and cyclohexene were formed. They found dicyclohexyl ketone to be reduced in a similar manner to form dicyclohexyl carbinol and cyclohexene. The action of cyclohexylmagnesium chloride<sup>11</sup> on cyclohexanone resulted in the formation of cyclohexene and cyclohexanol.

Oddo<sup>12</sup> found the chief product of the reaction between ethylmagnesium iodide and nitrobenzene to be ethylaniline. He<sup>13</sup> also studied the action of phenylmagnesium bromide on sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ) and found that benzenesulfinic acid was formed along with small amounts of chlorobenzene and diphenyl.

When tert-butylmagnesium chloride reacts with methyl formate Bouveault<sup>14</sup> found tert-butyl carbinol to be the chief product. Only a small quantity of the aldehyde was produced.

Franzen and Deibel<sup>15</sup> have shown that ethylmagnesium bromide reacts with azobenzene and with azotoluene

11. Sabatier and Mailhe, *compt. rend.*, 141, 298. (1905).

12. Oddo, *R. Accad. Lincei.*, (V), 13, 11, 220 (1904).

*J.C.S.*, 86, 882 (1904).

13. Oddo, *ibid.*, (V), 14, 169 (1905).

*J.C.S.*, 88, 400 (1905).

14. Bouveault, *Compt. rend.*, 138, 1108 (1904).

15. Franzen and Deibel, *Ber.*, 38, 2716 (1905).

to give a good yield of the corresponding hydrazo compound. They likewise observed a reducing action of ethylmagnesium bromide on benzaldazine with the formation of benzylidene benzylhydrazone. To explain the mechanism of the reaction they assumed the formation of butane and the addition of  $-Mg Br$  groups to the  $-N=N-$  and the  $-C=N-$  linkages.

Sachs and Sachs<sup>16</sup> treated p-dimethylamino benzaldehyde with various alkyl- and arylmagnesium halides at an elevated temperature and found that the oxygen atom could be replaced by 2 R groups from the  $RMgX$  compound employed. The yields of hydrocarbon were high in most cases.

Konowalow, Miller and Timtschenko<sup>17</sup> have found that ethylmagnesium iodide reduces fenchone to fenchyl alcohol and that tert-butyl- and tert-amylmagnesium bromide reduce benzophenone to benzhydrol.

Hale, McNally and Peter<sup>18</sup> report the formation of no tertiary alcohol when phenyl- and benzylmagnesium bromide are allowed to react with furfuraldehyde. The only products isolated were large quantities of diphenyl and dibenzyl.

16. Sachs and Sachs, Ber., 38, 517 (1905).

see also Sachs and Weigert, Ber., 40, 4361 (1907).

17. Konowalow, Miller and Timtschenko, J. Russ. Phys.-Chem. Soc., 38, 447 (1906). Centralblatt, I, 312 (1906).

18. Hale, McNally and Peter, Am. Chem. J., 35, 68 (1906).

It is possible that the failure to obtain the desired tertiary alcohols may have been due to the reducing action of the Grignard reagent.

In explaining the formation of triphenyl hydrazine from phenylhydroxylamine and phenylmagnesium bromide Busch and Hobein<sup>19</sup> postulate the intermediate formation of azobenzene after which phenylmagnesium bromide is assumed to add to the -N=N- linkage. Results which will be described in this paper make the latter assumption improbable.

The action of alkylmagnesium iodides and alkylzinc iodides on nitroparaffins has been studied by Bewad<sup>20</sup>. He found that substituted hydroxylamines were formed in all cases.

Wieland<sup>21</sup> studied the action of various Grignard reagents on benzonitrile oxide ( $C_6H_5C\bar{O}N=O$ ) and found that in every case benzonitrile and the ketone that would result from the reaction between benzonitrile and the RMgX compound were formed. Both aliphatic and aromatic Grignard reagents acted as reducing agents.

Pickard and Kenyon<sup>22</sup> report the formation of p-nitrosotoluene, p-tolyl hydroxylamine and p,p'-azoxytoluene when organomagnesium halides react with p-nitrotoluene.

19. Busch and Hobein, Ber., 40, 2099 (1907).

20. Bewad, ibid., 40, 3065 (1907).

21. Wieland, Ber., 40, 1667 (1907).

22. Pickard and Kenyon, Proc. of the Chem. Soc., 23, 153 (1907).

Staudinger<sup>23</sup> has obtained benzaldehyde by the reaction of benzamide chloroimide with magnesium followed by hydrolysis. While this is not a reduction by means of the Grignard reagent a reduction has taken place through the formation of the organomagnesium halide and its subsequent hydrolysis.

In preparing phenyl ethyl carbinol from benzaldehyde and ethylmagnesium iodide Schorigin<sup>24</sup> found the product to be contaminated by benzyl alcohol.

Letellier<sup>25</sup> found that the action of ethylmagnesium bromide on ethyl hydroxypivalate ( $\text{CH}_2\text{OH}\cdot\text{C}(\text{CH}_3)\cdot\text{CO}\cdot\text{OC}_2\text{H}_5$ ) gives in addition to the expected tertiary alcohol a considerable quantity of the glycol  $\text{CH}_2\text{OH}\cdot\text{C}(\text{CH}_3)_2\cdot\text{C}(\text{OH})(\text{C}_2\text{H}_5)_2$ . In contrast to the usual higher temperatures attending the reducing action of Grignard reagents he finds that reduction in this case is favored by low temperatures.

Egorowa<sup>26</sup> observed the formation of isobutylene which he explained as being due to the splitting of isobutylmagnesium chloride into  $\text{HMgCl}$  and the unsaturated hydrocarbon when this Grignard reagent reacts with ethyl oxalate.

Pope and Peachey<sup>27</sup> report the formation of trimethyl platonic iodide from methylmagnesium iodide and

22. Staudinger, Ber., 41, 2217 (1908).

24. Schorigin, *ibid.*, 41, 2717 (1908).

25. Letellier, *compt. rend.*, 146, 343 (1908).

26. Egorowa, J. Russ. Phys.-Chem. Soc., 41, 1454 (1909).

Centralblatt, 1, 1003 (1910).

27. Pope and Peachey, J.C.S., 95, 571 (1909).

platinic chloride which is, in a sense, a reducing agent.

Strecker<sup>28</sup> has shown that phenylmagnesium bromide will react with thionyl chloride ( $\text{SOCl}_2$ ) to form phenyl sulfoxide, some reduction taking place at the same time to form diphenyl sulfide.

The reduction of quinone by triphenylmethylmagnesium chloride has been reported by Schmidlin, Wohl and Thommen<sup>29</sup>. The triphenylmethyl ether of quinone and quinhydrone are formed.

Lederer<sup>30</sup> has ~~found~~ found that phenylmagnesium bromide reacts with telluric chloride ( $\text{TeCl}_4$ ) to form triphenyltelluronium chloride. This compound then will react with more phenylmagnesium bromide with the formation of diphenyl and diphenyl tellurium ( $\text{C}_6\text{H}_5$ )<sub>2</sub>Te.

In contrast to the work of Strecker<sup>28</sup>, Odde<sup>31</sup> reports that phenylmagnesium bromide reacting with thionyl chloride or sulfur dioxide yields diphenyl and in addition small amounts of phenyl sulfoxide and diphenyl. When ethylmagnesium iodide was used ethyl sulfide resulted.

In attempting to prepare certain alcohols by the action of various Grignard reagents on acetaldehyde

28. Strecker, Ber., 43, 1131 (1910).

29. Schmidlin, Wohl and Thommen, Ber., 43, 1298 (1910).

30. Lederer, ibid., 44, 2287 (1911).

31. Odde, Gazz. chim. ital., 41, 11 (1911).

J.C.S., 100, 286 (1911).

Pickard and Kenyon<sup>32</sup> obtained some very low yields. Their difficulty was due to a reducing action which they tried to circumvent by allowing an ether solution of the aldehyde and alkyl halide to react simultaneously on the magnesium. They<sup>33</sup> found the method to be without advantage.

Gorski<sup>34</sup> found that propyl iodide and magnesium will reduce  $\beta$ -benzpinacoline in dry toluene solution to form  $\beta$ -benzpinacoline alcohol. For the formation of triphenylmethane by the interaction of triphenylmethane ethyl ether and propylmagnesium iodide Gorski thinks it probable that a direct reduction of the ether takes place to form triphenylmethane, propene and ethoxymagnesium iodide.

Bennett and Turner<sup>35</sup> have shown that certain Grignard reagents reduce chromic chloride to chromous chloride and that the amount of hydrocarbon formed by the coupling of two R groups of the RMgX compound is comparable to the amount of reduction taking place.

Kötz, Blendermann, Rosenbusch and Sirringhaus<sup>36</sup> found that methylmagnesium iodide reduces  $\alpha$ -hydroxy cyclohexanone to cyclohexanone. The reduction is explained

32. Pickard and Kenyon, J.C.S., 99, 45, (1911).

33. Pickard and Kenyon, *ibid.*, 101, 620 (1912).

34. Gorski, J. Russ. Phys.-Chem. Soc., 45, 163 (1913).  
C.A., 7, 2225 (1913).

35. Bennett and Turner, J.C.S., 105, 1057 (1914).

36. Kötz, Blendermann, Rosenbusch and Sirringhaus,  
Ann., 400, 55 (1913).



on the basis of the formation of ethylene.

Jegorowa<sup>37</sup> observed that tertbutylmagnesium chloride acts on  $(\text{CH}_3)_2\text{C}\cdot\text{CO}\cdot\text{CHOH}\cdot\text{C}(\text{CH}_3)_2$  to form the corresponding glycol. He assumes the intermediate formation of  $\text{RMgCl}$  in the reaction.

