

THE ACTION OF RANEY NICKEL ON HALO-NITROBENZENES

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THE ACTION OF RANEY NICKEL ON HALO-NITROBENZENES

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CHAPTER I

INTRODUCTION

Many biphenyl derivatives are conveniently made by means of Ullman's method, which involves the treatment of aromatic halides with copper powder.¹ The formation of copper halide seems to be a contributing factor for the forward reaction. Since the heat of formation of nickel halides is higher than that of copper halides,² nickel is probably more reactive than copper towards halogen. Thus it may be possible that nickel may be better than copper in the Ullman reaction.

An active form of nickel is that developed by Raney, now commonly referred to as Raney nickel.³ By its normal method of preparation the finely divided nickel holds a considerable amount of hydrogen and may be referred as a hydrogen-rich Raney nickel. One may, however, take measures to remove this bound hydrogen and obtain a hydrogen-poor or a hydrogen-free Raney nickel.⁴ In this work it is proposed to investigate the action of both of these forms of Raney nickel on certain aromatic halogen compounds.

¹P. E. Fanta, Chem. Rev., 38, 139 (1946).

²N. A. Lange, Handbook of Chemistry, 7th edition (Sandusky, Ohio: Handbook Publishers, Inc., 1949), pp. 1581, 1593-94, 1599.

³M. Raney, U. S. Patent, 1,915,473 (June, 1933).

⁴H. Hauptmann and B. Wladislaw, J. Am. Chem. Soc., 72, 707 (1950).

CHAPTER II

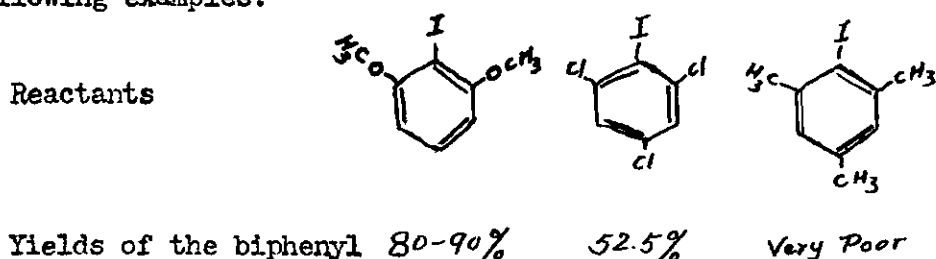
REVIEW OF LITERATURE

The Ullman reaction^{1,2} may be represented generally as:



where R and R' are aromatic radicals. The halogen atom must be active, and for this reason iodo-compounds are commonly employed. Good results can be obtained also with activated chloro-derivatives, especially if there is the nitro group in the ortho or para position. On the other hand, amino or hydroxyl groups will decrease the activity of halogen and hence poor yields of the biphenyl might be expected. Bromo-compounds are intermediate in activity.

The steric effects are very important too, as can be seen from the following examples:



This is in agreement with the relative sizes of the OCH₃, the Cl, and the CH₃ groups as reported by Gilman.³

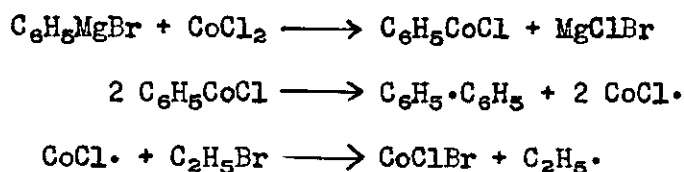
The metal used in the Ullman reaction is copper. Although there

¹F. Ullman and J. Bielecki, Ber., 34, 2174-85 (1901).

²P. E. Fanta, Chem. Rev., 38, 139 (1946).

³H. Gilman, Organic Chemistry, An Advanced Treatise, Vol. I (New York: John Wiley and Sons, Inc., 1943), p. 362.

is no direct information concerning the use of nickel instead of copper in the Ullman reaction, it would seem possible that nickel might be effective since certain condensations are brought about by the use of nickel or its compounds. For instance, nickel carbonyl⁴ has been found to be a catalyst in the formation of $\alpha\alpha'$ -binaphthyl from naphthalene. Under high pressure, nickel promotes the formation of biphenyl from benzene.⁵ Gilman⁶ found that the halides of Fe, Co, and Ni react with phenylmagnesium iodide to give quantitative yields of biphenyl. In the presence of these halides, Kharasch⁷ obtained good yields of biaryls by coupling phenylmagnesium halides with organic halides -- ethyl bromide, for example. He also stated that the order of increasing effectiveness of the metals is Fe, Co, Ni. With ethyl bromide, the mechanism suggested^{8,9} is as follows:



The coupling of allylic halides by nickel carbonyl in methanol

⁴J. Dewar and H. O. Jones, J. Chem. Soc., 85, 219 (1904); 91, 1104 (1910); and 97, 1101. (1916).

⁵J. P. Wibaut and H. M. Ramijn, Rec. Trav. Chim., 53, 584 (1934).

⁶H. Gilman, J. Am. Chem. Soc., 61, 957 (1939).

⁷M. S. Kharasch, J. Am. Chem. Soc., 63, 2316 (1941).

⁸M. S. Kharasch, D. W. Lewis, and W. B. Reynolds, J. Am. Chem. Soc., 65, 493 (1943).

⁹M. S. Kharasch, D. W. Lewis, and W. B. Reynolds, J. Am. Chem. Soc., 65, 498 (1943).

has been studied recently by Webb and Borchardt.¹⁰ A mechanism is proposed in which nickel carbonyl is activated by the solvent, *i. e.*, to a lower carbonyl compound, and complexes with two allylic halide molecules. The complex may then undergo electronic changes to form products.

In preparing Raney nickel catalyst,¹¹ some quantities of hydrogen are adsorbed on the surface and absorbed within the nickel structure. The amount of hydrogen thus held was determined by Mozingo, *et. al.*¹² They found that the amount held depended on the final temperature of preparation, namely, 170 or 460 ml. of hydrogen for every 4 g. of Raney nickel at 80° or 50° C. respectively. Thus Raney nickel freshly prepared at 50° contains so much hydrogen that its formula is nearly that of a compound Ni₂H.¹³ It is for this reason that Mozingo and co-workers¹⁴ were able to carry out hydrogenations with Raney nickel catalyst without any molecular hydrogen.

In addition to its reducing power, Raney nickel has a special affinity for sulfur in reactions with aromatic sulfur compounds.^{12, 15} Its deoxygenation of nitro groups on aromatic radicals to form azoxy

¹⁰L. D. Webb and G. T. Borchardt, Abstracts of Papers, September, 1950, Meeting of the American Chemical Society, Chicago, Illinois, p. 10N.

¹¹R. Mozingo, Organic Syntheses, Vol. 21 (New York: John Wiley and Sons, Inc., 1941), p. 15.

¹²R. Mozingo, D. E. Wolf, S. A. Harris, and K. Folkers, J. Am. Chem. Soc., 65, 1013 (1943).

¹³R. Schroter, Newer Methods of Preparative Organic Chemistry (New York: Interscience Publishers, Inc., 1948), p. 69.

¹⁴Mozingo, R., C. Spencer, and K. Folkers, J. Am. Chem. Soc., 66, 1859 (1944).

¹⁵H. Hauptmann and B. Wladislaw, J. Am. Chem. Soc., 72, 707 (1950).

compounds was recognized by Covert and Adkins.¹⁶ In most cases, azoxy compounds¹⁷ are prepared by reduction of the corresponding nitro compounds in alkaline solution.

¹⁶L. W. Covert and H. Adkins, J. Am. Chem. Soc., 54, 4116 (1932).

¹⁷H. E. Bigelow, Chem. Rev., 9, 117 (1931).

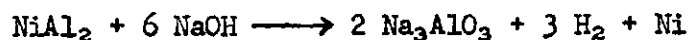
CHAPTER III

EXPERIMENTAL

A. Preparation of Raw Materials

1. Preparation of Raney Nickel Catalyst

Raney nickel was prepared by Mozingo's method.¹ The alloy was added in small portions to the moderately concentrated alkaline solution at 20° C. Further reaction took place by heating in a steam bath. The reaction is as follows:



The product was washed thirty times with 600 ml. portions of water, three times with 600 ml. portions of 95% ethyl alcohol and three times with absolute alcohol. The Raney nickel thus prepared was kept under absolute alcohol.