The action of tert-amylmagnesium chloride on ethyl oxalate has been studied by Wenus<sup>38</sup>. A reducing action took place with the formation of  $\text{C}_2\text{H}_5\text{O}\cdot\text{CO}\cdot\text{CHOH}\cdot\text{C}_5\text{H}_{11}$ , the free hydroxy acid and  $\text{C}_5\text{H}_{11}\cdot\text{CH}(\text{OC}_2\text{H}_5)\cdot\text{CO}\cdot\text{OH}$  which Wenus attributes to the reducibility of the tert-amylmagnesium chloride.

Wieland and Rosset<sup>39</sup> mention the fact that reduction of the nitroso group of certain compounds by  $\text{RMgX}$  compounds takes place instead of normal addition to the  $\text{NO}$  group. Phenylmagnesium bromide reacts with N-nitroso diphenylamine at  $-15^\circ\text{C}$ . to form triphenyl hydrazine, diphenyl and phenol.

In the preparation of certain tellurium compounds Lederer<sup>40</sup> has found that the Grignard reagent causes a reduction to take place. When di-p-tolyl phenyl-tellurium chloride is treated with an excess of phenylmagnesium bromide there is formed phenyl-p-tolyl

37. Jegorowa, J. Russ. Phys.-Chem. Soc., 46, 1319 (1914).  
Centralblatt, I, 1055 (1915).

38. Wenus, *ibid.*, 46, 1332 (1914). centralblatt, I, 1055 (1915).

39. Wieland and Rosset, *Ber.*, 49, 1117 (1915).

40. Lederer, *ibid.*, 49, 1615 (1916).

telluride and p-methyl diphenyl.~~XXXXX~~

Van Duin<sup>41</sup> heated cineole with methylmagnesium iodide and with ethylmagnesium iodide. A rather violent reaction occurred at high temperatures accompanied by the formation of the hydrocarbon  $C_{10}H_{16}$ . Attempts to reduce cineole by Sabatier and Senderen's hydrogenation method gave negative results.

Meerwein<sup>42</sup> was unsuccessful in preparing pinacones by the action of n-propyl- and n-butylmagnesium bromide on the diethyl ester of glycolic acid. He obtained instead the corresponding hydroxy ketones.

Danilov<sup>43</sup> was able to reduce benzhydryl isopropyl ketone to the corresponding alcohol by means of tert-isobutylmagnesium chloride when sodium amalgam had failed.

Hepworth<sup>44</sup> has studied the action of methylmagnesium iodide and ethylmagnesium bromide on nitrotoluene, p-nitrotoluene, o-nitrotoluene and  $\alpha$ -nitronaphthalene. With ethylmagnesium bromide and nitrobenzene he obtained ethyl aniline as Oddo<sup>12</sup> had done previously and found in addition some azobenzenes. With methylmagnesium iodide and nitrobenzene there was obtained methyl aniline and azobenzene. Analogous results

41. Van Duin, Proc. Acad. Sci. Amsterdam, 20, 66 (1917).

C.A. 11, 3259 (1917).

42. Meerwein, Ann., 419, 121 (1919).

43. Danilov, J. Russ. Phys.-Chem. Soc., 52, 369 (1920).

C.A., 18, 1489 (1924).

44. Hepworth, J.C.S., 117, 1004 (1920).

were observed with the other nitro compounds.

In a study of the organo derivatives of bismuth, Challenger and Allpress<sup>45</sup> have found that RMgX compounds often exert a reducing action. As an example, tri  $\alpha$ -naphthylbismuthine dibromide is reduced to tri  $\alpha$ -naphthyl bismuthine by phenylmagnesium bromide with the formation of magnesium bromide and bromobenzene.

Mikhailenko and Protosova<sup>46</sup> have found that a quantitative yield of dibenzyl can be obtained if a solution of benzyl chloride in ether is refluxed with magnesium and certain inorganic halides. When mercuric bromide cupric chloride are used they are reduced to the metal.

The action of methylmagnesium iodide and ethylmagnesium bromide on various alkyl nitrates has been studied by Hepworth<sup>47</sup>. No matter what ester was used the chief product in every case was  $\beta, \beta$ -dimethylhydroxylamine or  $\beta, \beta$ -diethylhydroxylamine.

Hepworth and Clapham<sup>48</sup> have found that alkyl- and arylmagnesium halides react with benzensulfochloride to form chiefly sulfoxides while sulfides were formed to a less extent. They also report a small amount of reduction of sulfoxides to sulfides by the action of the

<sup>45</sup>Challenger and Allpress, J.C.S., 119, 913 (1921).

<sup>46</sup>Mikhailenko and Protosova, J. Russ. Phys.-Chem. Soc., 53, 1, 347 (1921). C.A., 18, 2338 (1924).

<sup>47</sup>Hepworth, J.C.S., 119, 251 (1921).

<sup>48</sup>Hepworth and Clapham, *ibid.*, 119, 1188 (1921).

Grignard reagent.

Similar results were obtained by Wedekind and Schenk<sup>49</sup> in a study of the action of RMgX compounds on arylsulfochlorides. They found that phenylmagnesium bromide would reduce p-tolyl sulfochloride to form p-tolyl phenyl sulfoxide and diphenyl. p-tolyl phenyl sulfane was also formed. When alkylmagnesium halides were used in place of phenylmagnesium bromide the reaction products were di-p-tolyl disulfoxide and p-tolyl alkyl sulfide. The reducing action is based on the progressive addition of the RMgX molecule to the SO grouping followed by a splitting.

Hepworth<sup>50</sup> has reported the action of certain RMgX compounds on iodosobenzene ( $C_6H_5IO$ ) and iodoxybenzene ( $C_6H_5IO_2$ ). When alkylmagnesium halides were used reduction to iodobenzene resulted in all cases. Aryl-magnesium halides for the most part acted as reducing agents but with iodosobenzene the formation of a small amount of iodonium hydroxides was likewise observed.

Hess and Rheinboldt<sup>51</sup> found that ethylmagnesium bromide would reduce benzaldehyde to give yields of benzyl alcohol as high as 75% of the theoretical. They have shown that reduction is favored by high temperatures.

49. Wedekind and Schenk, Ber., 54, 1604 (1921).

50. Hepworth, J. C. S., 119, 1244 (1921).

51. Hess and Rheinboldt, Ber., 54, 2043 (1921).

Attempts to prepare HMgX did not meet with success.

Leroide<sup>52</sup> has shown that  $\alpha, \alpha$ -disubstituted esters react with alkylmagnesium halides to form the corresponding secondary alcohols instead of the tertiary alcohols which would result from a normal reaction between these compounds. Reduction of  $\alpha, \alpha$ -disubstituted ketones by RMgX compounds to give excellent yields of corresponding secondary alcohols is mentioned.

The reducing action of ethylmagnesium iodide on sodium methylete and on sodium amylate has been reported by Buylia and Olay<sup>53</sup> who find that ethylene and ethane are evolved from the former alcoholate and that ethylene and an unidentified liquid hydrocarbon are obtained when the latter alcoholate is used.

In preparing Grignard reagents from various olefinic halogen compounds and activated magnesium Krestinsky<sup>54</sup> has found that the formation of isocrotylmagnesium bromide is accompanied by the formation of isobutene, particularly when the temperature of the reaction mixture is allowed to rise. The formation of the unsaturated hydrocarbon is attributed to the action of HMgBr formed as an intermediate compound. In a like manner the formation of vinylmagnesium bromide is accompanied by the evolution

52. Leroide, Ann. chim., 16, 334 (1921).

53. Buylia and Olay, Annles. soc. espan. fis. quim., 20, 699 (1922). C.A., 17, 2413 (1923).

54. Krestinsky, Ber., 55, 2754 (1922).

See also Krestinsky, ibid., 55, 2762 (1922).

and Krestinsky, ibid., 55, 2770 (1922).

of ethylene and acetylene. Isocrotylmagnesium bromide acting on acetaldehyde was found to produce some ethyl alcohol along with the methyl isocrotyl carbinol.

Skrap and Moser<sup>55</sup> have found that the action of phenylmagnesium bromide on the acid chloride of benzoxazol 1-carboxylic acid when carried out warm results in a reduction to form benzoxazylmethyl alcohol. The anilide of benzoxazol 2-carboxylic acid appears to be reduced by methylmagnesium iodide to form the anil of benzoxazol 1-aldehyde. They regard the reduction as being due to the special influence of the benzoxazyl radical.

Wieland and Kögl<sup>56</sup> have studied the action of Grignard reagents on certain nitroso compounds. When p-nitroso dimethylaniline and phenylmagnesium bromide react some p,p<sup>1</sup>-azo dimethylaniline is formed. When p-tolylmagnesium bromide or ethylmagnesium bromide are the reagents used the azo compound is likewise formed. In an analogous manner p-azoisole was formed by the reaction of phenylmagnesium bromide with p-nitroso anisole.

Bredt-Savelsberg<sup>57</sup> has found that ethylmagnesium iodide with camphor yields a gas composed of ethylene and ethane. The ethylene was thought to have resulted

55. Skrap and Moser, Ber., 55, 1080 (1922).

56. Wieland and Kögl, ibid., 55, 1798 (1922).

57. Bredt-Savelsberg, J. prakt. chem., 107, 65 (1924).

from the reducing action of ethylmagnesium iodide.

When benzylmagnesium chloride reacts with benzil Banus and Vila<sup>58</sup> have observed a reduction to form the benzyl ether of benzoin.

Hess and Wustrow<sup>59</sup> have found that ethylmagnesium bromide, sec-butylmagnesium bromide, and isobutylmagnesium bromide will reduce crotonaldehyde and cinnamyl aldehyde to the corresponding alcohol. They have shown in a rather convincing way that the reduction is due to the loss of an unsaturated hydrocarbon from the R group of the RMgX compound after it has added to the aldehyde. The evolution of unsaturated hydrocarbon, and hence the reducing action, is favored by higher temperatures.

Rheinboldt and Roleff<sup>60</sup> have demonstrated that the loss of unsaturated hydrocarbon which accompanies the reducing action of alkylmagnesium halides takes place only when there is an addition compound of the Grignard reagent and the carbonyl group. Alcoholates of magnesium halides containing the same groups as the addition compound will not evolve an unsaturated hydrocarbon. Hydrogenmagnesium halide may thus be assumed to have existence as the addition compound of certain compounds containing the carbonyl group.

58. Banus and Vila, *Anales, soc. espan. fis quim.*, 22, 262 (1924). *C.A.*, 19, 59 (1925).

59. Hess and Wustrow, *Ann.*, 437, 256 (1924).

60. Rheinboldt and Roleff, *Ber.*, 57, 1921 (1924).

Gilman and Parker<sup>61</sup> have studied the action of organomagnesium halides with cupric chloride. In all cases except with the -OMgX compounds a coupling reaction took place, the cupric chloride being reduced at the same time to the cuprous state.

The zinc dialkyls exhibit a reducing action somewhat like that of the Grignard reagent. For example, chloral is reduced by zinc diethyl<sup>62</sup> to form trichloroethyl alcohol.

The large number of examples of reduction by means of the Grignard reagent emphasizes the importance of this reaction. In some cases it appears as a troublesome side reaction; in others it is the sole reaction. In view of the many types of compounds which undergo reduction by means of the Grignard reagent it is not possible to formulate a single mechanism applicable to all reactions. Thus, the theory that HMgX is responsible for the reducing action holds very well for aliphatic RMgX compounds in which R represents a hydrocarbon radicle of at least 2 carbon atoms. However, it is not readily applicable in explaining the reducing action of arylmagnesium halides or alkylmagnesium halides in which no hydrogen atoms are available for the formation of HMgX. Phenylacetylenemagnesium bromide

61. Gilman and Parker, J.A.S.S., 46, 2823 (1924).

This paper includes a review of the work done on the action of R.MgX compounds with metallic halides.

62. Garzaroli-Thurnlackh, Ann., 210, 83 (1881).

See also Schtscherbakow, Ber., 14, 1710 (1881).

Markownikow, Ber., 16, 2284 (1883).



will serve as an example of this latter type. The present study was undertaken with the purpose in view of determining the mechanism of reduction of some RMgX compounds. It may be divided into two parts., first, attempts to prepare HMgX, and second, the reduction of azo compounds.

A. The Existence of Hydrogenmagnesium Halides.

While the reducing action of the Grignard reagent has long been attributed to the formation of HMgX as an intermediate compound it has never been prepared in the free state. Hess and Rheinboldt<sup>64</sup> were unable to effect a direct preparation of hydrogenmagnesium halide. Likewise, Nelson and Evans<sup>65</sup> obtained negative results in an endeavor to prepare the HCl derivative of various metals using ether as a solvent.

Hess and Rheinboldt<sup>64</sup>, Hess and Winstrow<sup>66</sup>, and Rheinboldt and Roleff<sup>67</sup> have virtually proved the existence of HMgX as an addition compound. However, the preparation of hydrogenmagnesium halide as an individual compound would be a valuable substantiation of this theory of reducing action.

Some preliminary experiments in the direct preparation of hydrogenmagnesium bromide were carried out. Dry hydrogen bromide was passed into an ether solution containing

64. Reference 51.

65. Nelson and Evans, J.A.C.S., 39, 82 (1917).

66. Reference 59.

67. Reference 60.

activated magnesium. The flask was surrounded by carbon dioxide snow in ether. Assuming that  $\text{HMgBr}$  might be unstable even at this low temperature one run was made in which carbon dioxide snow was present during the passing in of the hydrogen bromide. No formic acid was formed in this experiment and no evidence of the formation of  $\text{HMgBr}$  was found in two other experiments carried out under slightly different conditions.

The difficulty of preparing free  $\text{HMgX}$  is not so surprising in view of the fact that magnesium hydride has never been isolated in any appreciable amount although traces of it have been found by spectrum analysis. Pfeiffer<sup>68</sup> has pointed out by a comparison of some inorganic compounds that beryllium and magnesium might better be grouped with zinc, cadmium and mercury instead of with calcium, strontium and barium.

Likewise, the lack of activity of dry hydrogen chloride is ~~is~~ demonstrated in the work of Bhagwat<sup>69</sup> where it has been shown that dry hydrogen chloride in isoamyl ether does not react with methylmagnesium iodide. However, dry hydrogen bromide does react with magnesium in ether solution at ordinary temperatures to liberate hydrogen.

68. Pfeiffer, *Z. anorg. chem.*, 37, 41 (1924).

69. Bhagwat, *J. C. S.*, 123, 1803 (1923).

In some recent work by Adams<sup>60-75</sup> and coworkers it has been shown that platinum oxide serves as an excellent catalyst for the reduction of many organic compounds. It was thought that such a reaction might be employed for the preparation of HMgX according to the equation:



Accordingly, the reduction of a variety of Grignard reagents was attempted. The ones chosen were chiefly those which often act as reducing agents. Benzylmagnesium chloride and triphenylmethylmagnesium chloride seemed especially suitable because of indications that the carbon-magnesium linkage in these compounds is weaker than in other RMgX compounds. Benzylmagnesium chloride is known to undergo a rearrangement in which the -MgCl group migrates to the ring and triphenylmethyl compounds have been shown to be easily dissociated to form triphenylmethyl as a free radical. In addition to the Grignard reagents, organomagnesium halides were used containing the <sup>and</sup> groups, -OMgX, -NMgX, ~~^~~ ethylzinc iodide and phenylcalcium iodide were also used.

Negative results were obtained in all cases with the

70. Voorhess and Adams, J.A.C.S., 44, 1397 (1922).
71. Carothers and Adams, *ibid.*, 45, 1071 (1923).
72. Adams and Shriner, *ibid.*, 45, 2171 (1923).
73. Kaufmann and Adams, *ibid.*, 45, 3029 (1923).
74. Carothers and Adams, *ibid.*, 46, 1675 (1924).
75. Shriner and Adams, *ibid.*, 46, 1683 (1924).

possible exception of triphenylmethylmagnesium chloride. Here an absorption of hydrogen corresponding to about 110 % of the theoretical amount was noted. Treatment with carbon dioxide for the purpose of holding any  $\text{HMgX}$  formed gave no formic acid in any case. In the reduction of triphenylmethylmagnesium chloride in a steam bath and followed by treatment with carbon dioxide the yield of triphenylacetic acid was only 5.3 % and ~~triphenylmethane~~ triphenylmethane was 66.3 % while a check run without catalytic reduction gave 28.9 % of triphenylacetic acid and 48.5 % of triphenylmethane. When separating the products of the reduction run the solvent, which consisted of ether and toluene, was removed by distillation. It was found to contain a small amount of a phenolic compound that readily reduced  $\text{KMnO}_4$  solution and formed with bromine water a derivative melting at  $95 - 96^\circ$  after a crystallization from ether.

Apparatus. The apparatus used was essentially the same as that described by Skita<sup>76</sup> and later modified by Lochte, Noyes and Bailey<sup>77</sup> and Voorhees and Adams<sup>70</sup>.

Hydrogen from a large tank was passed through sulfuric acid and into a reservoir until the pressure had reached approximately 3 atmospheres. The reservoir was a small oxygen cylinder equipped with 2 needle valves and a manometer arranged in such a manner that ~~the pressure in the~~

76. Skita, Ber., 45, 3589 (1912).

77. Lochte, Noyes and Bailey, ~~This Journal~~ 43, 2801 (1921).

the pressure in the cylinder could be determined by noting the change in volume of some inclosed air. One needle valve was for the inlet; the other for the outlet. A stopcock was placed in the incoming line so that the reservoir and drying line could be evacuated at one time. The outlet tube was made of copper<sup>tubing</sup> bent into a coil of several turns to give it flexibility. This tube was connected directly to the reaction flask through a rubber stopper. The rubber stoppers were boiled in sodium hydroxide solution before using. The reaction flask used for most of the runs was an ordinary 500 c.c. 3-necked Pyrex flask. The center stopper held the hydrogen inlet tube. One neck contained a solid rubber stopper and the other a rubber stopper holding a glass stopcock through which the flask was evacuated before the hydrogen was introduced. After most of the experiments had been carried out in ordinary Pyrex flasks with but little difficulty, a considerable amount of trouble started with the failure of the flasks to withstand the pressure. Finally a 500 c.c. single neck pressure flask was substituted with good results. In this case the stopper held both a glass stopcock and the copper inlet tube. The chief disadvantage<sup>s</sup> was that the contents had to be transferred to another flask before it was further treated.

The flask was fastened into a shaker to keep the contents well agitated during the treatment with hydrogen.

Preparation of the catalyst.

The platinum oxide used as a catalyst was prepared according to the optimum conditions described by Adams and Shriner<sup>72</sup>. The chloroplatinic acid which was employed was made from scrap platinum after it had been purified by a reduction with sodium formate following the directions given in Treadwell and Hall<sup>78</sup>.

The ferrous chloride used as an activator for the platinum oxide was not specially prepared. Ordinary C.P. material was kept in a desiccator and used as needed.

Activation of the catalyst by shaking with air or oxygen as suggested in certain of the papers by Adams and coworkers<sup>70-75</sup> was precluded by the nature of the materials to be reduced.

The activity of the catalyst was tested from time to time by check runs on benzaldehyde in ether solution.

Procedure.

The hydrogen reservoir and inlet line was evacuated and filled with hydrogen 4 consecutive times before the gas was considered pure enough for use. After once filling this reservoir with pure hydrogen it was not necessary to repeat the process.

In all cases the flask had a volume of 500 c.c. The 3 necked flask had the advantage as previously mentioned that no change was necessary for the subsequent treatments.

78. Treadwell and Hall's Analytical Chemistry  
Vol. I, p 285, (1921).

The catalyst was first placed in the flask. The amount of platinum oxide used was 0.23 gms. and in most cases there was added to the platinum oxide 0.13 gms. of ferrous chloride. The material to be reduced was next added. All soluble organomagnesium halides were filtered through glass wool to remove unused magnesium. Solvent was added until the total volume was about 260 c.c. When the flask was evacuated the ether boiled vigorously but this was allowed to continue until it was certain that all air was swept out. A mixture of air and hydrogen is easily exploded by the catalyst.