2. Preparation of H₂-free Raney Nickel

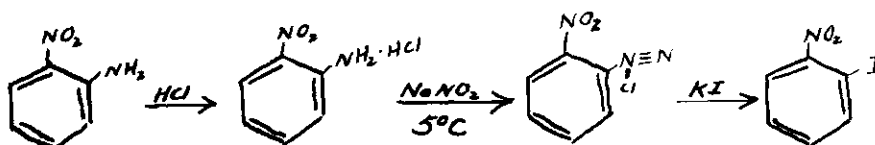
Hydrogen-free Raney nickel was prepared in an atmosphere of carbon dioxide. Six grams of Raney nickel suspended in absolute alcohol was placed in a three-neck reaction flask. After a few minutes, the nickel settled and as much of the alcohol was decanted as was possible without loss of metal. A few glass beads were added to prevent too much accumulation of nickel in the center of the flask which seemed to give rise to severe bumping when heat was applied. The

¹R. Mozingo, Organic Syntheses, Vol. 21 (New York: John Wiley and Sons, Inc., 1941), p. 15.

central neck of the flask was connected to a vacuum pump and a carbon dioxide generator, while the other two were equipped with a thermometer and a separatory funnel respectively. The reaction flask was first filled with carbon dioxide and then gently heated to 50°-60° C. under a vacuum of about 5 mm. A small stream of carbon dioxide was passed into the flask throughout the heating time. After the alcohol was removed, the lumps of nickel were gently broken to a powder by a glass rod and a grinding motion of the glass beads. Then the flask and contents were heated to 100° C. and kept there for one hour. They were further heated at 200° C. for one hour. After cooling slowly to room temperature, the vacuum pump was disengaged and the reaction vessel filled with carbon dioxide to atmospheric pressure.

3. Preparation of *o*-Iodo-nitrobenzene

The reactions are as follows:

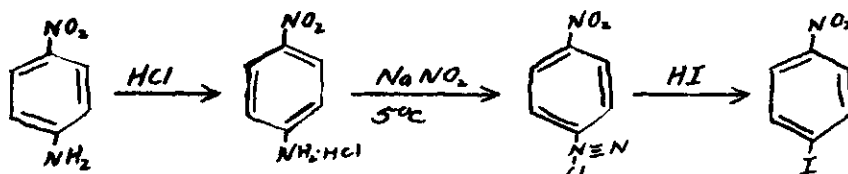


A solution was made by heating 30 g. of *o*-nitro-aniline with 60 ml. of concentrated hydrochloric acid. The hot solution was cooled to 30° C. with stirring, resulting in a thick, almost colorless paste of the hydrochloride. After adding 100-120 ml. of H₂O, 120 g. of ice was added. Forty-four ml. of a 5 N sodium nitrite solution was dropped in with vigorous stirring. Stirring was continued and more ice added as necessary (to keep temperature to 5° C.) until most of the material was in solution and all but a trace of the nitrite had been used. After filtration,

60 g. of KI was added. The yellow *o*-iodo-nitrobenzene was filtered from the solution and recrystallized from 70% ethyl alcohol. The yield was nearly quantitative.

4. Preparation of *p*-Iodo-nitrobenzene

The chemical reactions are as follows:



A mixture of 30 g. of *p*-nitroaniline, 70 ml. water and 70 ml. of concentrated hydrochloric acid was heated until solution was effected. The solution was cooled to room temperature. 200 g. of ice was added and then an amount of dry, technical sodium nitrite equivalent to 15 g. of pure sodium nitrite added in one portion with constant shaking. Shaking was continued until most of the precipitated material had redissolved and the mixture allowed to stand for about 10 minutes in an ice bath. Any residual undissolved material was removed by filtration. Twenty-eight g. of hydriodic acid was added. *p*-Iodo-nitrobenzene precipitated from the solution and after filtration was recrystallized from methyl alcohol.

B. The Reaction Procedures:

1. Hydrogen-free Raney Nickel with α -bromonaphthalene

Six grams of H₂-free Raney nickel was prepared as mentioned above. After cooling under a CO₂ atmosphere, 20 g. of α -bromonaphthalene was added to the reaction flask through the separatory funnel. The central neck was connected to a condenser. The mixture was stirred to a paste

and then heated to 210° C. and kept for 23 hours. After cooling, the flask was immersed in an oil bath for vacuum distillation. The immersion was done in such a way that the surface of the oil reached as high as possible on the necks of the flask. Distillation was carried out at 157-160° C. under 20 mm. pressure. Fourteen g. of a yellow oil collected in the receiver and was identified as unreacted α -bromonaphthalene.

After distillation, the reaction mixture was extracted twice with 100 cc. boiling benzene and this extract concentrated to a very small volume. About 2.4 g., apparently an organo-metallic compound, was collected by filtration.

The same procedure was carried out at 230° C. White fumes appeared and the reaction was stopped. A portion of the white fumes, condensed on the wall of the condenser, was identified as naphthalene.

2. Hydrogen-free Raney nickel with o-chloro-, o-bromo-, o-iodo-, and p-chloro-nitrobenzene.

a. Six g. of H₂-free Raney nickel was prepared in the same way as described above. The o-chloro-nitrobenzene (7.85 g.) placed in the separatory funnel was melted with a small flame and allowed to run down slowly into the reaction flask. The reaction temperature was controlled at 240-250° C. After heating for 2 hours, the mixture was extracted three times with boiling ligroin. On cooling and concentrating, only a tarry residue was obtained from which no pure compound could be isolated.

b. Ten g. of o-bromo-nitrobenzene was treated with 6 g. of H₂-free Raney nickel at 220-230° C. in a similar way. On cooling the ligroin

extract, 1.1 g. of 2,2'-dinitro-biphenyl was obtained (M.P. 123-4° C.).

c. o-Iodo-nitrobenzene (12.4 g.) was treated with 6 g. of the H₂-free Raney nickel at 120-130° C. for two hours. On cooling, 1.34 g. of 2,2'-dinitro-biphenyl was obtained from ligroin extraction.

d. When 7.85 g. of p-chloro-nitrobenzene reacted at 240-250° C. with 6 g. of H₂-free Raney nickel for 2 hours, the ligroin extract was only slightly colored. No product was found except a small quantity of tarry materials.

3. Reaction of H₂-rich Raney nickel with m-bromo-nitrobenzene

Five ml. nickel-alcohol mixture was placed in a 250 ml. three necked reaction flask. Excess alcohol was removed by decantation and 5 g. of m-bromo-nitrobenzene added in small portions. The flask was immersed in an oil bath to distill off the alcohol. After this operation, the reaction was carried out under several conditions by varying the temperature and time of reaction as shown below:

	Temperature	Time of Reaction
a.	100-160° C.	5 minutes
b.	155-165° C.	2 hours
c.	120-130° C.	2 hours
d.	105-115° C.	2 hours

At the end of the reaction period, 100 ml. of ligroin was added for extraction. The mixture was boiled for about 10 minutes and filtered. The process was repeated with 60-70 cc. ligroin and again repeated with 100 cc. ligroin. Upon cooling the ligroin solution in an ice box, crystals were obtained which were filtered off and purified by recrystal-

lization from 95% ethyl alcohol. The product was found to be 3,3'-dibromo-azoxybenzene.

The ligroin solution from the above filtration was further treated with 30% H_2SO_4 solution. The yellow solid formed was filtered off and the immiscible acid solution separated from ligroin by means of a separatory funnel. The yellow solid and the acid solution were set aside to be identified later. The ligroin solution was cooled again and a small amount of the azoxy compound crystallized out in the form of needles. After filtering off the crystals, the solution was concentrated to half of the original volume and cooled again. This time the small amount of crystals were found to be mainly 3,3'-dibromo-hydroazobenzene.

The remaining material in the above ligroin solution consisted of unreacted compound which was crystallized from the ligroin by repeating the concentrating and cooling processes.

4. Reaction of H_2 -rich Raney Nickel with halo-nitrobenzenes

a. For low melting solids - halo-nitrobenzenes with the omission of p-bromo- and p-iodo-nitrobenzene.

Three g. of Raney nickel in absolute alcohol was placed in the reaction flask and the excess alcohol removed by decantation. The fixed quantity of halo-nitrobenzenes (3.93 g. for chloro-nitrobenzenes, 5 g. for bromo-nitrobenzenes and 6.2 g. for iodo-nitrobenzenes with the mol ratio of nickel to the reactants equal to 2:1) was added in small portions with shaking and keeping the temperature of the mixture less than $60^\circ C$. This was done by the aid of a cold water bath. The total addition took 4-6 minutes. The reaction flask was then placed in a water bath at $80^\circ C$.

and the temperature raised to 95° C. within 6-8 minutes. The flask was immersed in a water bath as far as possible. In such an arrangement, by the vigorous stirring of the thermometer, the alcohol was removed within 6-8 minutes. The final temperature was usually about 95° C. or a little higher due to the exothermic reaction taking place. The reaction flask was removed from the water bath and cooled for about 5 minutes. It was next placed in an oil bath at 90°-100° C. and the temperature gradually raised to 110-115° C. within 20-30 minutes. No stirring was necessary. In some cases a vigorous reaction took place around 100-110° C. This was observed by the sudden rise in temperature and the evolution of a lot of gas bubbles. When this occurred, the flask was taken out quickly and allowed to cool in air or put into an ice-water bath if necessary. As the temperature began to drop, the flask was replaced in the oil bath. If a second vigorous reaction occurred, it was treated in the same way as before. The reaction temperature was kept at 110-120° C. for two hours. At the end of this time, three extractions with boiling ligroin with a total volume about 250 ml. were effected. The ligroin extract was placed in the cold (5-10° C.) for crystallization. The azoxy compound was collected by filtration and recrystallized from methyl alcohol.