After all of the air had been removed the stopcock was closed and hydrogen admitted from the reservoir. The increase in volume allowed an immediate partial drop in pressure. The flask was shaken and kept under a pressure of hydrogen for 4 hours. In the runs where reduction might have resulted in the formation of a gaseous hydrocarbon the supply of hydrogen was stopped, the pressure released, and the flask evacuated from time to time during the 4 hours.

In some of the experiments the reaction flask was surrounded by steam.

In each run as soon as the hydrogen treatment was finished the flask was equipped with a stirrer and placed in an ice bath where carbon dioxide was passed in for at least 2 hours<sup>79</sup>.

79. For a study of the optimum condition for the preparation of n-valeric acid from n-butylmagnesium bromide and carbon dioxide see Gilman and Parker, J.A.C.S. 46:2816 (1924).

After hydrolysis with dilute sulfuric acid the ether layer together with several ~~other~~ other extracts were filtered to remove the catalyst and then worked up to obtain the acids formed. Tests were made for formic acid in the ether layer and in the steam distillate from the water layer. The first 25 c.c. of the steam distillate was collected and tested; then 500 c.c. more was collected and concentrated by making alkaline and evaporating to dryness. The residue was taken up in a small amount of distilled water and tested for formic acid.

The tests used for detecting the presence of formic acid are described by Mulliken<sup>80</sup>. The one test is dependent on the reducing action of formic acid on a cold alkaline solution of potassium permanganate. The other test employs mercuric oxide which forms a compound with formic acid. Boiling the solution for half a minute or more causes free mercury to precipitate when formic acid is present. While the first test can not be considered as specific, negative results with both tests prove the absence of formic acid.

80. Mulliken's, Identification of Pure Organic Compounds, Vol. I, p 79 and 83 (1904).



Experimental Part.

Cyclohexylmagnesium bromide.

Cyclohexylmagnesium bromide was prepared from 35.9 gms. (0.22 moles) of bromocyclohexane and 5.4 gms. (0.22 moles) of magnesium. The solution was filtered from the unused magnesium and placed in the apparatus for reduction. Then 0.23 gms. of platinum oxide and 0.13 gms. of ferrous chloride was added. No appreciable absorption was noted during 4 hours run. At the completion of the hydrogen treatment the flask was placed in an ice bath and carbon dioxide passed in for 2 hours. The material was hydrolyzed with dilute sulfuric acid, the platinum oxide filtered off, and several ether extractions made. After drying over sodium sulphate the ether was removed by distillation and that part of the distillate coming over between 95° and 115° (B.P. of formic acid is 100°) was collected separately to be tested for formic acid.

The water layer was steam distilled and the first 25 c.c. collected in one portion and then 500 c.c. more was collected. This latter portion was made alkaline, evaporated to dryness, and taken up in a small amount of water to be tested for formic acid. None of the three samples gave a positive test for formic acid.

The yield of cyclohexane carboxylic acid was 16 gms. or 57 % of the theoretical.

Two other runs with cyclohexylmagnesium bromide were made in the same manner as described above except that no

ferrous chloride was used in one case and, in the other the solvent employed was benzene. There was no absorption of hydrogen and no formic acid found in either run. The yield of cyclohexane carboxylic acid from the run in benzene was 16.8 gms. or 64 % theoretical.

Isobutylmagnesium bromide.

Isobutylmagnesium bromide was prepared from 30.1gms. (0.22 moles) of isobutyl bromide and 5.4 gms. (0.22 moles) of magnesium. The same amount of catalyst was used as in the first run of cyclohexylmagnesium bromide. Since a reduction of this Grignard reagent would result in the formation of a gas, the flask was evacuated 4 times during a 5 hour run. No absorption of hydrogen was noted during any period and no formic acid was found following a treatment like that used in the first experiment.

n-Laurylmagnesium bromide.

n-Laurylmagnesium bromide was prepared in 0.1 molar quantity in the usual manner and the same procedure followed as in the first experiment. No hydrogen was absorbed and no formic acid formed. A yield of 84.1 % of n-tridecylic acid was obtained. This indicates a higher yield of Grignard reagent than that reported by Gilman and McCracken,<sup>81</sup>

81. Gilman and McCracken, J.A.S.S., 45, 2462 (1923).

They obtained a 73.7 % yield of n-laurylmagnesium bromide from n-lauryl bromide and magnesium.

Benzylmagnesium chloride.

A solution of 0.22 moles of benzylmagnesium chloride was prepared in the usual manner. The usual reduction procedure was followed. No hydrogen was absorbed and no formic acid formed. A 73.5 % yield of phenylacetic acid was obtained.

Phenylmagnesium bromide.

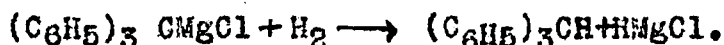
Phenylmagnesium bromide was prepared in 0.2 molar quantity in the usual manner. The customary reduction procedure was followed. No indication of hydrogen absorption, or of the formation of formic acid, was found. Benzoic acid was recovered in a yield of 21 gms. or 78.2 % of the theoretical. The fact that this yield is higher than Gilman and Parker<sup>79</sup> obtained in a similar reaction — they obtained 72.5 % of benzoic acid in a more accurate run — is probably due to the weighing of an impure product.

Triphenylmethylmagnesium chloride.

An ether solution of 0.22 moles of triphenylmethylmagnesium chloride was prepared in the usual manner. Since this Grignard reagent precipitates from ether it was not filtered before attempting the reduction. In a 4 hour reduction run no hydrogen was absorbed and no formic acid was formed after the carbon dioxide treatment.

About 1 gram of triphenyl acetic acid was separated in this reaction. Triphenylmethane was obtained in a yield of about 15 gms. The low yield of triphenylacetic acid was probably due to a poor reaction in ether solution with carbon dioxide.

A second run with triphenylmethylmagnesium chloride was carried out using the same quantities as in the run just described. The ether was replaced by toluene which completely dissolved the Grignard reagent when hot. After filtering through a glass wool it was subjected to reduction while surrounded by a steam bath. The treatment was continued for 7 hours during which time enough hydrogen was absorbed to correspond to a 110% reduction when calculated on the basis of the reaction:



Most of the absorption took place during the first 4 hours.

When the products were worked up a total of 2.2 gms. of triphenylacetic acid was obtained, a yield of 5.3%. There was also obtained 4.2 gms. (14.8% yield) of triphenylmethyl peroxide and 17.7 gms. (66.3% yield) of triphenylmethane.

The solvent from the ether extractions was removed by distillation and that portion coming over between 65° and 112° was caught separately. It contained a small amount of phenolic compound that readily reduced KMnO<sub>4</sub> solution. The distillate was combined

with a quantity of sodium hydroxide solution and evaporated to dryness. When taken up in a small amount of water, acidified with dil.  $H_2SO_4$ , and the water distilled over, the phenolic compound came over with it. Treatment with bromine water yielded about 0.5 gms. of substance, soluble in ether from which crystals were obtained melting at ~~85-86~~ 95-96°C. A mixture of the derivatives with tribromophenol melted at 80°.

In a check run of triphenylmethylmagnesium chloride in benzene solution using the same quantity of materials as was used in the 2 previous runs the Grignard solution was treated with carbon dioxide with the omission of the reduction. On working up the products there was obtained 12 gms. (28.9% yield) of triphenylacetic acid, 2 gms. (7.4 % yield) of triphenylmethyl peroxide, and 13 gms. (48.5 % yield) of triphenylmethane. Schmidlin<sup>82</sup> reports an 83 % yield of triphenylacetic acid in a somewhat similar run.

sec-Butylmagnesium bromide.

Sec. Butylmagnesium bromide was prepared in the usual manner in 0.22 molar quantity. The ether was replaced by toluene and the solution then filtered and subjected to reduction in the customary manner while the flask was surrounded by steam. During a 4 hour period the flask was evacuated 3 times to remove any

82. Schmidlin, Ber., 39, 628 (1906).

butane that might have formed. No drop in pressure was noted during any interval and after treatment with carbon dioxide no formic acid was found. A 40.1 % yield of active valeric acid was obtained.

Phenylcalcium iodide.

Phenylcalcium iodide was prepared in ether solution after the method of Beckmann<sup>83</sup> from 20.4 gms (0.1 moles) of iodobenzene and 4.gms.(0.1 moles) of freshly turned calcium. The material was subjected to reduction without filtering. No hydrogen was absorbed and no formic acid was found following the usual procedure. A 41 % yield of benzoic acid was obtained.

Ethylzinc iodide.

Ethylzinc iodide was prepared in ether solution after the method of Job and Reich<sup>84</sup> using 26.8 gms. of zinc-copper couple and 34.3 gms. (0.22 moles) of ethyl iodide. It did not absorb hydrogen and after treatment with carbon dioxide yielded 3-4 gms. of ethyl alcohol. Since alkylzinc iodides do not react with the carbonyl group the formation of propionic or formic acids would not be expected.

n-Butoxymagnesium iodide.

n-Butoxymagnesium iodide was prepared by adding 0.22 moles of n-butyl alcohol to an ether solution of 0.22 moles of ethylmagnesium iodide. During the 4

83.Beckmann,Ber.,38,904 (1905).

84.Job and Reich,Bull.soc.chim.,33,1414 (1923).

hour reduction period the flask was evacuated 3 times to remove any gas which might form if a reaction took place. No hydrogen was absorbed and after treatment with carbon dioxide the only substance obtained was n-butyl alcohol.

Diphenylaminomagnesium bromide.

Diphenylaminomagnesium bromide was prepared by the action of 37.2 gms. (0.22 moles) of diphenyl amine on 0.22 moles of ethylmagnesium bromide. There was no absorption of hydrogen and no formic acid formed. The diphenylamine was recovered, quantitatively.

Phenylacetylenemagnesium bromide.