The ligroin filtrate was treated twice with 60 ml. 30% H₂SO₄ solution and separated from the immiscible acid solution. If a solid salt was present, separation was carried out after removing the salt by filtration. The solid was boiled with a small quantity of ligroin (about 20-30 ml.) for a few minutes and filtered. The filtrate and the above ligroin solutions were mixed together and concentrated to half

the original volume. The solution was then cooled in an ice box and filtered. The process was repeated several times in order to remove as much solid as possible. The acid solution and the solid salt were kept in a cold place for the later determination of amine.

b. For high melting solids - p-bromo- and p-iodo-nitrobenzene

1. At higher temperature

The procedure was the same as described above except the reaction temperature was 120-130° C. and 165-175° C. for p-bromo-nitrobenzene and p-iodo-nitrobenzene respectively.

2. With small amounts of solvent

The same procedure was carried out except that one ml. and 3.5 ml. of xylene were added to the reaction mixture of p-bromo- or p-iodo- compound respectively after the removal of the alcohol. In these cases, the reaction temperature was 110-120° C.

c. With p-chloro-nitrobenzene under other conditions.

The same procedure was carried out with the variation of the amount of nickel and solvent. This is listed in the following table.

TABLE I

Reaction of p-Chloro-nitrobenzene with Raney Nickel

Exp. No.	g. Reactant	g. Nickel	Xylene	Reaction Temp.	Reaction Time
17	3.9	1.5		110-120° C.	2 hrs.
19	3.9	6.		110-120° C.	2 hrs.
20	3.9	3.	3.5 cc	110-120° C.	2 hrs.

In experiment (19), pp'-dichloro-azobenzene was found. This was recrystallized from ligroin several times and finally recrystallized from glacial acetic acid. The m.p. was 184-186° C.

C. The Quantitative Determination of Amine

The process described by Siggia² is based on the following reaction:



The primary amine was titrated with 1 N NaNO₂ in acid solution. The excess of HONO was indicated by an immediate blue color obtained with potassium-iodide-starch paper.

²S. Siggia, Quantitative Organic Analysis via Functional Group (New York: John Wiley and Sons, Inc., 1949), p. 70-73.

CHAPTER III

RESULTS AND DISCUSSION

A. Results:

A summation of the results of the experimental portion of this work is summarized in Tables II, III, and IV:

TABLE II

NAPHTHALENE FORMATION

Exp. No.	Reactants	Raney Nickel	Temp.	Time	Results
1	α -Br-C ₁₀ H ₇	H ₂ -free	230° C.		C ₁₀ H ₈
2	α -Br-C ₁₀ H ₇	H ₂ -free	210° C.	23 hrs	70% unreact. 12% organo- metallic comp.

TABLE III

BIPHENYL FORMATION

Exp. No.	Reactants	Raney Nickel	Temp.	Time	Results
3	o -Cl-C ₆ H ₄ -NO ₂	H ₂ -free	250°C.	2 hrs	No Biphenyl
4	o -Br-C ₆ H ₄ -NO ₂	"	210-220°C.	"	15-18% Biphenyl
5	o -I-C ₆ H ₄ -NO ₂	"	130-140°C.	"	20-22% Biphenyl
6	p -Cl-C ₆ H ₄ -NO ₂	"	250°C.	"	No Biphenyl

TABLE IV - H₂-RICH RANEY NICKEL WITH NITRO-HALOBENZENES

Exp. No.	Reactant	Mol Ratio ^a	Temp °C	Time	Hydrazo	Azoxy	Amine	Unreacted	N.B.
7	<u>o</u> -Cl-C ₆ H ₄ -NO ₂	2:1	110-120°	2 hrs			26.7%	51.7%	
8	<u>o</u> -Br-C ₆ H ₄ -NO ₂	2:1	"	"			24.0%	45.4%	
9	<u>o</u> -I-C ₆ H ₄ -NO ₂	2:1	"	"			12.2%	21.6%	14.4% Biphenyl
10	<u>m</u> -Cl-C ₆ H ₄ -NO ₂	2:1	"	"		55.2%	7.92%	4.06%	
11	<u>m</u> -Br-C ₆ H ₄ -NO ₂	2:1	"	"		39.6%	14.3%	1.86%	
12	<u>m</u> -Br-C ₆ H ₄ -NO ₂	2:1	100-160°	5 m.	8%	15.0%	17.5%	6.0%	
13	<u>m</u> -Br-C ₆ H ₄ -NO ₂	2:1	155-165°	2 hrs	2%	6.5%	13.6%	2.0%	
14	<u>m</u> -Br-C ₆ H ₄ -NO ₂	2:1	120-130°	"	10.1%	16.4%	24.7%	11.0%	
15	<u>m</u> -Br-C ₆ H ₄ -NO ₂	2:1	105-115°	"	9.0%	11.8%	30.7%	4.0%	
16	<u>m</u> -I-C ₆ H ₄ -NO ₂	2:1	110-120°	"		20.7%	12.9%	20.0%	
17	<u>p</u> -Cl-C ₆ H ₄ -NO ₂	1:1	"	"		20.3%	8.4%	65.0%	
18	<u>p</u> -Cl-C ₆ H ₄ -NO ₂	2:1	"	"		56.9%	7.8%	7.35%	
19	<u>p</u> -Cl-C ₆ H ₄ -NO ₂	4:1	"	"		6.9%	59.5%		21% azo-comp.
20	<u>p</u> -Cl-C ₆ H ₄ -NO ₂	2:1	"	"		37.8%	15.8%	33.2%	with 3.5 cc xylene
21	<u>p</u> -Br-C ₆ H ₄ -NO ₂	2:1	120-130°	"		24.5%	15.03%	8.53%	
22	<u>p</u> -Br-C ₆ H ₄ -NO ₂	2:1	110-120°	"		6.4%	19.3%	47.0%	with 1 cc xylene
23	<u>p</u> -I-C ₆ H ₄ -NO ₂	2:1	165-175°	"			4.22%	42.4%	
24	<u>p</u> -I-C ₆ H ₄ -NO ₂	2:1	110-120°	"			26.1%	55.5%	with 3.5 cc xylene

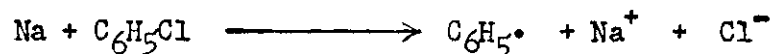
^aThe molar ratio of Raney nickel to reactant

B. Discussion of the Results

1. Naphthalene Formations:

α -Binaphthyl was prepared in 50% yield from α -bromonaphthalene by Schoepfle¹ by heating at 280-285°C. for 4-5 hours. The metal used was copper to which a small quantity of iodine was added. But, if nickel was used instead of copper, work found the reaction to be quite different. When the reaction temperature was kept above 230°C., naphthalene was formed, and at 210°C. for 23 hours, no noticeable amount of binaphthyl could be found.

The formation of naphthalene with hydrogen-free Raney nickel perhaps occurs through the free radical mechanism. Bachmann and Clarke² believe that $C_6H_5\cdot$ exists as an intermediate in the reaction of chlorobenzene with sodium:



Hence the products are benzene, bi-phenyl, *o*-diphenyl benzene, *p*-diphenyl benzene, and triphenylene and so on. The existence of a free radical is further indicated in that if the above reaction is carried out in the presence of excess toluene, one obtains nearly 50% of benzene and no biphenyl.

There has been no report that nickel forms an organo-metallic compound like that of Mg in $\alpha-C_{10}H_7MgBr$. So it might be possible that nickel at higher temperature reacts with the bromine of α -bromonaphthalene and leaves the naphthyl free radical which then takes hydrogen

¹C. S. Schoepfle, J. Am. Chem. Soc., 45, 1566 (1923).

²W. E. Bachmann and H. T. Clarke, J. Am. Chem. Soc., 49, 2089 (1927).

from another α -bromonaphthalene to form naphthalene.