Phenylacetylenemagnesium bromide was prepared by allowing 11.22 gms. (0.11 moles) of phenylacetylene to react with 0.11 moles of ethylmagnesium bromide. An oily layer of Grignard reagent was formed under the ether. There was no drop in pressure during a 4 hour reduction period. The material was next treated with carbon dioxide for 3 hours and subjected to reduction for another 4 hours/ period after adding a fresh supply of catalyst. Again no hydrogen absorption was observed. Then 21.2 gms. (0.2 moles) of benzaldehyde was added along with another fresh quantity of catalyst. As before no hydrogen was absorbed giving evidence that Grignard reagents poisons the catalyst for the reduction of the acetylenic linkage or of the carbonyl group of the aldehyde. This is in opposition to the results obtained in the hot reduction of triphenyl-

methylmagnesium chloride although it is quite possible that in this case no catalyst was necessary for the reduction to take place.

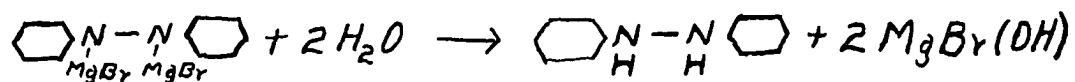
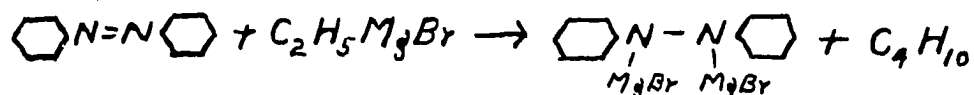
Summary.

I. Attempts have been made to prepare  $\text{HMgX}$ ,  $\text{HCaX}$  and  $\text{HZnX}$  by subjecting a number of organometallic halides to catalytic reduction. Negative results were obtained in all cases except in a hot reduction of triphenylmethylmagnesium chloride where 110 % of the theoretical absorption of hydrogen was observed. No direct evidence of the presence of  $\text{HMgCl}$  was found, however.



B. The Reduction of Azo Compounds.

Franzen and Deibel<sup>1b</sup> have shown that azobenzene and p, p'-azotoluene react vigorously with ethylmagnesium bromide to give the corresponding hydrazo compounds. With no other experimental evidence than this they proposed the following scheme as the mechanism for the reducing action:



They<sup>2</sup> also found that one of the =C=N- groups of benzaldazine (C<sub>6</sub>H<sub>5</sub>·CH=N-N=CH·C<sub>6</sub>H<sub>5</sub>) was reduced by ethylmagnesium bromide and assumed the mechanism of reduction to be the same for this compound as for azobenzene.

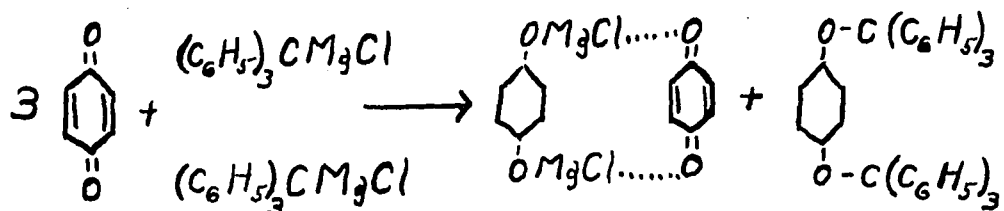
In work done up to that time on the reaction of the Grignard reagent there was no experimental evidence to show that the Grignard reagent would react in such a manner and even up to the present time there has been but little work that indicates that the Grignard reagent undergoes reactions of this sort.

The most nearly comparable reaction is found in the behavior of triphenylmethylmagnesium chloride with quinone. The reaction involves the use of three molecules of quinone and two molecules of triphenyl-

<sup>1b</sup> Franzen and Deibel, Ber., 38, 2716 (1905).

<sup>2</sup> Franzen and Deibel, ibid., 38, 2717 (1905).

methylmagnesium chloride in which quinhydrone and the triphenylmethyl ether of quinone are formed, thus:



In this scheme two -MgX groups are removed from two molecules of RMgX compound and bring about the reduction of quinone by addition to the two oxygen atoms. This then reacts with a second molecule of quinone to form quinhydrone. The two R groups from the Grignard reagent, instead of combining with each other to form the hydrocarbon R-R, as Franzen and Deibel have assumed in the reduction of azobenzene, also add to the oxygen atoms of a third molecule of quinone to form the corresponding ether. The probability that the mechanism of reaction in this case is as indicated is further supported by the well known tendency of triphenylmethyl to split off as a free radicle.

The reduction of arylsulfochlorides by phenylmagnesium bromide has a point in common with the postulate of Franzen and Deibel<sup>1,2</sup> for the reduction of azobenzene since the hydrocarbon diphenyl is formed. Wedekind and Schenk<sup>3</sup> explain the reduction

<sup>3</sup>Wedekind and Schenk, Ber., 54, 1604 (1921).

on the assumption that after the chlorine atom is replaced by a phenyl group two molecules of phenylmagnesium bromide add to the  $>S(=O)_2$  grouping; the resulting compound then is assumed to lose diphenyl so that reduction to the aryl phenyl sulfoxide takes place. If an addition takes place as assumed in this reaction, the R groups from two molecules of RMgX attaching themselves to the sulfur atom and at the same time the -MgX groups attaching themselves to the two oxygen atoms, one would expect to find the hydrocarbon which forms to be composed of the two hydrocarbon radicals which split off most easily. Then, by interchanging the R groups of the arylsulfochloride and the Grignard reagent, a hydrocarbon composed of two R groups from the RMgX compound should form in one case; in the other, the hydrocarbon should be composed of the aryl group of the arylsulfochloride and one R group of the RMgX compound. No such experimental proofs as this has been made. Related studies on the mechanism of addition to the  $S=O$  group are now in progress in this Laboratory.

No reaction which conforms any more closely to the postulate of Franzen and Deibel than the two just described were found. As Hess and Rheinboldt<sup>4b</sup> have pointed out, the reduction of azobenzene by ethylmagnesium bromide can readily be explained on

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

the assumption that ethylene and  $\text{HMgBr}$  are formed and that the  $\text{HMgBr}$  adds to the azo grouping. The theory of  $\text{HMgX}$  formation is not new and excellent evidence for its existence as an addition compound to the carbonyl group has been presented by many workers. The work of Hess and Rheinboldt<sup>4b</sup>, Hess and Winstrow<sup>5b</sup>, and Rheinboldt and Roloff<sup>6b</sup> is particularly convincing in the proof of the mechanism of reduction on the basis of the formation of  $\text{HMgX}$ .

As has been mentioned previously in this paper<sup>7b</sup>, the theory of  $\text{HMgX}$  formation is limited by the nature of the Grignard reagent in question. Many  $\text{RMgX}$  compounds are of such a nature that a splitting to form  $\text{HMgX}$  and an unsaturated hydrocarbon cannot be satisfactorily accomplished. Typical examples would be arylmagnesium halides and compounds of the type  $\text{RCH}_2\text{MgX}$ ,  $\text{CH}_3\text{MgX}$ , and  $\text{RC}\equiv\text{CMgX}$  where R represents an aryl group. Here the formation of  $\text{HMgX}$  becomes tenable only when the radicals which split off condense with each other. Thus two molecules of phenylmagnesium bromide could ~~be~~ form two molecules of hydrogenmagnesium bromide and one molecule of diphenylene ( $\text{C}_6\text{H}_4=\text{C}_6\text{H}_4$ ). However, no such compound as this has ever been obtained.

<sup>5b</sup>Hess and Winstrow, Ann., 437, 256 (1924).

<sup>6b</sup>Rheinboldt and Roloff, Ber., 57, 1921 (1924).

<sup>7b</sup>This paper, page 16.

Therefore, the assumption that  $\text{HMgX}$  is responsible for the reducing action of ethylmagnesium halides on azobenzene can be used satisfactorily in connection with the behavior of most aliphatic Grignard reagents but it cannot be extended to include aromatic Grignard reagents and Grignard reagents of the type mentioned above.

In the present work the action of a variety of organo-magnesium halides on azobenzene has been studied. Nearly all of the Grignard reagents tried were found to be good reducing agents and in no case was the formation of an unsaturated hydrocarbon observed. This practically eliminates the  $\text{HMgX}$  theory. Instead, the results all support the postulate of Franzen and Deibel that the reduction of each molecule of azobenzene is brought about by two molecules of  $\text{RMgX}$  which react in such a way that two  $-\text{MgX}$  groups add to the  $-\text{N}=\text{N}-$  linkage, the hydrocarbon  $\text{R}-\text{R}$  being formed at the same time. The azobenzene complex then yields hydrazobenzene on hydrolysis. It was found that the yield of the hydrocarbon  $\text{R}-\text{R}$  was in good agreement with the amount of reduction which takes place.

It has been shown by Meisenheimer and Casper<sup>8a</sup> that all reactions of the Grignard reagent probably involve a preliminary addition with magnesium

<sup>8a</sup>Meisenheimer and Casper, Ber., 54, 1655 (1921).  
See also references 4, 5<sup>b</sup> and 6<sup>b</sup> of this paper.

functioning as the central atom. It is assumed that a similar reaction takes place with azobenzene and the  $\text{RMgX}$  Grignard reagent so that one molecule of  $\text{RMgX}$  adds to each nitrogen atom. This complex then rearranges to form  $\text{C}_6\text{H}_5 \cdot \text{NMgX} \cdot \text{NMgX} \cdot \text{C}_6\text{H}_5$  and the hydrocarbon  $\text{R-R}$ .

It was found that the speed of reaction of various Grignard reagents towards azobenzene varied widely. Ethylmagnesium bromide reacted almost immediately with the formation of a white precipitate and a gas. No refluxing was required. With phenylmagnesium bromide there was a slight elevation of temperature when azobenzene was added but no precipitate formed until after about three hours of refluxing in ether. The reactivity of methylmagnesium iodide<sup>9b</sup> was intermediate between that of ethylmagnesium bromide and phenylmagnesium bromide when based on the appearance of the white precipitate of  $\text{C}_6\text{H}_5 \cdot \text{NMgX} \cdot \text{NMgX} \cdot \text{C}_6\text{H}_5$ .

Since azobenzene reacts with the Grignard reagent in a more sluggish manner than most other types of reactive compounds and, since the speeds of reaction of azobenzene with various Grignard reagents have reasonably wide variations, it seems probable that this reaction would be of value in determining the

<sup>9b</sup>Cilman and Hoyle, J.A.C.S., 44, 2621 (1922)., have pointed out that ethylmagnesium bromide is more reactive than methylmagnesium iodide toward phenylacetylene.

strength of the carbon-magnesium bond in RMgX compounds. Accordingly a measure of the relative reactivity of these compounds could be obtained.

Phenylacetylenemagnesium bromide was the only Grignard reagent tried which did not reduce azobenzene. The reason for the failure of this compound to react is not evident. A possible explanation is that this Grignard reagent is not a very reactive one. The closely related styrylmagnesium bromide was not very reactive toward azobenzene although a good amount of reduction was obtained in the usual 8 hour refluxing period. None of the organometallic halides other than the Grignard reagents (RMgX) gave any evidence of reduction. The list of compounds tried included those containing such groups as -NMgX, -OMgX, -SMgX, -CaX, and ZnX.

The fact that the reduction of the azo to the hydroazo grouping was always accompanied by an equivalent yield of hydrocarbon strongly indicates the formation of the intermediate compound  $C_6H_5 \cdot NMgX \cdot NMgX \cdot C_6H_5$ . Additional evidence for the existence of this compound has been gained by the treatment of the reaction mixture with benzoyl chloride before hydrolysis. In experiments where this modification was used one of the products was always a good yield of dibenzoyl hydrazobenzene. As a supplementary experiment it was found that an ether solution of hydrazobenzene and benzoyl chloride, under the condition of the reduction runs, gave no dibenzoyl

hydrazobenzene.

Other attempts to replace the -MgX groups to form known compounds were not so successful. When acetyl chloride or acetic anhydride were used, the monoacetyl derivative, which is higher melting and less soluble than the diacetyl derivative, was always obtained in low yields (20-25%) and a large amount of an oil was left. Much difficulty was experienced in obtaining crystals of diacetyl hydrazobenzene from this oil. None of the methods such as the use of a variety of solvents, concentrations and temperatures, and finally a vacuum distillation met with any success until water was employed as a solvent. A hot water extract of the oil was boiled with boneblack and, after filtering, was allowed to evaporate slowly. In about ten days some crystals of diacetyl hydrazobenzene were obtained. The position and number of -MgX groups is, therefore, virtually proved, by the use of benzoyl chloride and acetic anhydride.

When diethyl sulfate was the reagent used for replacement of the -MgX groups some material was obtained through a vacuum distillation that possessed the proper physical constants. However it did not respond to a color test on treatment with dilute acids, a property which Wieland and Fressel<sup>10<sup>b</sup></sup> describe as being

<sup>10<sup>b</sup></sup>Wieland and Fressel, Ann., 392, 133 (1912).



especially characteristic for sym-diphenyl diethyl hydrazine.

When the intermediate compound was treated with phenyl isocyanate a reaction took place but the results are rather confusing. The intermediate compound obtained by the action of phenylmagnesium bromide on azobenzene, when treated with phenyl isocyanate, yields a substance melting at  $175^{\circ}$ . In addition some carbanilide was formed. When the intermediate compound obtained from ethylmagnesium bromide and azobenzene, was treated with phenyl isocyanate there resulted some of the tri-polymer of phenyl isocyanate  $(C_6H_5CNO)_3$  and two other compounds, one melting at  $178-9^{\circ}$  (mixed melting point with the  $175^{\circ}$  compound was  $160-165^{\circ}$ ) and another melting at  $185-186^{\circ}$ . When hydrazobenzene was treated with ethylmagnesium bromide the two hydrogen atoms of the  $-NH.NH-$  group should be replaced by  $-MgBr$  groups to give the same intermediate compound as is obtained in the reaction of azobenzene with ethylmagnesium bromide. Treatment of this compound with phenyl isocyanate gave, besides carbanilide, a product melting at  $212^{\circ}$ . None of the products of these reactions has the properties of the di-phenylisocyanate derivative of hydrazobenzene which has been described in the literature as a very insoluble, amorphous substance melting at  $218-220^{\circ}$ .

It will be seen that the best results were obtained with benzoyl chloride where a well defined, crystalline

substance, quite insoluble in ether and easily purified by crystallization from alcohol, is obtained. The ease with which reduction of the azo grouping takes place with the more active alkylmagnesium halides, in which the hydrocarbon obtained as a byproduct is evolved as a gas, together with the smooth reaction of the reduction product with benzoyl chloride to give good yields of the dibenzoyl derivative suggests an application of this method for the preparation of the dibenzoyl derivative of hydrazo compounds. It would have particular value where the hydrazo compound is unstable but where the corresponding azo compound is available.

In order to determine whether the reduction of azobenzene by the Grignard reagent could be extended to other azo compounds, a few other reactions were tried. Franzen and Deibel<sup>11<sup>b</sup></sup> have already shown that ethylmagnesium bromide will reduce p,p<sup>1</sup>-azotoluene to the corresponding hydrazo compound. Phenylmagnesium bromide has been found to produce the same result. Benzylmagnesium chloride was shown to reduce p-dimethylaminoazobenzene to the hydrazo compound which was converted to the dibenzoyl derivative by treatment with benzoyl chloride. Likewise diazoaminobenzene was reduced by ethylmagnesium bromide and the intermediate compound so formed yielded sym-diphenyl tribenzoyl triazane when treated with benzoyl chloride.

11<sup>b</sup>.Reference 1.<sup>b</sup>

Experimental Part.

Reaction of Methylmagnesium iodide and azobenzene.

When 0.1 mole of azobenzene was added slowly to 0.22 moles of methylmagnesium iodide a reaction took place with the evolution of a gas, but it was decidedly more sluggish than a similar reaction using ethylmagnesium bromide.

After refluxing 8 hours<sup>12<sup>b</sup></sup> the material was hydrolyzed with ammonium chloride solution. Several ether extractions were made and the ether solution was washed with water, dried over sodium sulfate and the ether then was distilled off. A crystal mass formed from which there was obtained 6.0 gms. or a 32.6% yield of hydrazobenzene by filtering and washing the crystals with ether. The hydrazobenzene was identified by a mixed melting point. By means of a vacuum distillation 10.5 gms or 57.7% of azobenzene was recovered.

Reaction of n-butylmagnesium bromide with azobenzene.

An ether solution of 0.22 moles of n-butylmagnesium bromide and 0.1 mole of azobenzene was allowed to react in the usual manner. After refluxing for 8 hours the material was hydrolyzed with  $\text{NH}_4\text{Cl}$  solution. The ether extracts were worked

<sup>12<sup>b</sup></sup>The volume of ether used as a solvent was 250-300 c.c. in all experiments.

up in the usual manner. There was obtained 9.0 gms. or a 48.9% yield of hydrazobenzene, 3.5 gms. of aniline (identified by conversion to the hydrochloride) and a recovery of 2.3 gms. or 12.6% of azobenzene. No n-octane was found.

In view of the fact that some aniline was formed another run was made using 0.1 mole of azobenzene and 0.44 moles of n-butylmagnesium bromide. This time the Grignard reagent was filtered through glass wool which removed all of the larger particles of unused magnesium.

When the products were worked up from this run 9.7 gms. or a 52.7% of hydrazobenzene along with 1.8 gms. of aniline and 1. gm. or 8.8% of n-octane was obtained. It is probable that the formation of aniline was due to the reduction of hydrazobenzene by the action of the small amount of magnesium with the  $\text{NH}_4\text{Cl}$  solution since a smaller quantity of aniline was formed when the quantity of Grignard reagent was doubled. In the run using the smaller amount of Grignard reagent the magnesium had not been removed by filtration. The low yield of hydrocarbon, even though a fractionating column was used in separating the ether from the products, can be accounted for by the high volatility of this hydrocarbon.

Reaction of cyclohexylmagnesium bromide and azobenzene.

An ether solution of 0.33 moles of cyclohexyl-

magnesium bromide was refluxed for 8 hours with 0.1 mole of azobenzene. The reaction mixture was worked up in the usual manner, after hydrolysis with ammonium chloride solution, and there was obtained 5.2 gms., or 28.3% of hydrazobenzene, 5.0 gms. or 30.1% of dicyclohexyl, 0.9 gms. of aniline and 5.0 gms. or 27.5% of azobenzene. A troublesome emulsion, which caused some of the ether layer to be lost, partially explains the low yields.

Reaction of phenylmagnesium bromide and azobenzene.

An ether solution of 0.22 moles of phenylmagnesium bromide and 0.1 mole of azobenzene was refluxed for 8 hours. At the time the azobenzene was added to the phenylmagnesium bromide there was a slight elevation of temperature but no precipitate was formed until the solution had been refluxed for nearly 3 hours.

The apparatus was so arranged that any escaping gases would have to pass through a solution of bromine in carbon tetrachloride. No appreciable amount of gas was evolved and on working up the carbon tetrachloride solution no bromo derivatives were obtained.

The material was hydrolyzed with ammonium chloride solution and then worked up as usual. There was obtained 7.5 gms., or 41% of hydrazobenzene, 7.8 gms or 50.6% of diphenyl, and 8.2 gms or 45.5% of azobenzene was

recovered. The separation was effected by first crystallizing out as much hydrazobenzene as possible and then subjecting the mother liquor to vacuum distillation.

Reaction of p-tolylmagnesium bromide and azobenzene.

p-Tolylmagnesium bromide in 0.22 molar quantity was refluxed with 0.1 mole of azobenzene for 8 hours. On hydrolysis with ammonium chloride solution and on working up the ether extract in the usual manner there was obtained 10.5 gms., or a 54.6% yield, of hydrazobenzene, 5.6 gms. or a 30.8% yield of p,p<sup>1</sup>-ditolyl, 1 gm. of aniline and 4.5 gms. or 24.7% of azobenzene.