2. Biphenyl Formation:

Di-nitrobiphenyls have been synthesized from the corresponding halo-nitrobenzenes by Ullman's method. The reaction conditions and results are summarized in the following table:

TABLE V

BIPHENYL FORMATION BY ULLMAN METHOD

Radicals	Halogens	Temperature	Conditions	Yields	Reference
<u>o</u> -NO ₂ -C ₆ H ₅ -	Cl	210-245°C	with dry sand	60%	3
	Br	200-220°C		75%	3
	I	134°C	vigorous		4
<u>m</u> -NO ₂ -C ₆ H ₅ -	Br	257°C	slow reaction		4
	I	210-225°C		26-52%	5,6,3
<u>p</u> -NO ₂ -C ₆ H ₅ -	Br	255°C	slow reaction		4
	I	220-235°C		52%	3

From the above table it is clear that the variation of reaction temperature is closely related to the activities of the halogens. The influence of the nitro-group on the activity of halogen is especially strong when in the o-position. This is probably due to the strong electron attracting effect of the nitro-group. From Table V, the yields of biphenyl formed from the three o-halo-nitrobenzenes as in such a way as to indicate

³F. Ullman and I. Bielecki, Ber. 34, 2174 (1901).

⁴L. Mascarelli, E. Longo, and A. Ravera, Gazz. Chim. Ital., 68, 33, (1938).

⁵W. M. Cumming and G. D. Muir, J. Roy. Tech. Coll. (Glasgow), 4, 61 (1937).

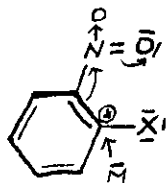
⁶G. Schieman and W. Roselius, Ber. 65, 737 (1932).

Cl < Br < I.

It was pointed out previously that the nickel is more active than copper towards bromine in formation of their bromides. Thus the lower yields of biphenyls in the case of nickel would seem to indicate a different reaction mechanism from that offered for the usual Ullman reaction. The mechanism of the Ullman reaction is not definitely known, but there are three possibilities advanced, namely:⁷

- a. Free radicals
- b. Organo-metallic compounds of moderate stability
- c. Organo-metallic complexes of transitory existence.

In the first case, high yields of biphenyl will not be likely since free radicals readily lead to polymerization and hence by-products. Organo-copper compounds have been studied by Gilman and Straley⁸ who point out that although well characterized RCu and R₂Cu compounds are known to undergo coupling to yield R-R compounds, it is not known whether organo-metallic compounds of such types are formed as intermediates in the Ullman reaction. A nucleophilic attack by copper was proposed for the possible mechanism involving a metallic complex of transitory existence. This may be illustrated as follows:



In short, the organo-metallic intermediate mechanisms, whether

⁷P. E. Fanta, Chem. Rev., 38, 139 (1946).

⁸H. Gilman and J. M. Straley, Rec. Trav. Chim., 55, 821 (1936).

moderately stable or of transitory existence, seem to be a more probable course of the Ullman reaction than the free radical mechanism. From the lack of evidence that a nickel-metallic compound may exist in the form of Ar-Ni-X and from the observed formation of naphthalene, the free radical hypothesis seems to be indicated as the course of nickel reacting with halo-nitro-benzenes at high temperature.

3. The Reaction of Hydrogen-Rich Raney Nickel with halo-Nitrobenzenes

The reaction of H_2 -rich Raney nickel with halo-nitrobenzenes is rather complex. It may involve:

- a. The reduction due to hydrogen held by nickel
- b. The reduction due to hydrogen possibly formed by the reaction of nickel and alcohol which is held on the surface of nickel
- c. Nickel oxidized by the nitro group of halo-nitrobenzenes.

All these are exothermic and make the reactions difficult to control. Furthermore, since this is a heterogeneous reaction, a small change of reaction procedure might cause a great change of products. However, from the experiments 11-15 shown in Table IV, it seems true that the lower the reaction temperature, the greater the amounts of known reduction products one obtains.

The exothermic reaction took place vigorously at two stages. One occurred during the addition of the bromo-nitrobenzene, the reaction temperature increasing from room temperature to 80°C . The other occurred after the alcohol was removed, the reaction temperature rising from 100°C . to more than 200°C . within a few minutes. From these experiences, it was possible to fix each step of the reaction procedure under very carefully controlled conditions in order to get a general process for

the reaction. This enables one to make a comparison between various halo-nitrobenzenes. From the experiments 11-15, the most favorable reaction temperature is 110-120° for the formation of azoxy-benzenes and the most favorable molar ratio (nickel to reactant) is 2:1.

4. The Formation of Azoxy Compounds

The amount of hydrogen held by Raney nickel prepared at 80° C. is approximately 170 ml. per 4 g. nickel.⁹ This may be represented as Ni₅H. Hence, the 2 equivalent moles of nickel used in these experiments contain only 1/5 mol of hydrogen. This amount of hydrogen is not enough to reduce one mol of reactant to the amine, because one mol of reactant contains one nitro-group requiring 3 moles of hydrogen for the amine formation. Actually some amine was found in addition to the azoxy compound in the experiments. Thus the reduction must be due to other factors, perhaps to deoxygenation by nickel. Furthermore, deoxygenation by nickel to form azoxy compound is perhaps taking place before the reduction of hydrogen, otherwise, the amine would not be formed.

The reduction of halo-nitrobenzene by hydrogen with Raney nickel as catalyst has been studied by Winans,¹⁰ Baty,¹¹ and Anglade.¹² Some of their results may be listed as follows:

a. o- and p-chloro-nitrobenzene are quantitatively reduced to

⁹R. Mazingo, J. Am. Chem. Soc., 65, 1013 (1943).

¹⁰C. F. Winans, J. Am. Chem. Soc., 61, 3564 (1939).

¹¹M. Baty, Bull. Soc. Chim., 5, 1276 and 1600 (1938).

¹²M. Anglade, Bull. Soc. Chim., 6, 473 (1939).

the chloroanilines.

- b. The p-bromo-compound is not so smoothly reduced as chloro-compound, the yield being 83%.
- c. o-iodo-nitrobenzene gives only 23% iodoaniline.

Although their data are not comprehensive enough for any general rule to be deduced, the reducibility of the nitro-group seems to decrease from the chloro-nitrobenzenes to the iodo-nitrobenzene. In comparing the results of this present work, the reducibilities of the reactants generally follow this rule.

In order to suggest a possible explanation of this, the three azoxy compounds formed from the m-halo-nitrobenzenes may be taken as examples. Since the melting point of the three m-halo-nitrobenzenes and the melting point of the three mm'-di-halo-azoxybenzenes are not much different in each series, if the reactions are controlled to the same conditions, the different yields of reduced compounds would be due to the different effect of the halogens. The different effect may be interpreted by the electronic theory through the inductive effect of the halogens towards the nitro-group in the m-position. It might be expected that the more loosely the oxygen is attached to the nitrogen by the $N \rightarrow O$ bond, the more easily it may be removed by nickel. Since chlorine has a higher inductive effect than bromine which in turn has a higher inductive effect than iodine, the oxygen in $N \rightarrow O$ bond in iodo-nitrobenzene is the most difficult to be removed. Therefore, the best yield of azoxy compound might be expected in the case of m-chloro-nitrobenzene.

In the chloro- series, m- and p-nitro-halobenzenes gave roughly

the same results. Thus the reduction takes place as if the chloro-radical has no different influence. Or it may be explained that the net result of the resonance and inductive effect of the chloro radical to p-nitro-group is roughly equal to its inductive effect in the m-position.

In experiments 7, 8, and 9, although the formation of amines is reasonable, yet there was no o-halo-azoxy compound found. This might be due to steric hindrance. Since the deoxygenation plays a very important part in the formation of azoxy compound and the deoxygenation cannot be done without bi-molecular combination, steric hindrance might be expected to have some influence. The lack of o-haloazoxy compound formation might also be due to the electronic effect of the nitro-group. The nitro radical is a strong electron seeking group and its effect is especially noted in o-nitro-compounds. In such compounds both the inductive and resonating effects will pull electrons strongly from the radical in the o-position. Hence the electron density over N \rightarrow O bond is expected to be increased. Therefore, the nitro group in the o-position is more difficult to reduce.

CHAPTER V

SUMMARY

- A. In the Ullman reaction, it seems that nickel cannot replace copper. It is perhaps due to the fact that nickel and copper react with aromatic halides in different ways.
- B. The formation of naphthalene at a temperature which is lower than that of normal Ullman reaction may be explained by the free radical intermediate formation.
- C. At higher temperature, certain activated *o*-halo-nitrobenzenes form small amounts of the biphenyls. That those yields are much lower than that of Ullman reaction is perhaps due to the different mechanism involved. The mechanism of the Ullman reaction, although not clearly known, is preferably explained by a metallic complex intermediate while the reaction with nickel is perhaps due to free radical intermediates.
- D. When the *m*- and *p*-halo-nitrobenzenes, having no steric hindrance and ortho-effect, are used, a series of reduced products is obtained. The reducibilities of halo-nitrobenzenes are closely related to their activities and may be explained by the electronic theory.

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