Reaction of phenylacetylenemagnesium bromide and azobenzene.

Phenylacetylenemagnesium bromide was prepared by the action of 22.4 gms. (0.22 moles) of phenylacetylene on an ether solution of 0.22 moles of ethylmagnesium bromide. A smooth reaction took place and was insured of completion by refluxing for 2 hours. Then 0.1 mole of azobenzene was added and refluxing continued for 8 hours. After hydrolysis with ammonium chloride solution and working up the reaction products in the usual manner there was recovered 21.0 gms. or 94% of phenylacetylene. Azobenzene was recovered quantitatively.

A repeat run in which the reaction mixture was refluxed for 16 hours gave similar results.

Reaction of acetylenemagnesium bromide ( $\text{MgBrC}\equiv\text{CMgBr}$ ) and azobenzene.

Acetylenemagnesium bromide was prepared by bubbling

a pure stream of acetylene into 0.22 moles of ethylmagnesium bromide for 2 hours. A white precipitate formed. Then 0.1 mole of azobenzene was added. During the addition of the first part of azobenzene a saturated gas was evolved. This soon stopped and no further evidence of reaction was noted during the 8 hour refluxing period.

When the material was hydrolyzed with a solution of ammonium chloride a small amount of gas was formed. After working the products up in the usual manner 0.9 gm., or 4.9%, of hydrazobenzene and 14.9 gms, or 81.9%, of azobenzene was recovered. Undoubtedly what little reduction which took place was due to the action of ethylmagnesium bromide which had not reacted with the acetylene.

Reaction of diphenylaminomagnesium bromide and azobenzene.

Diphenylaminomagnesium bromide was prepared from the action of 0.22 moles of diphenylamine with 0.22 moles of ethylmagnesium bromide. To this reaction mixture was added 0.1 mole of azobenzene and the material refluxed for 8 hours. There was no evidence of reaction. Following the usual procedure for hydrolysis and ether extraction there was recovered 94.5% of azobenzene and 91.7% of diphenylamine. No hydrazobenzene was found.

Reaction of n-butoxymagnesium iodide and azobenzene.

n-Butoxymagnesium iodide was prepared by allowing 0.22 moles of n-butyl alcohol to react with 0.22 moles of ethylmagnesium iodide. Then 0.1 mole of azobenzene

was added and the material refluxed for 8 hours. Following the usual procedure for hydrolysis and for working up the products there was obtained, besides most of the n-butyl alcohol, a 93.4% recovery of azobenzene.

Reaction of p-thiocresylmagnesium iodide and azobenzene.

By adding 0.22 moles of p-thiocresol to 0.22 moles of ethylmagnesium iodide there was obtained p-thiocresylmagnesium iodide. To this solution was added 0.1 mole of azobenzene and the solution refluxed for 8 hours. There was no evidence of reaction. When the reaction mixture was hydrolyzed and worked up in the usual manner azobenzene was recovered quantitatively besides an 80% recovery of p-thiocresol. From 4 gms. of an oil which was also obtained some crystals of p,p<sup>1</sup>-ditolyl disulfide were formed. This was no doubt due to the oxidation of p-thiocresol.

Reaction of phenylcalcium iodide and azobenzene.

Phenylcalcium iodide was prepared after the method of Beckmann<sup>136</sup> from 67.3 gms. (0.33 moles) of freshly distilled iodobenzene and 13.2 gms. (0.33 moles) of metallic calcium. Then 0.1 mole of azobenzene was added and the reaction mixture refluxed for 12 hours. Following the usual procedure for hydrolysis and for working up the products there was obtained 14 gms, or 21.5% of unused iodobenzene in addition to an almost quantitative recovery of azobenzene.

<sup>136</sup>Beckmann, Ber., 38, 904 (1905).



Reaction of ethylzinc iodide and azobenzene.

Following the method of Job and Reich<sup>14b</sup> ethylzinc iodide was prepared from 34.3 gms. (0.22 moles) of ethyl iodide and 28.8 gms. of zinc-copper couple. After adding 0.1 mole of azobenzene the solution was refluxed for 12 hours. No evidence of reaction was noted. The material was hydrolyzed with ammonium chloride solution and 17.1 gms. or 94% of azobenzene was recovered.

Reaction of phenylmagnesium bromide and p,p<sup>l</sup>-azotoluene.

To an ether solution of 0.11 moles of phenylmagnesium bromide was added 10.5 gms. (0.05 moles) of p,p<sup>l</sup>-azotoluene in benzene solution since it was more readily soluble in benzene. After refluxing for 8 hours the material was hydrolyzed and worked up as usual. The only crystals which could be separated from the residue were p,p<sup>l</sup>-azotoluene. The fact that no p,p<sup>l</sup>-hydrazotoluene was isolated was doubtless due to its solubility which is greater than that of p,p<sup>l</sup>-azotoluene and to its ease of oxidation to form p,p<sup>l</sup>-azotoluene.

Evidence of reduction was found in the formation of 5.7 gms. or a 74% yield, of diphenyl and in the formation of 2.8 gms., or a 26.15 yield, of p-toluidine during a vacuum distillation of the reaction mixture. p-Toluidine was converted to the hydrochloride for identification.

<sup>14A</sup>Job and Reich, Bull. soc. chim., 33, 1414 (1923).

An approximation of the amount of reduction may be obtained from the fact that p,p'-hydrazotoluene breaks up into p,p'-hydrazazotoluene and p-toluidine when heated. Thus a 26.1% yield of p-toluidine indicates the previous existence of a like amount of p,p'-hydrazotoluene.

Reaction of phenylmagnesium bromide, azobenzene, and benzoyl chloride.

An ether solution of 0.1 mole of azobenzene and 0.22 moles of phenylmagnesium bromide was refluxed for 8 hours. The reaction mixture was then treated with 30.8 gms. (0.22 moles) of benzoyl chloride in a small quantity of ether. A vigorous reaction followed and a dark tarry mass was formed. The material was refluxed with stirring for 4 hours.

When the material was hydrolyzed with ammonium chloride solution ~~in~~ a large quantity of solid material formed. It was separated by filtration and allowed to dry. In this way there was obtained 16.5 gms. of substance melting at 152-155°. After crystallization from alcohol it melted at 159-160° and was shown to be dibenzoyl hydrazobenzene by a mixed melting point. The dibenzoyl hydrazobenzene used for the mixed melting point was prepared after the method of Freundler<sup>156</sup>.

The ether extracts were washed with dilute ammonium<sup>156</sup> Freundler, Compt. rend., 136, 1553 (1903).

hydroxide and then with water. After following the usual procedure for working up the products there was obtained 4.5 gms. more of dibenzoyl hydrazobenzene making a total yield of 21 gms., or 54% of the theoretical.

The remaining material, on vacuum distillation, yielded 17.4 gms. or 60% of diphenyl. There was also obtained 2 gms., or 11% of ~~para~~ azobenzene and 4.5 gms. of benzanilide which no doubt resulted from the decomposition of dibenzoyl hydrazobenzene during the distillation. <sup>16b</sup>

Reaction of styrylmagnesium bromide, azobenzene, and benzoyl chloride.

Styrylmagnesium bromide was prepared from 0.22 moles of freshly distilled  $\beta$ -bromostyrene and 0.22 moles of magnesium. A 0.1 molar quantity of azobenzene was added and the material refluxed for 8 hours. Then 0.22 moles of benzoyl chloride was added and the reaction mixture stirred without heating for 4 hours. A vigorous reaction took place when the benzoyl chloride was added.

When the material was hydrolyzed and worked up in the usual manner 18.8 gms., or a 48% yield, of dibenzoyl hydrazobenzene was obtained. 1,4-Diphenylbutadiene was obtained in 77.7% yield and 24.2% of azobenzene was recovered.

<sup>16b</sup>Stern, Ber., 17, 379 (1884), has reported a related reaction. When monoacetyl hydrazobenzene is heated it decomposes to give azobenzene and acetanilide.

Reaction of phenylacetylenemagnesium bromide,  
azobenzene, and benzoyl chloride.

Phenylacetylenemagnesium bromide was prepared from 0.22 moles of phenylacetylene and 0.22 moles of ethylmagnesium bromide. The ether which had been used as a solvent was replaced by benzene and 0.1 mole of azobenzene was added. During the 16 hours refluxing there was no evidence that a reaction had taken place.

In order to be sure that phenylacetylenemagnesium bromide was still present after the refluxing a small amount of solution was removed and treated with carbon dioxide. After hydrolysis, phenylpropionic acid was obtained and identified by a mixed melting thus proving the presence of phenylacetylenemagnesium bromide. Some azobenzene was also recovered.

Hoping to isolate any small amount of reduction product by conversion to dibenzoyl hydrazobenzene there was added to the reaction mixture 30.8 gms. (0.22 moles) of benzoyl chloride. The reaction was not a vigorous one.

When the material was hydrolyzed with ammonium chloride solution and worked up as in the previous benzoyl chloride run there was obtained 0.4 gms. of benzamide which was doubtless due to a reaction of the ammonium hydroxide used to remove excess benzoyl chloride. There was recovered 17.7 gms. (94.2%) of azobenzene and 15 gms of liquid boiling between 150° and 210° was obtained. This liquid in all probability was formed by the action of

benzoyl chloride and phenylacetylenemagnesium bromide and was not studied further.

Reaction of ethylmagnesium bromide, diazoaminobenzene and benzoyl chloride.

To a solution of 0.33 moles of ethylmagnesium bromide there was added 0.1 mole of diazoaminobenzene. A reaction took place, although not a vigorous one, with the evolution of a gas. Since no large quantity of precipitate had formed, refluxing was continued for 16 hours. Then 0.33 moles of benzoyl chloride was added and a vigorous reaction took place.

After hydrolysis with ammonium chloride solution the reaction mixture was worked up in the usual way. There was obtained a total of 16 gms., or a 31.3% yield, of sym-diphenyl tribenzoyl triazane. It crystallizes from alcohol in needles melting at 160-161°. When hydrolyzed by boiling with concentrated hydrochloric acid a 2 gm. sample of this product yielded 1.6 gms. of benzoic acid, 0.6 gms of aniline hydrochloride and some ammonium chloride.

There was also obtained 2.5 gms. of benzanilide and 8.0 gms. of benzamide from the reaction mixture.

Reaction of benzylmagnesium bromide, p-dimethylaminoazobenzene, and benzoyl chloride.

To an ether solution of 0.22 moles of benzylmagnesium chloride there was added 0.1 mole of p-dimethylaminoazobenzene in benzene solution since it was more readily

soluble in benzene. The material was refluxed for 8 hours after which 0.22 moles of benzoyl chloride was added and refluxing continued for another 8 hour period. An amorphous precipitate had formed.

The material was hydrolyzed with an ammonium chloride solution and worked up in the usual manner. When most of the solvent had been removed by distillation 5.gms. of crystalline material was obtained. It was found to be composed of 3.0 gms. benzamide and 1.9 gms. of a substance which melted at 160-161° when crystallized from alcohol. It was fairly soluble in ether and formed a crystalline precipitate when treated with dry hydrochloric acid. No doubt this material was the dibenzoyl derivative of p-dimethylaminoazobenzene since it was prepared in the way that had given good yields of other dibenzoyl derivatives.

The remainder of the reaction mixture did not crystallize well so it was vacuum distilled to obtain the other products. In this way 12 gms., or a 66% yield, of dibenzyl was obtained. After the dibenzyl had distilled over, the residue came over through the wide range of 140-280° at 3m.m. From this distillate there was obtained a small amount of benzanilide which was identified by a mixed melting point. There was also obtained a small amount of another substance melting at 223-225°. This was very likely the benzoyl derivative of p-dimethylamino aniline<sup>174</sup>

174Hornstein, Ber., 29, 1479 (1896).

$((\text{CH}_3)_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5)$ , which is described as melting at  $228^\circ$ .

Reaction of ethylmagnesium bromide, azobenzene and acetyl chloride.

To an ether solution of 0.22 moles of ethylmagnesium bromide was added 0.1 mole of azobenzene. After about 10 c.c. of the azobenzene solution had been added the evolution of a gas began and a white crystalline precipitate commenced to form. To insure complete reaction the material was refluxed for 8 hours although very little gas was evolved after all of the azobenzene had been added. Practically all of the color of azobenzene disappeared.

The reaction mixture was then treated with 19.5 gms. (.25 moles) of freshly distilled acetyl chloride. A vigorous reaction took place. After refluxing for 8 hours the material was hydrolyzed with an ammonium chloride solution.

All gas evolved from the beginning of the experiment until after hydrolysis was bubbled through a solution of bromine in carbon tetrachloride. The bromine solution lost only a little of its color and a small amount of hydrogen bromide was formed. When the solution was worked up 12.2 gms. of liquid boiling between  $80^\circ$  and  $165^\circ$  was obtained. At no point was the temperature constant. Undoubtedly the gas evolved was a saturated hydrocarbon and what bromo derivative that formed was the result of a substitution reaction.

The ether extract from the original reaction mixture was worked up in the usual way. After standing for a few days, 5.6 gms., or 25.6%, of monoacetyl hydrazobenzene<sup>18<sup>Δ</sup></sup> had formed. Its identity was proved by a mixed melting point.

The remaining oil did not crystallize after standing for several months. Various solvents such as glacial acetic acid, dilute acetic acid, alcohol, benzene, and ether were employed and the solution seeded with diacetyl hydrazobenzene<sup>19<sup>Δ</sup></sup> but none of this compound could be made to crystallize.

In another run following the method used in the one just described except that 0.33 moles of acetyl chloride was used there was obtained 5.6 gms. or 24.7% of monoacetyl hydrazobenzene. The same viscous oil was obtained as described in the previous run.

An attempt to purify the material by vacuum distillation was unsuccessful. It distilled over through the wide range of 160° to 210° at 3 m.m. The distillate appeared to be the same viscous oil. All attempts to crystallize it were unsuccessful.

18<sup>Δ</sup>. Monoacetyl hydrazobenzene used for the mixed melting point was prepared after the method of Stern, Ber., 17, 379 (1884).

19<sup>Δ</sup>. Diacetyl hydrazobenzene was prepared after the method of Schmidt and Schultz, Ann., 207, 320 (1881).



In a third run, following the same procedure as in the previous runs and substituting 0.25 moles of freshly distilled acetic anhydride, 5.0 gms, ~~xxx~~ or a yield of 22.1%, of monoacetyl hydrazobenzene was obtained besides the usual heavy oil. This time the heavy oil was extracted with hot water and this hot water extract boiled with boneblack for an hour. The resulting solution (about 1 liter) was filtered and allowed to evaporate. After about 10 days some crystals were obtained which melted at 104-105°. They were shown to be diacetyl hydrazobenzene by a mixed melting point.

Reaction of phenylmagnesium bromide, azobenzene, and acetyl chloride.

Using 0.22 moles of phenylmagnesium bromide and 0.1 mole of azobenzene the usual reaction occurred. The material was refluxed for 8 hours and then 0.33 moles of acetyl chloride was added. Refluxing was continued for 8 hours.

When the products were worked up 4.6 gms. or a 20% yield of monoacetyl hydrazobenzene was obtained besides the same heavy oil described in other runs. By vacuum distillation there was obtained 12.3 gms. or 80% of diphenyl besides 1.0 gms or 5.5% of azobenzene.

Reaction of phenylmagnesium bromide, azobenzene, and diethyl sulfate.

An ether solution of 0.22 moles of phenylmagnesium bromide and 0.1 mole of azobenzene was refluxed for 8

hours. Then 0.33 moles of diethyl sulfate was added slowly and the mixture refluxed for 8 hours.

After hydrolysis with ammonium chloride solution the residue from the ether extractions was vacuum distilled. Diphenyl was obtained in a yield of 12.5 gms. or 81.1%.

A fraction of 2.5 gms. of liquid was obtained between 140° and 155° at ~~xxxx~~ 1.5 m.m. (B.P. of sym-diphenyl diethyl hydrazine is 141° at 1 m.m.) On a redistillation 1.5 gms. of product was obtained distilling at 140-145° at 1.5 m.m. It was probably sym-diphenyl diethyl hydrazine, but it did not give the characteristic color reaction with acetic acid which Wieland and Fressel<sup>20</sup> mention.

Reaction of phenylmagnesium bromide, azobenzene, and phenyl isocyanate.

After 0.22 moles of phenylmagnesium bromide and 0.1 mole of azobenzene had been refluxed in ether for 8 hours, 26.2 gms. or 0.22 moles of phenyl isocyanate was added and refluxing continued for 4 hours. On hydrolysis with ammonium chloride solution 14 gms. of ether insoluble material was obtained. It melted at 170° and when recrystallized from either alcohol or benzene it melted sharply at 175°. When heated, an odor of phenyl isocyanate was produced and a red color appeared. Diphenyl diisocyanate (C<sub>6</sub>H<sub>5</sub>CNO)<sub>2</sub> also melts at 175° but the  
20<sup>o</sup> Wieland and Fressel, Ann., 392, 133 (1912).

product did not give the reactions described for this compound.

The ether solution yielded ~~12.3~~ 12.3 gms. of a mixture from which azobenzene was removed by washing with petroleum ether. The residue after recrystallizing from alcohol gave 3.5 gms. of pure benzanilide doubtless due to a reaction between unused phenylmagnesium bromide and phenyl isocyanate. There was also obtained some carbanilide and 5 gms. of diphenyl.

Reaction of ethylmagnesium bromide, azobenzene, and phenyl isocyanate.

An ether solution of 0.22 moles of ethylmagnesium bromide and 0.1 mole of azobenzene was refluxed for 8 hours. Then 0.22 moles of phenyl isocyanate was added and refluxing continued for 4 hours. The reaction product was hydrolyzed with ammonium chloride solution and 11 gms. of ether insoluble material was obtained. From this there was isolated a small amount of the tri-polymer of phenyl isocyanate  $(C_6H_5CNO)_3$  melting at 275-276°. It was identified by a mixed melting point. There was also obtained by repeated crystallizations from benzene and alcohol 2 other compounds. One of these came out in needle-like crystals from alcohol and melted at 178-9°. A mixed melting point with the 175° compound obtained in the previous run was 160-165°. The other product was also crystallized from alcohol and melted at 185-186°.

The ether extract from the original reaction mixture yielded a heavy oil from which the only product obtained was azobenzene.

Reaction of ethylmagnesium bromide, hydrazobenzene, and phenyl isocyanate.

To an ether solution of 0.22 moles of ethylmagnesium bromide there was added 0.1 mole of hydrazobenzene. A vigorous reaction took place with the evolution of a gas. The material was refluxed for 2 hours to insure completion of the reaction. Then 0.22 moles of phenyl isocyanate was added and the reaction mixture refluxed for 4 hours more.

The material was hydrolyzed with ammonium chloride solution and 14 gms. of ether insoluble substance was obtained. It melted between 185° and 220°. After several recrystallizations from benzene and also from alcohol, the only products which could be isolated were carbanilide and a material which crystallized from benzene and melted sharply at 212°. It was almost completely insoluble in alcohol and was fairly soluble in benzene. It does not have the properties of the di-phenyl isocyanate derivative of hydrazobenzene which is described as a gray, amorphous substance insoluble in benzene and melting at 218° to 220° 21<sup>b</sup>.

21<sup>b</sup>. Goldschmidt and Rosell, Ber., 23,487 (1890).

Summary.

I. The reducing action of a number of Grignard reagents with azo compounds has been studied. All results indicate the mechanism of reduction to be:

