STUDIES OF DIAZO, TRIAZO, AND PENTAZO COMPOUNDS.

by

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CHAPTER I

REDUCTION OF DIAZONIUM SALTS TO HYDROCARBONS WITH ALKALINE FORMALDEHYDE.

Introduction and History

The reduction of diazonium salts by alcohol was observed by Griess[1] who obtained benzene from phenyldiazonium salts and dinitrophenol from diazodinitrophenol. The production of the hydrocarbon or complete elimination of the diazonium group by the action of alcohol was, for many years, regarded as a general reaction, in spite of the observation of Wroblewski[2], who found that the diazonium salt of chlorotoluidine gave, not the chlorohydrocarbon, but the corresponding chlorophenetole. Four years later Hayduck[3] showed that when o-toluidinesulphonic acid was diazotized, and the resulting diazonium salt boiled with alcohol, phenetolsulphonic acid was obtained.

The experiments of E. and O. Fischer[4] demonstrated that when the diazonium compound of paraleucaniline was boiled with alcohol the three diazo-groups were eliminated with the formation of triphenylmethane.

However, examples of the formation of ethers in this reaction were becoming numerous, among which may be mentioned the cases of m-amino-

benzenedisulphonic acid[5], cumidinesulphonic acid[6], aminotetramethyl benzene, cumidine[7], and β-toluidinesulphonic acid[8], all of which yielded, when diazotized and treated with alcohol, the corresponding ethyl ethers.

Therefore, the reaction with alcohol may proceed in two ways, according to the equations:

$$RN_2X+C_2H_5OH \rightarrow RH+CH_3CHO+N_2+HX \quad (I)$$

$$RN_2X+C_2H_5OH \rightarrow ROC_2H_5+N_2+HX \quad (II)$$

where R denotes a hydrocarbon radical and X an acid radical. I is called the hydrogen reaction and II, the alkoxy reaction.

Remsen[9] and his students made a thorough investigation of the reaction and concluded that the second of the above equations represented the normal reaction and that the ether was the major product in most cases. The extent to which the hydrogen reaction or alkoxy reaction will occur between any diazonium salt and an alcohol is somewhat complicated and depends on many factors, such as the character of the radical (R), the nature of the alcohol, and the pressure at which the reaction is carried out.

The substitution of carboxyl, halogen, or

nitro groups in the radical (R) tends to induce the complete elimination of the diazo group and this influence is greatest when these radicals are in the ortho position to the diazo group, with less influence exhibited in the meta position, and least in the para position as illustrated by Cameron[10] in the case of the chlorophenyldiazonium nitrates when he found that the ortho- and meta- compounds yielded only chlorobenzene with ethyl alcohol, but the para- compound gave rise to the formation of a little p-chlorophenetole. In the case of 2, 4, 6-tribromophenyldiazonium sulfate, the yield of tribromobenzene[11] is 75-78% of the theoretical quantity.

The tendency toward the formation of hydrocarbons is increased as the molecular weight of the alcohol increases. Phenyl diazonium chloride and sulfate with methyl alcohol yield amiole as the sole product, no benzene being formed[12]. With ethyl alcohol the chief product is phenetole but a little benzene is also obtained. Phenyl diazonium chloride with normal and iso-propyl alcohols yields phenyl

propyl ethers but no trace of propaldehyde or acetone; amyl alcohol gives both phenyl amyl ether and valeraldehyde or its condensation products; and benzyl alcohol gives benzaldehyde with only a little phenyl benzyl ether[13]. Glycerol behaves like propyl alcohol, giving the monophenyl ether, while mannitol and benzoin are not attacked[14]. Phenol behaves similarly, thus, when a solution of phenyl diazonium sulphate is warmed with phenol, diphenyl ether[15] is obtained. In alkaline solution, however, phenol gives hydroxyazobenzene.

If such substances as sodium methoxide[16], sodium hydroxide[17], or zinc dust[17] are added to the alcohol, the alkoxy reaction is almost entirely inhibited and the reaction proceeds mainly with the elimination of the diazonium group. Thus in the case of p-tolyl diazonium nitrate and sulfate the ordinary treatment with methyl alcohol results in the production of a good yield of the methoxy product but with the addition of any of the above mentioned substances, no alkoxy compound is

obtained but the product consists mainly of toluene[17].

The reduction of diazonium salts to the corresponding hydrocarbon may, of course, be effected by reducing agents instead of alcohol. Baeyer and Pfitzinger[18] reduced the diazonium salt to the hydrazine with stannous chloride and removed the $NHNH_2$ group by oxidation with boiling copper sulfate solution. By treating phenyldiazonium formate with stannous formate solution, benzene[19,20], together with a little biphenyl is produced. Reduction may also be effected by adding sodium stannite[21] to a solution of the diazonium salt in sodium hydroxide, by the use of hypophosphorous acid[22], an alkaline solution of sodium hyposulphite[23], and also when diazides of sulphonic acids are boiled with copper powder and formic acid[24].

Brewster and Poje[25] recommended, inasmuch as the hydrogen reaction involved a reduction of the carbon atom to which the diazonium salt is joined, that a reducing agent stronger than alcohol should be used and they gave their results using an alkaline solution of

formaldehyde as the reducing agent. They reported a variety of compounds which had been deaminated in yields of 50-80% as given in Table I.

The first chapter of this thesis is the result of a series of investigations to extend the method of Brewster and Poje and determine the limitations of their reagent for the reduction of diazonium salts. The experimental method is described by reproducing here their typical experiment.

"Deamination of p-Toluidine to Toluene

A solution of 0.5 mole (53.5 g.) of p-toluidine in 150 cc. of concentrated hydrochloric acid and 400 cc. of water was chilled by the addition of 400 g. of ice and diazotized in the usual manner with 36 g. of sodium nitrate. A solution of 100 g. of commercial sodium hydroxide in 600 cc. of water was then prepared and placed with 500 g. of shaved ice into a 5-liter flask which was fitted with a mechanical stirrer. The stirrer was started and 75 cc. of formalin (37% formaldehyde) added. The solution

of p-tolydiazonium chloride was then poured in a slow stream into the rapidly stirred alkaline solution of formaldehyde. The rapid escape of nitrogen caused considerable frothing. After all of the diazonium chloride solution had been added the stirring was continued for two or three minutes, after which the stirrer was removed, the mouth of the flask covered with a watch glass and the reaction mixture allowed to stand with occasional shaking for thirty to forty minutes. The toluene in the upper oily layer was then removed by distillation in steam, separated from the water, dried and distilled."

This method was finally adopted for this work after many variations in the above procedure had been tried and the affect of these variations on the yield of hydrocarbon had been determined. Their procedure will be referred to as the "standard procedure."

Since all the compounds obtained by deamination in this investigation had been synthesized previously and their

Table I[X]

Yield of Deaminated Products from Diazonium Salts

Amino compound	Product and % yield	
Aniline	Benzene	60
o-Toluidine	Toluene	80
p-Toluidine	Toluene	80
o-Anisidine	Anisole	75
p-Anisidine	Anisole	72
o-Phenetidine	Phenetole	75
p-Phenetidine	Phenetole	65
2,4-Dimethylaminobenzene	m-Xylene	80
p-Chloroaniline	Chlorobenzene	50
o-Chloroaniline	Chlorobenzene	55
4-Amino diphenyl ether	Diphenyl ether	60
2-Amino diphenyl ether	Diphenyl ether	60
2-Amino-4'-methyl diphenyl ether	4-Methyl diphenyl ether	50
4-Amino-4'methyl diphenyl ether	4-Methyl diphenyl ether	50
2,5-Dichloroaniline	p-Dichlorobenzene	10
Anthranilic acid	Benzoic acid	25
o-Nitroaniline	Nitrobenzene	20
m-Nitroaniline	Nitrobenzene	10
p-Nitroaniline	Nitrobenzene	10

X From J. A.C.S. 61 2419 (1939)

physical constants recorded, no analyses were made in this part of this research.

In all cases, the yields reported in this paper for liquid products were for the redistilled product collected over a range of five degrees near the boiling point. For solid products, the yields are for products whichnhave been recrystallized once.

EXPERIMENTAL PROCEDURE:

Deamination of p-chloroaniline

To study the affects on yield of hydrocarbon the variation of quantities of chemicals used, and their order of mixing, on the method of deamination used by Brewster and Poje, p-chloroaniline was selected as standard since they recorded a yield of 50% deamination from this product and it was also readily obtainable. It was an amine which, according to their results, should readily show an increase or decrease in yield of the hydrocarbon reaction with changes in experimental procedure.

a. Time Necessary for Complete Reaction

The method of Brewster and Poje was repeated several times using 0.5 mole p-chloroaniline and the yields of chlorobenzene, boiling from 129-133°, were 27 to 29 grams (48-52% of the theoretical). The reaction was complete thirty-five

minutes after all the formalin had been added and allowing the reaction mixture to stand for longer periods of time did not increase the yield of chlorobenzene.

b. Effect of Alkali Concentration

The procedure was then repeated varying the concentration of alkali used. Runs were made using 70, 150, and 200 grams of sodium hydroxide. The yields of chlorobenzene, b.p. 129-133°, were as follows:

Grams of NaOH added	Grams of Chlorobenzene
70	20
100	28
150	28
200	28

The solution containing 70 grams of sodium hydroxide was nearly neutral to litmus after all the diazonium salt had been added. Therefore one hundred grams of sodium hydroxide seems sufficient for the reaction.

c. Effect of Formalin Concentration

The next test was for the purpose of determining the optimum concentration of

formalin for the reaction. These results are shown below:

cc. of Formalin	Yield of Chlorobenzene
40	20.0 grams (36%)
80	28.0 (50%)
160	28.0 (51%)

d. Effect of Temperature of Reduction

To determine the effect of the temperature of reduction on the yield of chlorobenzene, runs were made maintaining the alkali and formalin mixture at 0°, 25°, and 50° and these results are tabulated below.

Temperature of Reduction	Yield of Chlorobenzene
$0^{\circ}C$	27-29 gms (48-52%)
$25^{\circ}C$	29-30 gms (52-53%)
$50^{\circ}C$	22-24 gms (40-43%)

Therefore the best yields are obtained by maintaining the temperature so that it does not exceed 25°.

e. Variations in the Order of Adding Ingredients

The yields obtained by variations in the order of adding the ingredients were then

determined. Addition of the formaldehyde to the diazonium salt solution before adding the salt solution to the alkali gave yields identical to those obtained with the standard procedure. Addition of the alkali solution to a mixture of the diazonium salt and formalin greatly reduced the yield giving yields of 15-16 grams (27-29%) of chlorobenzene. By adding the diazonium salt solution to the alkali followed by addition of the formalin to this mixture, gave yields comparable to the standard procedure (48-52%).

f. Variation in Acid Used

Substituting 350 grams of 40% hydrobromic acid for 150 cc. hydrochloric acid in the standard procedure gave identical yields of chlorobenzene to those of the standard procedure while equivalent quantities of nitric acid gave only slightly lower yields.

The effect of acetic acid on the reaction was also determined. However the tendency towards the formation of diazo-amino compounds during diazotization increases in using an organic acid, and Cain in "The Chemistry of the

Diazo-Compounds" states that if two and a half equivalents of acetic acid are substituted for the same equivalent quantity of hydrochloric acid, in the case of aniline only about twenty percent of the aniline is converted into the diazonium salt; the diazotization is complete only by the use of eleven equivalents of acetic acid. Therefore for this experiment, 330 cc. of glacial acetic acid were used. Even with this quantity of acetic acid some diazoamino compound was formed in the diazonium salt solution as evidenced by the slight yellow precipitate formed. The quantity of sodium hydroxide was increased to 260 grams. The yield of chlorobenzene by this method was only 7-10 gms (13-18%).

Replacement of the p-chlorodiazonium chloride by the sulfate reduced the yield of hydrocarbon as Brewster and Poje noted in the case of the p-tolydiazonium salt. The use of the sulfate salt reduced the yield from 48-52 % to 35-40%. The addition of excess sulfate ion by the addition of 1 gram mole of sodium sulfate further reduced the yield of chloro-

benzene to 30-35% which is similar to the results of Brewster and Poje.

g. Influence of Other Substances

As previously mentioned, addition of zinc dust to the alcohol increased the yields of hydrocarbon when alcohol was used as reducing agent. Addition of zinc dust and sodium stannite to the alkaline formaldehyde did not increase the yield of hydrocarbon as was also reported by Brewster and Poje.

Using the "standard procedure" various amines were diazotized and reduced and the results are given in Table II.

TABLE II

Yield of Deaminated Products from Diazonium Salts

Amino Compound	Product	% Yield Alkaline Formaldehyde	% Yield in Literature	Literature Modification
Amino p-Xylene (p-Xylidine)	p-Xylene	83		
m-Toluidine	Toluene	80		
o-Ethylaniline	Ethylbenzene	65		
p-Ethylaniline	Ethylbenzene	60		
p-Amino-Diethylaniline	Diethylaniline	60		
4-Chloro-2-Aminoanisole	4-Chloroanisole	52		
p-Bromoaniline	Bromobenzene	50	68	A[10]
m-Chloroaniline	Chlorobenzene	50	75.6,92.7	B[10]
p-Aminobiphenyl	Biphenyl	46		
o-Aminobiphenyl	Biphenyl	43		
Cumidine	Isopropylbenzene	40		
p-Iodoaniline	Iodobenzene	20		

A.-- Ethyl Alcohol

B.-- 75.6% yield from m-Chlorophenyldiazonium nitrate + Ethyl alcohol.

92.7% yield from m-Chlorophenyldiazonium sulfate + Ethyl alcohol.

TABLE II ((Cont'd)

2,5-Dimethoxy aniline	p-Dimethoxyaniline	20		
β-Napthylamine	Napthalene	10		
2,4-Dimethyl-6-bromoaniline	3,5 Dimethylbromobenzene	9	N.Y.R.	C[26]
α-Napthylamine	Napthalene	7	N.Y.R.	D[22]
Benzidine	Biphenyl	5	60,80-85	D[22],A[
p-Aminobenzoic acid	Benzoic acid	20		
p-Amino acetanilide	Acetanilide	15		
p-Amino ethylbenzoate	Ethylbenzoate	15		
p-Amino acetophenone	Acetophenone	2		
Arsanilic Acid	Phenylarsinic acid	2.5	50	E[27]
p-Amino benzophenone	Benzophenone	1		
2,4,6-Tribromoaniline	s-Tribromobaniline	5	75	A[11]
2,6-Dibromo-4 methyl aniline	3,5-Dibromotoluene	5	N.Y.R.	A[28,21
3,5-Dibromo-4-aminoanisole	3,5-Dibromoanisole	5		
3,5-Dibromo-2-aminophenetole	3,5-Dibromophenetole	5		
2,4-Dibromo-6-methylaniline	3,5-Dibromoluene	7	N.Y.R.	C[29]
3,5-Dibromo-2-aminoanisole	3,5-Dibromoanisole	8		

N.Y.R.- no yield recorded.

C------ Steam distilled HCl salt of amine.

D------ Calcium hypophosphite and sulfuric acid.

E------ Sodium hypophosphite and hydrochloric acid.

Discussion:

In the experimental procedure, the usual precautions were observed. The diazonium salt solution — alkaline formaldehyde mixture was usually allowed to set for twelve hours before steam distillation to insure complete reaction. Such precaustions as diazotizing the α- and β- napthylamines, and benzidine at 10^0 rather than at 0^0 - 2^0, as is done for most amines, was observed. For substances like α- napthylamine, the sodium nitrite was added all at once, taking care to have sufficient ice in the solution to prevent much temperature rise, which prevents formation of diazoamino compounds .

In most cases there was a smooth evolution of the nitrogen as the diazonium salt solution was added to the alkaline formaldehyde. However, in some cases, notably α- and β- napthylamines, p-aminoacetanilide, o- and p- aminobiphenyl, p-aminoacetophenone, p-phenylenediamine, and benzidine, the frothing was excessive. In the case of p-phenylenediamine the frothing was so excessive that the reaction could not be

carried out. As an example, a 0.25 mole quantity of the diazonium salt solution of p-phenylenediamine produced over ten liters of foam. In some cases a drop or two of isoamyl alcohol would remove the foam but the phenylenediamines could not be controlled by such an addition.

The loss of material in the reaction was accounted for by the formation of tarry substances which were chiefly polymers of the aromatic radical and remained in the flask after steam distillation. In the reduction of phenyl diazonium chloride a considerable quantity of biphenyl was isolated and identified; p-iodo phenyldiazonium chloride gave a considerable quantity of 4,4'-diiodobiphenyl and benzidine gave some 4,4'-dihydroxybiphenyl. In most cases the black tarry matter left in the distillation flask gave no recognizable product on extraction with organic solvents.

In the case of p-amino acetophenone, addition of small quantities of the diazonium salt to the alkaline formaldehyde gave a deep red coloration and with further addition, the solution became a deep purple. There was

only slight evolution of gas as the diazonium salt was added but on standing the solution foamed all over the laboratory desk. By stirring the mixture for two hours after all the diazonium salt was added, this excessive frothing was prevented but the yield of acetophenone was practically negligible (about 2 cc. from 0.25 mole of p-amino-acetophenone). No other recognizable product was isolated.

On the addition of the diazonium salt of arsanilic acid to the alkaline formaldehyde a clear dark reddish brown solution was formed. The phenyl arsinic acid was obtained by a modification of the method of Bertheim[27] in isolating this acid from the reduction of diazophenylarsinic acid with sodium acid phosphate and hydrochloric acid. The phenyl arsinic acid was precipitated with zinc acetate after acidifying the solution with acetic acid. This zinc salt was then digested with sodium carbonate solution, filtered from zinc carbonate, the filtrate acidified with sulphuric acid, and the phenylarsinic acid

collected and weighed. This method gave a much better yield of phenyl arsinic acid than was obtained by merely acidifying the reduced mixture and collecting the precipitated acid.

The benzoic acid obtained by the reduction of the diazonium salt of p-amino-benzoic acid was isolated by acidifying the reduced solution and extracting the precipitate with hot water. A similar procedure was used to isolate the acetanilide obtained by the reduction of the diazonium salt of p-amino-acetanilide except that the original solution did not require neutralization.

In cases where the deaminated product was an ester such as in the reduction of the diazonium salt of methyl p-aminobenzoate, the reduced solution was neutralized before steam distillation to prevent hydrolysis of the ester.

The reduction of the diazonium salts of p-aminophenylbenzyl ether and p-amino-phenyl-allyl ether gave no recognizable yields of phenyl benzyl ether and phenyl allyl ether respectively.

The various bromo-derivatives of the toluidines, phenetidines, and anisidines gave poor yields of the brominated hydrocarbons. In these cases, large quantities of black tarry matter were obtained and the products were obtained by solvent extraction of these tars.

From the data of Tables I and II, it is seen that diazonium salts containing electron donor groups substituted in the benzene nucleus generally give good yields of hydrocarbon on reduction with alkaline formaldehyde while diazonium salts containing electron acceptor groups give poor yields of hydrocarbons. These results may partially be explained on the basis that electron acceptor groups displace electrons from the nitrogen atom toward the ring thereby strengthening the carbon-nitrogen bond causing the reduction to proceed with the formation of azo, hydrazo, and hydrazine type compounds which rearrange and condense with the formation of unidentifiable products as found in these

cases.

Diazonium salts containing electron donor groups in the benzene nucleus may displace electrons from the benzene ring thereby weakening the carbon-nitrogen bond and facilitating the evolution of nitrogen with a subsequent increase in hydrocarbon yield. This would seem to be substantiated by the fact that the reduction of phenyl diazonium salts gives a yield of hydrocarbon intermediate between that of diazonium salts containing electron donor substituted groups and those containing electron acceptor groups.

CHAPTER II

TRIAZO DERIVATIVES OF MORPHOLINE

Introduction

During the course of this investigation, diazonium salts were added to various primary and secondary amines and it was found that compounds were formed by the reaction of diazonium salts with morpholine. These compounds, derived by coupling the diazonium salts with morpholine, were not listed in the literature so an investigation of their properties was made.

Gerland[30] in 1853 prepared hydroxybenzoic acid from aminobenzoic acid and observed the formation of a red, intermediate product, the quantity of which was found to increase by working with cold solutions. Gerland was unable to decide as to the constitution of this substance owing to the wide variation in the analytical determinations. The further investigation of this compound was suggested to Griess by Kolbe[31] with the result that diazoaminobenzoic acid was isolated. Griess then extended this work so carefully that he discovered a new class of compounds, to which the name "diazo" was given. Historically,

therefore, the diazoamino compounds were known before the diazonium salts had been isolated.

In most laboratory preparations, diazoamino compounds are formed by the condensation of the diazonium salt with primary or secondary amines in the presence of sodium acetate or by the addition of an alkali nitrite to a solution of an amine containing no free mineral acid. They may also be prepared by the addition of a neutralized diazonium salt solution to two moles of the amine. The acid eliminated by the coupling reaction is neutralized by the excess amine.

The primary monoamines of the benzene series all yield diazoamines, those containing the groups Cl, NO_2, CN, etc., most readily, but the alkylated monoamines of this series show a tendency to form azo-compounds; for example, methylaniline, when treated with diazobenzene-sulphonic acid, yields a mixture of the diazoamino-compound,

$$HO_3SC_6H_4N_2N(CH_3)C_6H_5$$

and the isomeric aminoazo-compound,

$$HO_3SC_6H_4N_2C_6H_4NHCH_3$$ [32,33]

Since morpholine is a cyclic, secondary, aliphatic amine, only triazo compounds would be formed by reacting a diazonium salt with the amine. In most cases, nearly quantitative yields of diazo/amino compounds were obtained and the yields are reported for products which have been recrystallized once.

The melting points of the compounds were determined using a sulfuric acid bath and a thermometer which had been checked with melting points of well known, chemically-pure chemicals over most of the range used in this investigation. The melting points listed are uncorrected temperature readings for substances which have been recrystallized several times from the organic solvent listed in each preparation.

Molar weight determinations were made by determining the freezing point depression of a weighed quantity of chemically pure, thiophene free benzene by a weighed quantity of the triazo compound. In some cases, the triazo-compound was not sufficiently soluble in benzene to allow a molar weight determination in this solvent. The cryoscopic formula,

$$M = \frac{100\ Cw}{dW}$$

was selected from Cohen[34]. In this formula, w is the weight of substance and W the weight of solvent, d the freezing point depression, and C the coefficient for the solvent determined for the standard conditions (i.e. for the weight of substance which produces 1^{0} depression in 100 grams of solvent) and M is the molecular weight. The value of C, using benzene as solvent, is 50. This value of C was checked by determining the freezing point depression of benzene by napthalene.

Nitrogen analyses were made by the method of Dumas. The percentage of nitrogen was calculated as follows:-

v was the observed volume of nitrogen
B was the height of the barometer in mms.
t was the temperature of the measured gas
f was the vapor tension of the potash solution, which may be taken without serious error to be equal to that of water.

As the weight of 1cc. of nitrogen at 0^{0} and 760 mms. is 0.00126 grams, the percentage weight of

nitrogen in the substance w will be given by the expression,

$$\frac{v \times 273 \times (B-f)}{(273 + t)\ 760} \times \frac{.00126 \times 100}{w}$$

All weighings of reactants and products were made on a triple-beam platform balance sensitive to 0.1 gram. Samples for analytical determinations were weighed on an analytical balance.

The nomenclature adopted for use in naming the compounds prepared in this part of the investigation was similar to that of Jacobs and Heidelberger[35] who worked with diazoamino-derivatives of arsanilic acid.

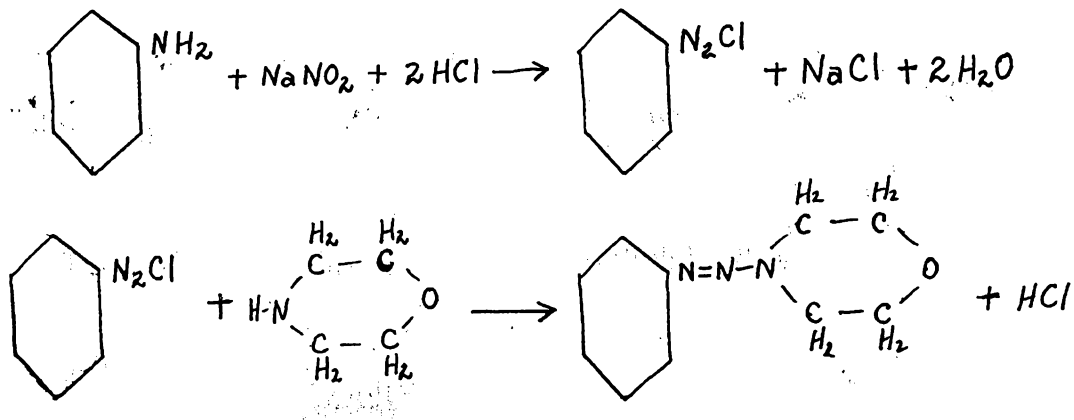
EXPERIMENTAL

In this investigation, the usual procedure was followed in the diazotization process. Water and the amine were mixed and 2½ equivalents of hydrochloric acid was slowly added to the well stirred mixture. In most cases the amine salt would dissolve in the quantity of water present. This solution was then cooled to 0°C and a slight excess of an equivalent of sodium nitrite solution was slowly added so that the temperature did not exceed 2°C. The solution was then allowed to stand for fifteen minutes before the excess acid was neutralized. The solution was then slowly added, with stirring, to the morpholine solution and kept at 0°C for at least fifteen minutes before filtering off the solid or separating the oil formed by the reaction.

The procedure will be described in detail in the preparation of the first two derivatives. The other derivatives were made in an analagous manner unless otherwise mentioned.

Preparation of Diazobenzene-morpholine

Reaction.--



Procedure.--In a 500 cc. flask fitted with a mechanical stirrer and a dropping funnel were placed 50 cc. of water, 9.3 grams (0.1 gram mole) of aniline, and 35 grams (30 cc., 0.346 gram moles) of concentrated hydrochloric acid (sp. gr. 1.18). After this solution had been cooled to 0°C, the stirrer was started, and a solution of 7.2 grams (0.104 gram moles) of sodium nitrite in 30 cc. of water was added from the separatory funnel at such a rate that the temperature of the solution did not exceed 2° C. This solution was allowed to stand for ten minutes after all the sodium nitrite solution had been added. The excess acid was neutralized with 1 N sodium hydroxide solution.

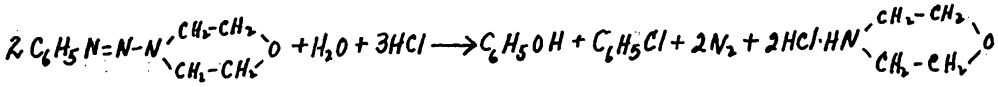
The neutralized diazonium salt solution was added to a well stirred, cold solution of 75 cc. of water and 17 cc. (0.2 gram mole) of morpholine. The diazobenzene-morpholine formed at once as a yellow oil which floated on the surface of the solutions. On standing, the yellow oil solidified on the surface of the ice cold mixture. The yellow diazobenzene-morpholine was filtered on a Buchner funnel, washed with cold water, and sucked as dry as possible. The solid melted to a brown oil at room temperature. The yellow solid was recrystallized from ether and melted at 28°C. The yield of recrystallized diazobenzene-morpholine was 15 grams (80% of the theoretical amount).

The diazobenzene-morpholine was distilled under reduced pressure and boiled at 158-160° C under 15 mm. pressure. The diazobenzene-morpholine underwent slight decomposition on distillation at reduced pressure, giving a product which was a viscous, light brown oil, which melted at 15°C.

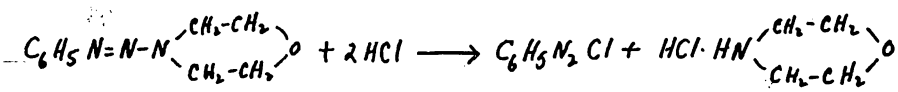
The molar weight of the purified diazo-

benzene-morpholine was determined by the cryoscopic method and 0.5047 grams of diazobenzene-morpholine gave a freezing point depression of 0.78° in 16.76 grams of benzene. These data correspond to a molar weight of 193. The calculated molar weight is 190.

The diazobenzene-morpholine was insoluble and stable in boiling water and could be steam distilled from a neutral or slightly alkaline solution. The steam distillation proceeded slowly. In boiling, dilute hydrochloric acid, the compound decomposed with the formation of morpholine hydrochloride, phenol, and chlorobenzene as represented by the equation,

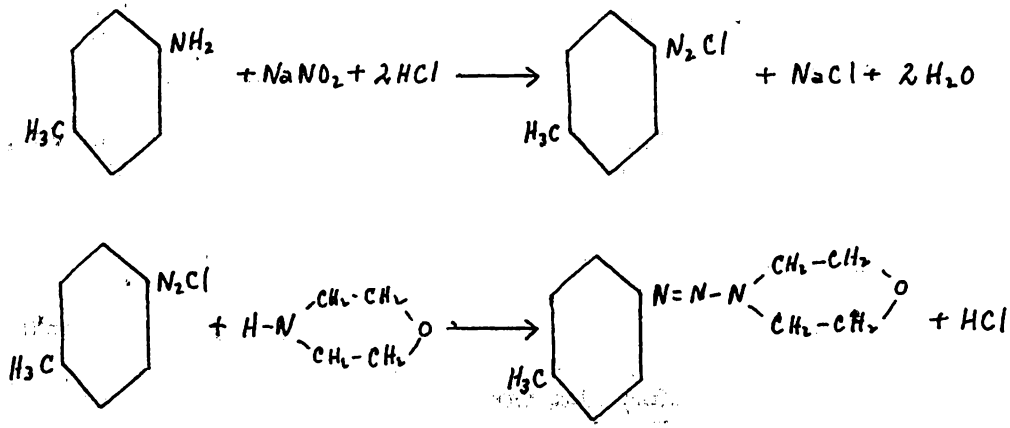


In cold, concentrated hydrochloric acid, the diazobenzene-morpholine decomposes to phenyl diazonium chloride and morpholine hydrochloride as represented by the equation,



Preparation of Diazobenzene-(4-methyl)-morpholine

Reaction.--



Procedure.--In a 500 cc. flask provided with thermometer, stirrer, and a dropping funnel were placed 50 cc. of water and 30 cc. of concentrated hydrochloric acid. To this solution, 10.7 grams (0.1 gram mole) of p-toluidine was added. The resulting solution was cooled to 0° C and the stirrer started. A solution containing 7.2 grams (0.104 gram moles) of sodium nitrite was added to the solution from the separatory funnel at such a rate that the temperature of the solution did not exceed 2° C. After allowing fifteen minutes for the completion of the reaction, the excess acid was neutralized with 1 N sodium hydroxide solution.

The neutralized diazonium salt solution

was added to a well stirred, cold solution containing 50 cc. of water and 17 cc. (0.2 gram mole) of morpholine. The cream colored, crystalline diazobenzene-(4-methyl)-morpholine was collected with suction and dried in air. After drying, it weighed 17.5-18.5 grams (85-90% of the theoretical amount) and melted at 46° C. After several recrystallizations from Skelly solvent (petroleum fraction of boiling point 90-100°C--largely heptane), the light cream colored, crystalline diazobenzene-(4-methyl)-morpholine melted at 48.5°C.

Using 16.4 grams of benzene, 0.1284 gram of product gave a freezing point depression of 0.195° in this quantity of solvent. This corresponds to a molar weight of 201 compared to the calculated molar weight of 205.

Nitrogen analysis data, obtained by the Dumas combustion method, were as follows:

Weight of sample = 0.2006 gram

cc. of nitrogen = 37.9 cc.

Room temperature = 30°C

Vapor tension of water at 30°C = 31.5 mm. of Hg[36]

Barometric pressure = 740 mm. Hg.

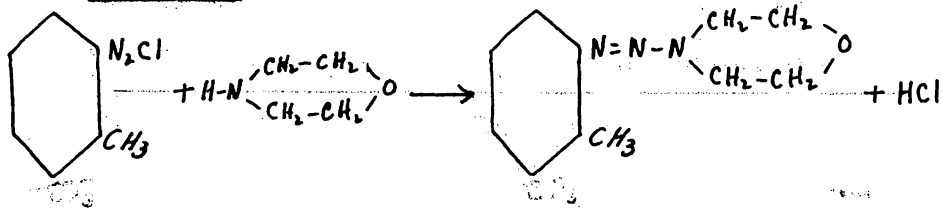
These data give a percentage of nitrogen equal to 20.0% . The calculate percentage of nitrogen in diazobenzene-(4-methyl)-morpholine is 20.5%.

Approximately the same yields of diazobenzene-(4-methyl)-morpholine were obtained by adding a diazonium salt solution to an equivalent quantity of morpholine in the presence of a large excess of sodium acetate. Comparable yields were also obtained by the addition of unneutralized diazonium salt solution to a large excess of morpholine. In this case, the excess morpholine served as a neutralizing agent toward the excess acid.

The diazobenzene-(4-methyl)-morpholine was insoluble and stable in boiling water and could be steam distilled from neutral or slightly alkaline solution. Concentrated hydrochloric acid dissolves the compound with evolution of of nitrogen. Warm, dilute hydrochloric acid decomposed the compound with vigorous evolution of gas forming a dark brown oil. This oil was found to contain p-toluidine, p-cresol, p-chlorotoluene, and morpholine.

Preparation of Diazobenzene-(2-methyl)-morpholine

Reaction.--



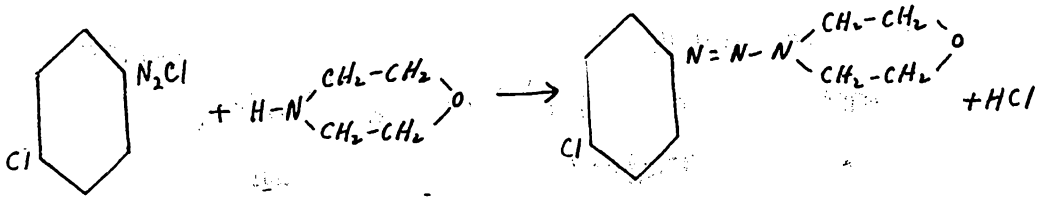
Procedure.--A solution of 10.7 grams (0.1 gram mole) of freshly distilled o-toluidine, 30 cc. of hydrochloric acid, and 50 cc. of water was cooled to 0°C and diazotized in the usual manner with sodium nitrite solution. After standing for ten minutes, the excess acid was neutralized with normal sodium hydroxide solution.

The neutralized diazonium salt solution was added to a cold solution of 17 cc. of morpholine and 50 cc. of water. The diazobenzene-(2-methyl)-morpholine settled to the surface of the solution in the form of dark red crystals. The solution was extracted with ether and dried over calcium chloride. The ether was distilled off and the residue chilled. The dark red precipitate was recrystallized from ether and melted at 18°C. The yield of diazobenzene-(2-methyl)-morpholine was 15 grams

(73% of the theoretical amount).

Preparation of Diazobenzene-(4-chloro)-morpholine

Reaction.--



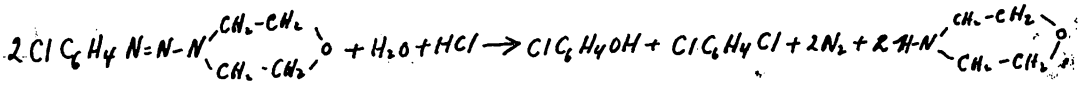
Procedure.--The diazobenzene-(4-chloro)-morpholine was prepared in the same manner as the previously listed derivatives. As the diazonium salt solution was added to the morpholine solution, the solution became milky and soon a cream colored precipitate settled to the surface. One tenth gram mole of p-chloro-aniline gave 20.5 grams of diazobenzene-(4-chloro)-morpholine (91% of the theoretical yield) which melted at 53°C. Recrystallization from ethyl alcohol gave cream colored, microscopic crystals melting at 54.5°C.

In the molar weight determination, 0.1000 gram of the purified product dissolved in 13.60 grams of benzene lowered the benzene freezing point by 0.17° which corresponds to a molecular weight of 216. The calculated molar weight is 225.

For analysis, a 0.2060 gram sample of the product was mixed thoroughly with 15 grams of sodium peroxide, 1 gram of potassium nitrate, and 0.5 gram of cane sugar in a Parr bomb. The bomb was clamped shut and the contents fused by heating in a Bunsen burner. The contents of the cooled bomb were dissolved in hot water. The solution was boiled to remove the excess hydrogen peroxide and 50 cc. of a saturated solution of hydrazine sulfate added. After the solution was acidified with nitric acid, it was filtered to remove carbon and other foreign matter. The halide was then precipitated with a slight excess of silver nitrate solution. The solution was heated to coagulate the precipitated silver chloride, cooled, and the precipitate was filtered into a prepared Gooch crucible, and dried at 110-115° C for one hour. The silver chloride weighed .1333 gram which corresponds to a percentage of chlorine in the original sample equal to 16.0%. The calculated percentage of chlorine is equal to 15.8%.

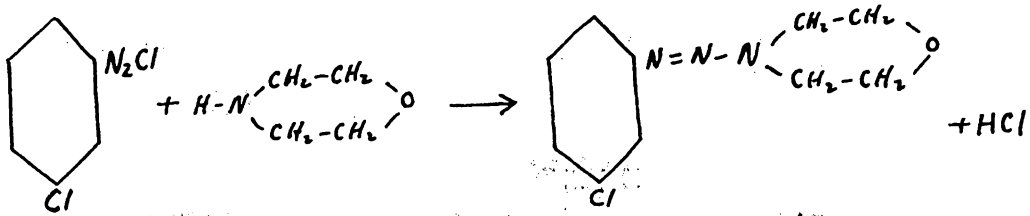
The diazobenzene-(4-chloro)-morpholine was

stable in boiling water and steam distilled very slowly. It evolved nitrogen in warm 10% hydrochloric acid with the formation of p-dichlorobenzene, p-chlorophenol, and morphopline according to the equation,



Preparation of Diazobenzene-(3-chloro)-morpholine

Reaction.--



Procedure.--The yield of diazobenzene-(3-chloro)-morpholine from 12.8 grams (0.1 gram mole) of m-chloroaniline by the above reaction was 15.4 grams (75% of the theoretical amount). The product separated as a yellow oil which solidified to a tan crystalline solid if the solution was maintained at 0° C. This tan solid melted to a light yellow oil at the laboratory temperature. The solid, recrystallized from ether, melted at 24-25° C.

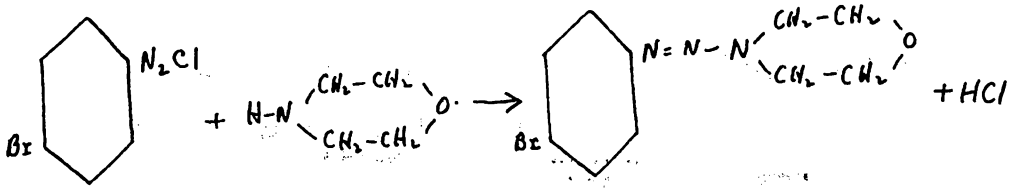
The crude diazobenzene-(3-chloro)-morpholine was dissolved in benzene and dried over calcium chloride. After filtering, the benzene was removed by distillation on a steam bath, and the residue was fractionally distilled under reduced pressure. The diazobenzene-(3-chloro)-morpholine distilled at 130-135° C/14 mm. The yield was 16.8 grams (75% of the theoretical amount).

The compound was analyzed by the Parr bomb method described previously. A 0.2006 gram sample gave 0.1290 gram of silver chloride which corresponds to a percentage of chlorine in the original sample equal to 15.9%. The calculated percentage of chlorine in diazobenzene-(3-chloro)-morpholine is 15.8%.

Diazobenzene-(3-chloro)-morpholine was stable in boiling water but was decomposed by boiling, 10% hydrochloric acid with the formation of m-dichlorobenzene, m-chlorophenol, and morpholine.

Preparation of Diazobenzene-(4-bromo)-morpholine

Reaction.--



Procedure.--The diazotization of 17.2 grams (0.1 gram mole) of p-bromoanilinenand the coupling of the diazotized solution with morpholine formed a white, viscous solution. A white precipitate settled to the surface of the solution. After the mixture had been stirred for fifteen minutes, the precipitated diazobenzene-(4-bromo)-morpholine was filtered with suction, washed with water, and pressed thoroughly on a Buchner funnel. The yield was 21.7 grams (80.5% of the theoretical amount) of product which melted at 86-88° C. Recrystallization of the crude product from ethyl alcohol gave white, microscopic crystals melting at 88.5° C. These crystals darkened and assumed a light brown color on exposure to light for a few days.

Combustion analysis for the determination of nitrogen gave the following data:

Weight of sample = 0.2010 gram

cc. of nitrogen = 30.2 cc.

Room temperature= 32° C

Vapor tension of H_2O at 32°C = 35.3 Hg[36]

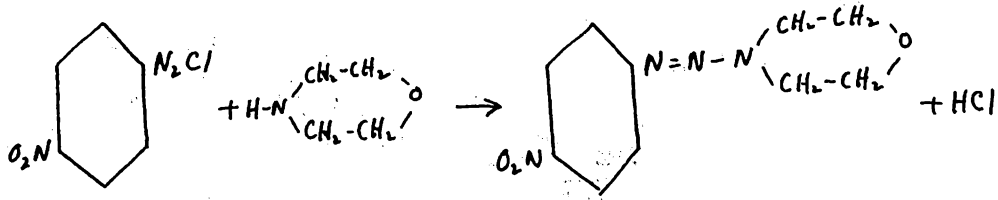
Barometric pressure = 736 mm. Hg

These data give the percentage of nitrogen in the sample as 15.6%, which is also the calculated percentage of nitrogen in the compound.

This compound, like the others in this series, is stable in boiling water but decomposes in acid solutions with the formation of p-bromochlorobenzene, p-bromophenol, and morpholine.

Preparation of Diazobenzene-(4-nitro)-morpholine

Reaction.--



Procedure.--This compound was prepared in an analagous manner to the others in this series with the exception that the amine was diazotized at 10° C to avoid the formation of the diazoamino-compound. In this procedure, it was necessary to add a larger volume of water to the morpholine

solution than was added in other preparations to prevent complete solidification of the solution before all of the diazonium salt solution had been added to the morpholine solution. The product was isolated as a canary yellow, crystalline precipitate. The yield of diazobenzene-(4-nitro)-morpholine from 0.1 mole of p-nitroaniline was 20.3 grams (90% of the theoretical amount). It was recrystallized from ethyl alcohol forming long, yellow-orange needles which melted at 133.5° C.

The following data were obtained by Dumas combustion analysis:

Weight of sample = 0.2038 gram

cc. of nitrogen = 46.7 cc.

Room temperature = 35° C

Vapor tension of water at 35° C = 41.8 mm. Hg[36]

Barometric pressure = 739 mm. Hg

Observed percentage of nitrogen = 23.5%

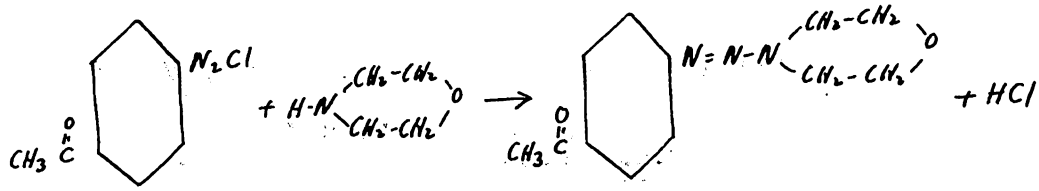
Calculated percentage of nitrogen = 23.7%

The diazobenzene-(4-nitro)-morpholine appeared to dissolve slightly in boiling water with the formation of a yellow colored solution.

There was no evolution of gas in boiling water and the compound would not steam distill. In hot, 10% hydrochloric acid solution the compound decomposed with the evolution of gas forming p-nitrophenol, p-chloronitrobenzene, and morpholine.

Preparation of Diazobenzene-(4-acetyl)-morpholine.

Reaction.--



Procedure.--In carrying out the above reaction, 13.5 grams (0.1 gram mole) of p-aminoacetophenone was diazotized in the usual manner and the excess acid neutralized. On the addition of small quantities of the diazonium salt solution to the morpholine solution, a purple colored solution was formed. As more of the diazonium salt solution was added, the solution changed from deep purple to yellow in color and soon assumed a permanent orange-yellow color. The precipitate formed in the reaction settled out very slowly. The light tan colored precipitate was collected

on a Buchner funnel and dried in air. The yield of diazobenzene-(4-acetyl)-morpholine was 18 grams (87.5% of the theoretical amount) and melted at 85°C. The product was recrystallized from Skelly solvent and melted at 92° C. The product crystals were very fine and had the appearance of a fine powder. The product was stable in boiling water but was decomposed by acids.

Combustion analysis for nitrogen gave the following data:

Weight of sample = 0.2034 gram

cc. of nitrogen = 35.9 cc.

Room temperature = 36° C

Vapor tension of H_2O at 36°C = 44.6 mm. Hg.[36]

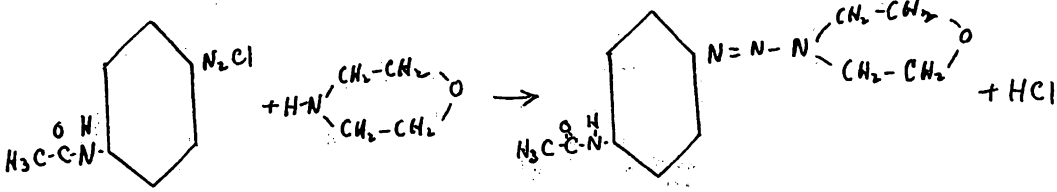
Barometric pressure = 731.7 mm. Hg.

Observed % of nitrogen = 17.8%

Calculated % of nitrogen = 18.0%

Preparation of diazobenzene-(4-acetamino)-morpholine

Reaction.--



Procedure.--The diazonium salt solution prepared from 15.0 grams (0.1 gram mole) of p-aminoacetanilide was purple in color and contained a slight precipitate so it was filtered before the excess acid was neutralized. The neutralized diazonium salt solution was then added to the morpholine solution with the formation of a purple solution. The solution was filtered on a Buchner funnel and 22.8 grams (92% of the theoretical amount) of diazobenzene-(4-acetamino)-morpholine was obtained. The melting point of this product was 174-175°C.

The compound was only slightly soluble in Skelly solvent and very soluble in ethyl alcohol, so 50% ethyl alcohol was used as the solvent for recrystallizations. After repeated recrystallizations from ethyl alcohol, small, shiny, pink platelets melting at 178°C were obtained.

Combustion analysis for nitrogen gave the following results:

Weight of sample = 0.2102 gram

cc. of nitrogen = 44.2 cc.

Room temperature = 30°C.

Vapor tension of water at 30°C = 31.5 mm. Hg.[36]

Barometric pressure = 740 mm. Hg

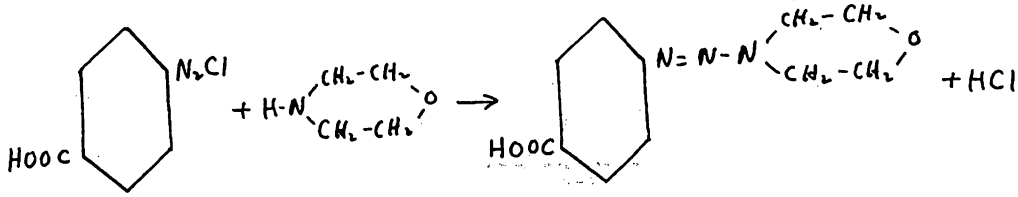
Observed % of nitrogen = 22.2%

Calculated % of nitrogen = 22.6%

The diazobenzene-(4-acetamino)-morpholine stable in boiling water but decomposes in warm, dilute acids. With cold, concentrated acids, the compound forms the diazonium salt and the morpholine salt of the acid.

Preparation of Diazobenzene-(4-carboxyl)-Morpholine

Reaction.--



Procedure.--This compound was prepared from diazotized p-aminobenzoic acid in a manner identical to the method used for other compounds in this series with one precaution. Precautions were taken in neutralizing the excess acid in the diazonium salt solution so that only the excess hydrochloric acid was neutralized. This was done by calculating the quantity of excess hydrochloric acid and adding an equivalent amount of 1 N sodium hydroxide solution. Addition of larger amounts of sodium hydroxide caused the formation of the sodium salt of diazobenzene-(4-carboxyl)-morpholine when the diazonium salt solution was added to the morpholine. After the addition of the diazonium salt solution to the morpholine, the solution was acidified with dilute acetic acid. The pink precipitate settled very slowly from the solution and filtered very slowly.

The diazobenzene-(4-carboxyl)-morpholine was recrystallized from ethyl alcohol with the formation of pink, microscopic crystals which melted at 169°C. The yield was 21.2 grams (90% of the theoretical amount) from 13.7 grams (0.1 gram mole) of p-aminobenzoic acid.

Combustion analysis for nitrogen gave the following data:

Weight of sample = 0.2040 gram

cc. of nitrogen = 33.8 cc.

Room temperature = 30°C

Vapor tension of water at 30°C = 31.5 mm. Hg[36]

Barometric pressure = 740 mm. Hg

Observed % of nitrogen = 17.5%

Calculated % of nitrogen = 17.9%

The diazobenzene-(4-carboxyl)-morpholine dissolved with decomposition in glacial acetic acid. The first step in the decomposition is probably analagous to the others in this series, i.e. formation of diazonium salt and morpholine salt, followed by a decomposition of the diazonium salt solution at room temperature. It is stable in boiling water. In hot, dilute

hydrochloric acid the compound decomposes with the formation of the morpholine salt, and a substance which melts at 240°C. This substance melting at 240°C was found to be p-chlorobenzoic acid.

3.3 grams of diazobenzene-(4-carboxyl)-morpholine was dissolved in 100 cc. of water and 1 cc. portions of this solution were treated with 2 drops of 0.1 molar solutions of various cations. These results are given in Table III.

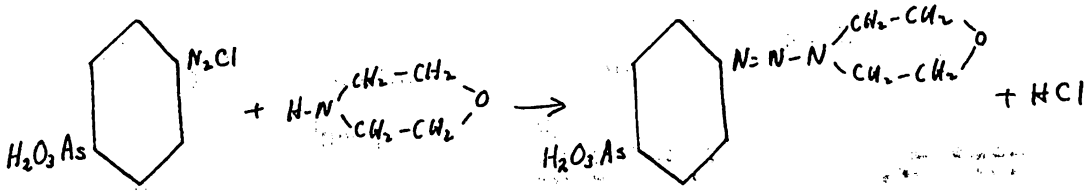
Table III

Action of Various Cations on a Solution of Diazobenzene-(4-carboxyl)-morpholine

Cation	Precipitate
Sn^{++++}	heavy, white
Sn^{++}	white, gelatinous
Sr^{++}	white, granular
Zn^{++}	white
Ag^{+}	heavy, white
K^{+}	none
Ni^{++}	flaky
Hg^{+}	heavy, white
Cu^{++}	green
Fe^{+++}	brown
Fe^{++}	brown
Pb^{++}	white
Mg^{++}	small, platelets
Mn^{++}	small, granular
Hg^{++}	slight, fine
Co^{++}	heavy, flaky
Cr^{+++}	curdy, gray
Ca^{++}	granular
Cd^{++}	white
Bi^{++}	curdy, white
Ba^{++}	granular
Al^{+++}	flocculent
NH_4^{+}	none

Preparation of Diazobenzene-(4-arsinic acid)-morpholine

Reaction.--



Procedure.--A solution of 21.7 grams (0.1 mole) of arsanilic acid dissolved in 20 cc. of concentrated hydrochloric acid and 30 cc. of water was diazotized with an aqueous solution of 7.2 grams sodium nitrite. When the arsanilic acid was completely diazotized, the color of the solution changed from an orange to a yellow color. The excess acid was neutralized with a solution containing 4 grams of sodium hydroxide.

The neutralized diazonium salt solution was added to a solution of 9 cc. morpholine, 40 cc. of water, and 4 grams of sodium hydroxide. The separation of the sodium salt from this reaction mixture was facilitated by the addition of 20 cc. of saturated sodium acetate solution. A viscous, dark tan solution was formed. The solution was allowed to stand for fifteen minutes with occasional stirring to insure complete reaction. The light tan precipitated sodium salt was

filtered off and dried on a porous plate. Some of the sodium salt placed in an oven at 110°C darkened slightly in color after forty-five minutes. The yield of the sodium salt of diazobenzene-(4-arsinic acid)-morpholine was 30 grams (80% of the theoretical yield).

The free acid was obtained from the sodium salt by dissolving the sodium salt in water and acidifying. The free acid was precipitated in the form of light tan colored platelets which melted with decomposition at 179°C after recrystallization from dilute ethyl alcohol. The free acid was practically insoluble in water but was appreciably soluble in methyl and ethyl alcohols.

Several analyses of the sodium salt gave a percentage of nitrogen lower than the calculated percentage for this compound. However a sample which had been dried on a porous plate and then dried in a vacuum oven at 60°C gave the calculated percentage of nitrogen on analyses. Investigation revealed that the sodium salt precipitated as a hydrate and analyses indicated that the

hydrate contained approximately three molecules of water for each molecule of sodium salt.

Nitrogen analysis by the combustion method gave the following results for the anhydrous sodium salt:

Weight of sample = 0.1286 gram

cc. of nitrogen = 15.0 cc.

Room temperature = 29°C

Vapor tension of water at 29°C = 36.0 mm. Hg

Barometric pressure = 742.6 mm. Hg

Observed % of nitrogen = 12.5%

Calculated % of nitrogen = 12.5%

The free acid was stable in boiling water but was decomposed by acids. The free acid formed insoluble salts with all of the heavy metals as shown in Table IV.

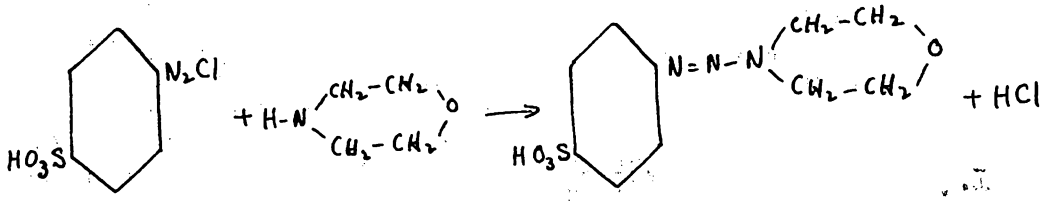
Table IV

Description of Insoluble Salts Formed by Cations With the Sodium Salt of Diazobenzene-(4-arsinic acid)-Morpholine

Cations	Precipitate
Sn^{++++}	slight, white
Sn^{++}	slight, white
Sr^{++}	very slight, white
Zn^{++}	flocculent, yellow
Ag^{+}	crystalline, white
K^{+}	none
Ni^{++}	flocculent, brown
Hg^{+}	gray
Cu^{++}	green
Fe^{+++}	red
Fe^{++}	grey-blue
Pb^{++}	white
Mg^{++}	slight, white
Mn^{++}	brown
Hg^{++}	yellow
Co^{++}	pink
Cr^{+++}	heavy, green
Ca^{++}	slight, white
Cd^{++}	crystalline, white
Bi^{++}	heavy, white
Ba^{++}	slight, yellow
Sb^{+++}	white
Li^{+}	none

Preparation of Diazobenzene-(4-sulfonic acid)-morpholine

Reaction.--



Procedure.--Nineteen and one-tenth grams (0.1 gram mole) of sulfanilic acid was added to a solution of 25 cc. hydrochloric acid and 50 cc. of water. The amine was diazotized in the usual manner. The diazo anhydride separated in the form of fine, white needles. The diazoanhydride was filtered off and mixed with 20 cc. of water. To this solution, 9 cc. of morpholine and 30 cc. of a saturated sodium acetate solution was added. The light yellow colored sodium salt of diazobenzene-(4-sulfonic acid)-morpholine was filtered from the solution. The sodium salt was recrystallized from a 50% ethyl alcohol solution forming white, crystalline needles.

Analysis of the sodium salt for nitrogen by the combustion method gave the following results:

Weight of sample = 0.2001 gram

cc. if nitrogen = 27.2 cc.

Room temperature = 28°C

Vapor tension of water at 28°C = 28.1 mm. Hg[36]

Barometric pressure = 738 mm. Hg

Observed % of nitrogen = 14.5%

Calculated % of nitrogen = 14.3%

An attempt was made to prepare the free acid by neutralizing a concentrated aqueous solution of the sodium salt with acetic acid but the free acid was too soluble to be isolated.

Three grams of the sodium salt was dissolved in 100 cc. of distilled water and various cations were added to small samples of this solution. These results are given in Table V.

An attempt was made to prepare the free acid by adding the diazo anhydride to morpholine. Apparently two precipitates were formed. These precipitates were separated into two portions due to their difference in solubility in ethyl alcohol. The portion of the precipitate which was least soluble in ethyl alcohol, was neutral to litmus, and decomposed at 122°C in a melting point bath. It appeared to be a mixture of a salt and some unreacted diazoanhydride. The

salt may have been formed by the neutralization of the free sulfonic acid by morpholine. The alcohol soluble precipitate was a compound which was faintly acidic and recrystallization from ethyl alcohol gave small, white platelets. These platelets were alkali soluble, water soluble, and soluble in alcohol. In a melting point apparatus, these platelets darkened in color at 160°C and decomposed at 177°C with evolution of gas. These crystals were believed to be the free acid.

Table V

Action of Various Cations on a Solution of the Sodium Salt of Diazobenzene-(4-sulfonic acid)-morpholine

Cation	Precipitate
Sn^{++++}	slight, gelatinous, white
Sn^{++}	slight, white
Sr^{++}	long, white needles
Zn^{++}	none
Hg^{+}	dark gray
Ni^{+++}	white needles
K^{+}	none
Ag^{+}	white, crystalline
Cu^{++}	slight, green
Fe^{+++}	flocculent, red
Fe^{++}	slight, flocculent, brown
Pb^{++}	heavy, white, crystalline
Mg^{++}	none
Mn^{+++}	none
Hg^{++}	none
Ba^{++}	heavy, white, crystalline
Bi^{++}	heavy, white
Li^{+}	none
Cd^{++}	none
Ca^{++}	white needles
Cr^{+++}	none
Co^{++}	none
Al^{+++}	white, crystalline
NH_4^{+}	none
Sb^{+++}	white, curdy

CHAPTER III

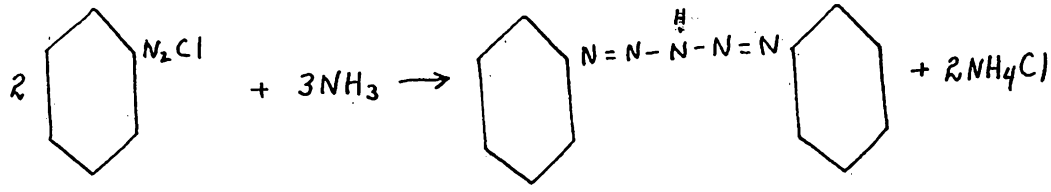
PREPARATION OF SOME PENTAZO COMPOUNDS

Introduction and History

This chapter is the result of an investigation begun with the purpose of determining the feasibility of using liquid ammonia as a solvent for carrying out the reactions that are typical of the diazonium salts. It was found that compounds were formed on adding diazonium salts to liquid ammonia so a few of these compounds were investigated.

Griess[37] examined the action of concentrated aqueous ammonia on phenyldiazonium nitrate and obtained an extremely unstable compound which decomposed into phenol, aniline, and nitrogen. He was unable to identify the substance due to inconsistent analytical data.

Many years later von Pechman and Frobenius[38] repeated the experiments of Griess and found that the substance, which Griess was unable to identify, was bisdiazobenzeneamide, the reaction proceeding as follows--



They prepared bis-p-diazotolylamide by the dropwise addition of a concentrated p-tolyldiazonium chloride solution, prepared from 10 grams of p-toluidine, into 500 grams of aqueous ammonia of specific gravity 0.88. They recorded the formation of a yellow colored solution which evolved gas relatively easy and formed a yellow precipitate. They obtained 2.5 grams of the bis-p-diazotolyamide. It possessed acid characteristics so it was purified by digestion with warm, dilute sodium hydroxide. For the analysis, it was forced out of acetone solution by means of ice water. For combustion analysis, it was mixed with a large quantity of copper oxide and burned in the usual manner. They reported that the substance was formed as yellow needles from acetone by means of water and exploded at 82-83°C in a melting point apparatus.

The equation for its decomposition was given as,

$$CH_3C_6H_4N{=}N{-}\overset{H}{N}{-}N{=}NC_6H_4CH_3 + H_2O \rightarrow CH_3C_6H_4OH + CH_3C_6H_4NH_2 + 2N_2$$

In this investigation, the same product

was formed when solid diazonium salts were added to anhydrous liquid ammonia. The yields of pentazo-compound were comparable to those of Pechmann and Frobenius.[38]

The first step involved the preparation of pure, solid diazonium salts. Several methods were tried in the preparation of the solid diazonium salts and two of the methods were found to give nearly quantitative yields of solid salt. One of these methods required isoamyl nitrite and the other required ethyl nitrite as a source for nitrous acid.

Isoamyl nitrite was prepared by an adaptation of the method of Noyes[39] for n-butyl nitrite. 380 grams (5.5 moles) of C.P. sodium nitrite and 1.5 liters of water were placed in a 3 liter, three-necked, round-bottomed flask, fitted with a mechanical stirrer, a separatory funnel extending to the bottom of the flask, and a thermometer. The flask was surrounded by an ice-salt mixture, and the solution was stirred until the temperature reached 0°C. A mixture of 100 cc. of water, 136 cc. (250 g., 2.5 moles) of concentrated sulfuric acid, and 545 cc. (440

grams, 5 moles) of commercial isoamyl alcohol was cooled to 0°C and by means of the separatory funnel was introduced slowly beneath the surface of the nitrite solution, with stirring. The alcohol solution was added slowly enough so that practically no gas was evolved, and the temperature remained at ± 1°C. This required approximately two hours. The resulting mixture was allowed to stand in the ice-salt bath until it separated into two layers. The isoamyl nitrite layer is separated by means of a separatory funnel, washed twice with 50-cc. portions of a solution containing 2 grams of sodium carbonate and 25 grams of sodium chloride. It was then dried over anhydrous sodium sulfate.

Ethyl nitrite was prepared by the method of Semon and Dawerell[40]. Two solutions were prepared. Solution I contained 620 grams (9 moles) of sodium nitrite, 210 grams (4.6 moles) of alcohol, and water to make a total volume of 2.5 liters. Solution II contained 440 grams of sulfuric acid and 210 grams of alcohol, diluted with water to 2.5 liters. The ethyl nitrite was generated in gaseous form by allowing solution III to flow into

solution I. In some cases the ethyl nitrite gas was condensed and added to the solution to be diazotized; and in other cases, the ethyl nitrite was bubbled into the amine solution.

The method used most commonly in the preparation of the solid diazonium salts was the method suggested in Cohen's "Theoretical Organic Chemistry." This method, described for the preparation of solid phenyl diazonium sulfate, is as follows: "15 grams of aniline are mixed with 140 grams of pure ethyl alcohol, and 30 grams of strong sulfuric acid are added. The alcoholic solution of aniline sulfate is cooled to 35°, and 20 grams of amyl nitrite are then slowly added. Amyl nitrite is hydrolyzed in presence of sulfuric acid, and is the source of nitrous acid. If, after the addition of amyl nitrite, the liquid is cooled in ice, a mass of crystals separates, which is the benzene diazonium sulfate. It is filtered and washed with a little alcohol." In this investigation, isoamyl nitrite was used in place of amyl nitrite and ether was added after all the isoamyl nitrite had been added which was found to increase

the yield of diazonium salt.

The ether method used for the preparation of solid diazonium salts was the method of Smith and Waring[41] which is as follows:

"5 grams of aniline hydrochloride is suspended in a mixture of 30 ml. glacial acetic acid and 30 ml. anhydrous, peroxide free dioxane. The mixture is cooled in an ice-salt mixture and ethyl nitrite bubbled in until all the solid has disappeared. The complete diazotization of the hydrochloride coincides with the disappearance of the solid phase and the first appearance of excess ethyl nitrite. Instantaneous coloration of starch-potassium iodide paper produced by 1 drop of solution shows complete reaction. 150 ml. of dry dioxane at room temperature is added in one portion to the completely diazotized solution and the phenyldiazonium chloride precipitates out. The solid is filtered on a Buchner and washed twice with 2-25 cc. portions of dry dioxane. The yield of dry salt is 95% of the theoretical yield."

EXPERIMENTAL

In a preliminary trial, one gram of solid phenyldiazonium sulfate was placed in a Dewar flask and an attempt was made to condense liquid ammonia in the flask as it was removed from a large ammonia cylinder. However, as the first drops of liquid ammonia came in contact with the solid diazonium salt, a vigorous explosion resulted and the Dewar flask was shattered.

Another trial was made in which small quantities of phenyldiazonium sulfate were added, by means of a spatula, to a Dewar flask filled with liquid ammonia. A vigorous reaction, causing much spattering, resulted on addition of of the salt to the liquid ammonia. A heavy precipitate settled to the bottom of the flask. Small quantities of the diazonium salt held on a spatula over the Dewar flask would turn dark brown and sometimes appeared as if it charred in the ammonia vapors. On standing, bubbles of gas were evolved from the precipitate which had settled to the bottom of the liquid ammonia

solution. The precipitate was filtered off and any inorganic salts were removed by extraction with water. The liquid ammonia filtrate was allowed to evaporate and the resulting residue combined with the precipitate previously filtered from the solution. This solid underwent partial decomposition in any of the common organic solvents. On standing, the odor of phenol became apparent.

These results were similar to those obtained by Griess[37] so the method of von Pechmann and Frobenius was used to isolate the bis-diazophenylamide. The precipitates were extracted with 3% sodium hydroxide solution maintained at 40-50°C for ten minutes in contact with the precipitates. This solution was filtered and the solution neutralized with very dilute acetic acid gave a canary yellow precipitate. The precipitate remaining after the sodium hydroxide extraction was largely diazoaminobenzene mixed with small quantities of phenol and aniline which were probably decomposition products of some of the pentazo-

compound. On dissolving the canary yellow compound in acetone at room temperatures, the compound immediately decomposed with the vigorous evolution of nitrogen. It was found that the compound could be dissolved in cold acetone without decomposition, from which it was reprecipitated with ice water. This precipitate was found to be exceedingly difficult to dry. It decomposed when placed in a drying oven which was maintained at 60°C. When it had been dried on a porous plate, it could not be removed from the plate as scraping or rubbing the dry, purified product produced decomposition with explosive violence. Occasional success in drying was finally obtained by drying in a vacuum desiccator containing calcium chloride.

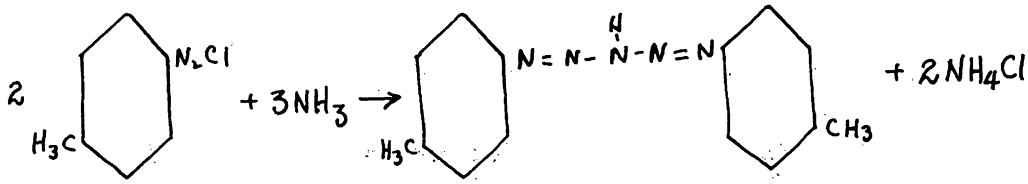
To be certain that the presence of water did not cause the reaction of the phenyl-diazonium chloride with ammonia in the manner just mentioned, special precautions were taken to carry out the experiments under anhydrous conditions. These trials gave the same results as those previously described and the yields of bis-diazobenzeneamide were comparable with

those obtained in the presence of water. The addition of ammonium chloride, an acid in the ammonia system, did not appreciably alter the yields. Addition of potassium iodide to the ammonia, previous to the addition of the diazonium salt, gave no recognizable yield of iodobenzene.

These experiments indicated that liquid ammonia could not be used as a solvent for the diazo reactions because the ammonia and diazonium salt reacted too easily with the formation of diazoamino and pentazo compounds. A search of the literature revealed that only a few pentazo compounds and their derivatives had been prepared. An attempt was then made to prepare some additional pentazo compounds and their derivatives.

Preparation of Bis-p-diazotolylamide

Reaction.--



Procedure.--The procedure used in this preparation is nearly identical to that of von Pechmann and Frobenius. Ten and seven tenths grams (0.1 gram mole) of p-toluidine were dissolved in 30 cc. of concentrated hydrochloric acid and 30 cc. of water. The solution was diazotized at 0°C with a solution containing 7.2 grams of sodium nitrite. This solution was added very slowly from a separatory funnel to 800 cc. of concentrated aqueous ammonia (sp.gr. 0.88) at 0°C. The ammonia solution was continuously stirred during the addition. The solution became yellow in color and a precipitate settled out when the stirring motor was stopped. Bubbles of gas escaped from the solution. The solution was filtered leaving a yellow precipitate which gradually darkened in air. The filtrate was allowed to stand and an

additional quantity of precipitate settled out which was combined with the first precipitate. The precipitates were then digested with warm, 3% sodium hydroxide solution forming a yellow filtrate and an orange-brown precipitate. The orange-brown precipitate was found to be principally p-dimethyldiazoaminobenzene. The yellow, alkaline filtrate was carefully neutralized with very dilute acetic acid solution and a canary yellow precipitate was formed. This precipitate was filtered off, dissolved in ice-cold acetone, and reprecipitated with ice water.

The purified p-diazotolylamide was extremely difficult to dry. As previously mentioned, the pentazo compound could not be dried on a porous plate as it could not be removed without explosive decomposition of the product. On one occasion some of the pentazo compound had been dried on a porous plate and the plate was being placed on the laboratory desk when it exploded violently. Apparently slight vibrations are sufficient to cause it to explode. Moderate success in drying the

product was obtained by drying the product on a watch glass placed in a vacuum desiccator over calcium chloride. Generally, the compound had undergone partial decomposition before it was completely dry. Melting point determinations were made and the compound exploded in the melting point bath at temperatures from 81 to 84°C. The yields of pentazo compound were ffom 2 to 3 grams (17-25.4% of the theoretical yield).

For analysis, the pentazo compound was weighed out on glazed paper and the sample distributed between three combustion boats. The boats were then filled with copper oxide powder and placed in the combustion furnace and nitrogen determined by Dumas method. The compound was ignited very carefully. Occasionally whentthe samples in all of the boats were ignited simultaneously, the explosion was sufficient to blow out the stoppers in the ends of the combustion tube. By carefully igniting the contents of each combustion boat indivually, the combustion proceeded in the normal manner. Data obtained by combustion of the pentazo

compound were as follows:

Weight of sample = .2014 gram

cc. of nitrogen = 52.5 cc.

Room temperature = 32°C

Vapor tension of water at 32°C = 35.3 mm. Hg[36]

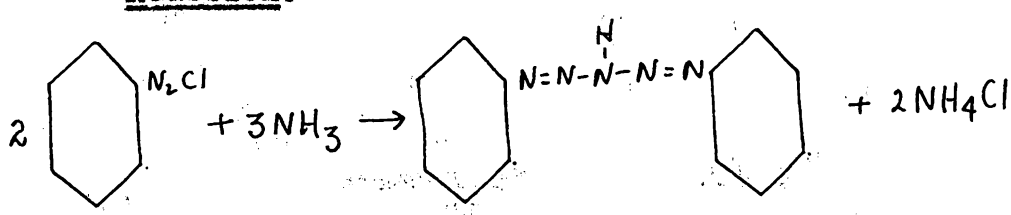
Barometric pressure = 736. mm. Hg

Observed % of nitrogen = 27.1 %

Calculated % of nitrogen = 27.7%

Preparation of Bis-diazobenzeneamide [1.5-Diphenyl-pentazdiene-(1,4)]

Reaction.--



Procedure.- Nine and three-tenths grams (0.1 gram mole) of aniline was dissolved in 30 cc. of concentrated hydrochloric acid and 30 cc. of water. The solution was diazotized at 0°C with a solution containing 7.2 grams of sodium nitrite. This solution was added dropwise from a separatory funnel to 800 cc. of concentrated aqueous ammonia (sp.gr. 0.88) at 0°C. The yellow precipitates obtained in the same manner as in the previous

preparation, were extracted with warm, 3% sodium hydroxide solution. The yellow colored sodium hydroxide extract was neutralized with dilute acetic acid solution and a yellow precipitate was formed which was very unstable. The substance was insoluble in water but dissolved with decomposition in alcohol, ether, and other organic solvents. It decomposed in a melting point bath at 72°C.

The following Dumas nitrogen combustion data were obtained:

Weight of sample = 0.2006 gram

cc. of nitrogen = 57.4 cc.

Room temperature = 30°C

Vapor tension of water at 30°C = 31.5 mm. Hg[36]

Barometric pressure = 737 mm. Hg

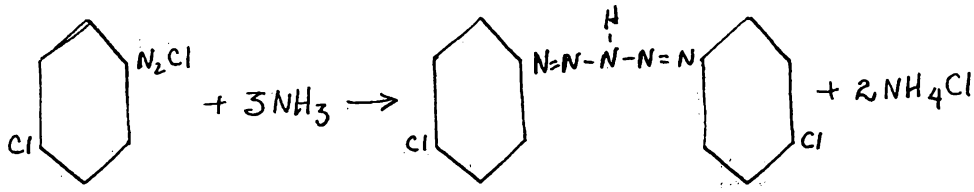
Observed % of nitrogen = 30.2%

Calculated % of nitrogen = 31.1%

On standing or on treatment with dilute acids the bis-diazobenzeneamide decomposed into aniline, phenol, and nitrogen.

Preparation of Bis-p-diazochlorobenzeneamide, [1,5 bis-(4-chlorophenyl)-pentazdiene-(1,4)]

Reaction.--



Procedure.--In a solution containing 50 cc. of water and 30 cc. of concentrated hydrochloric acid was dissolved 12.8 grams (0.1 gram mole) of p-chloroaniline. The amine was diazotized in the usual manner with a solution containing 7.2 grams of sodium nitrite. The diazotized amine solution was added to 800 cc. of concentrated aqueous ammonia of specific gravity equal to 0.88. At first, the solution assumed a yellow color, bubbles of gas escaped from the solution, and a yellow precipitate was formed. The yellow precipitate was filtered from the orange colored filtrate. On standing, a small quantity of precipitate was formed in the filtrate which was filtered off and combined with the first precipitate.

The combined precipitates were extracted with warm, 3% sodium hydroxide solution. The

alkali-insoluble residue was found to be largely p-diazoaminochlorobenzene. The sodium hydroxide extract solution was neutralized with very dilute acetic acid solution. A canary yellow precipitate was formed which was dissolved in cold acetone and reprecipitated with ice water. The precipitate was dried in a vacuum desiccator over calcium chloride. 1.5 grams of dry precipitate was obtained. This compound was very explosive when placed on a spatula and held in a flame. It decomposed when pressed with a spatula. The product exploded at 90-91°C in a melting point apparatus. It was slightly soluble in cold alcohol but dissolved with decomposition when the solution was heated.

The bis-p-diazochlorobenzeneamide was analyzed for nitrogen by Dumas' method in the same manner as the previous derivatives. On analysis, the following data were obtained:

Weight of sample = .2012 gram

cc. of nitrogen = 43.8 cc.

Room temperature = 28°C

Vapor tension of water at 28°C = 28.1 mm. Hg[36]

Barometric pressure = 739 mm. Hg

Observed % of nitrogen = 23.3%

Calculated % of nitrogen =23.8%

The pentazo compound decomposed in boiling water or dilute acids with the formation of nitrogen, p-chlorophenol, and p-chloroaniline.

Attempts to Prepare Other Pentazo Compounds

Attempts were made to prepare several other pentazo compounds but these attempts proved unsuccessful. In most cases, the precipitate formed by the addition of the diazonium salt solution to the concentrated aqueous ammonia was decomposed before it could be isolated. In these cases, decomposition occured before all of the diazonium salt solution had been added to the ammonia. Diazonium salts of 4-amino-1,3-dimethylbenzene, p-anisidine, and p-phenetidine added to concentrated aqueous ammonia formed precipitates which immediately decomposed. Both concentrated aqueous ammonia and liquid ammonia were used with the same results.

von Pechmann and Frobenius[38] reported that p-nitrophenyldiazonium chloride and concentrated aqueous ammonia formed only p-dinitrodiazoamino-

benzene. In this investigation, p-dinitrodiazoaminobenzene was the only product which was isolated and identified but on several occasions, it seemed very probable that a very unstable pentazo compound was formed. In several experiments an alkali soluble compound was obtained from the p-nitrophenyldiazonium chloride-ammonia reaction, which would decompose immediately forming large quantities of black ash. A small sample of this product was placed in a drying oven (maintained at 60°C) where it exploded with the deposition of this black ash all over the inside of the oven.

An attempt was made to prepare 3-benzyl-1,5-diphenyl-pentazdiene-(1,4) by the reaction of phenyldiazonium chloride on benzyl amine. By coupling the reactants in the mole ratio of 1 mole phenyldiazonium chloride to 2 moles of benzyl amine, p-diazotolylbenzylamine was formed as had been observed by Goldschmidt and and Badl[43] according to the equation,

$$C_6H_5N_2Cl + 2\,C_6H_5CH_2NH_2 \longrightarrow C_6H_5N{=}N{-}\overset{H}{N}{-}CH_2C_6H_5 + C_6H_5CH_2NH_2\cdot HCl$$

The product melted at 77°C when recrystallized from ether and ligroin.

The addition of 2 moles phenyldiazonium chloride to 3 moles of benzylaamine with the hope of obtaining the pentazo compound according to the equation,

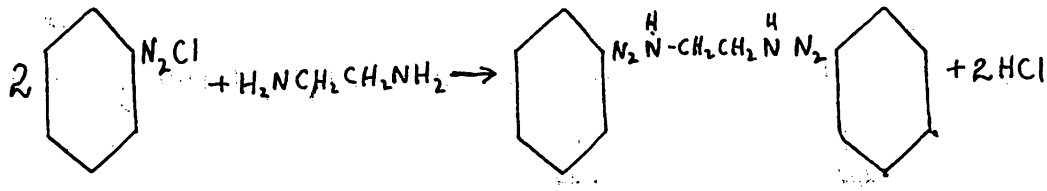
$$2C_6H_5N_2Cl + 3C_6H_5CH_2NH_2 \longrightarrow C_6H_5N_2\overset{\overset{C_6H_5}{|}}{\underset{\underset{CH_2}{|}}{N}}N_2C_6H_5 + 2C_6H_5CH_2NH_2\cdot HCl$$

gave a reddish brown precipitate which decomposed with the formation of benzyl amine and phenol.

Attempts were made to prepare a pentazo compound by coupling four molecules of phenyldiazonium chloride with one molecule of ethylene diamine. In most cases, the brown colored precipitates formed in the reaction decomposed too easily to be positively identified. However, using these reactants in the ratio of 2 moles of diazonium salt to three moles of the amine, a solid compound was obtained which was examined and found to be α, β -bis-benzenediazoaminoethane. This procedure will be described on the following page.

Preparation of α,β-Bis-benzenediazoaminoethane

Reaction.--



Procedure.--Nine and three-tenths grams (0.1 gram mole) of aniline was dissolved in a solution of 30 cc. of hydrochloric acid and 50 cc. of water. This solution was cooled to 0°C and a solution containing 7.2 grams of sodium nitrite (0.104 gram mole) was added slowly so that the temperature of the solution did not exceed 2°C. This solution was allowed to stand for fifteen minutes. It was then added to a cold solution containing 20 cc. of pyridine, 11.7 grams (0.15 gram mole) of ethylene diamine monohydrate, and 100 cc. of water. At once a dark tan precipitate was formed which was filtered from the greenish-blue filtrate. The precipitate was only slightly soluble in most organic solvents but was recrystallized from Skelly solvent. The crystals were shiny platelets with a light tan color. The crystals exploded at 127°C in a melting point bath.

The α,β-bis-benzenediazoaminoethane was extremely unstable in acids. Inacids it liberated nitrogen with the formation of aniline as the only recogniable product.

Forster, Fierz, and Hoshua[43] obtained this same product from phenylmagnesiumbromide and 1,2-diazoethane. They recrystallized the crude product from petroleum ether (b.p. 80-100°C) and found it required 2 liters of solvent to dissolve 8 grams of the α,β-bis-benzoldiazoamino-ethane. They reported that it melted with vigorous gas evolution at 128°C and was unstable in acids. They reported that 8% hydrochloric acid caused liberation of two-thirds of the nitrogen with the formation of aniline.

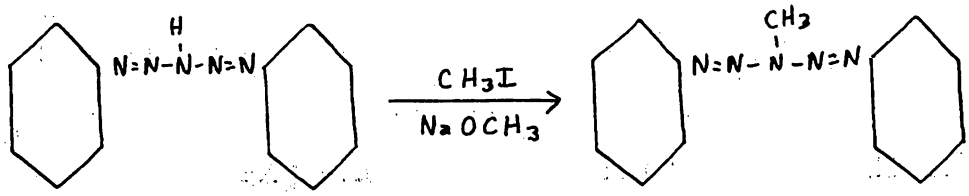
Derivatives of Pentaaz Compounds

A survey of the literature revealed that several pentazdiene compounds had been prepared in which the third nitrogen contained some organic radical. These compounds were quite stable. Since the hydrogen on the third nitrogen of the pentazdiene (1,4) compounds was acidic, it seemed feasible that stable derivatives of these compounds could easily be prepared.

The following reagents were added to small quantities of pentazo compound dissolved in benzene or in sodium methylate--methyl alcohol solution: acetic anhydride, monochloroacetic acid, phenylisocyanate, phenylisothiocyanate, benzoyl chloride, bromine in carbon tetrachloride, phosgene in toluene, benzyl chloride, methyl iodide, ethyl iodide, and alcoholic silver nitrate. Of these reagents, only the latter three gave products which were derivatives of the pentazo compound. Benzoyl chloride and carbonyl chloride gave small quantities of precipitates but the products formed underwent decomposition so that the analytical data could not be interpreted.

Preparation of 3-Methyl-1,5-diphenyl-pentazdiene-(1,4)

Reaction.--



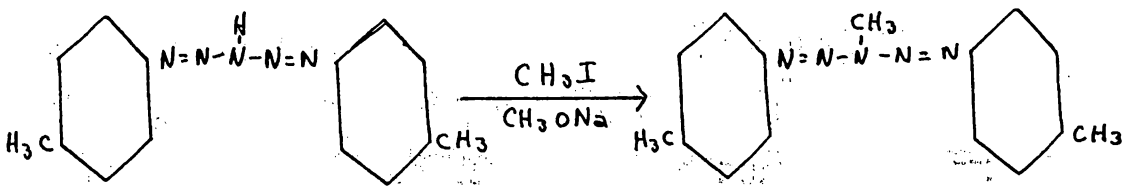
Procedure.--One gram of pure bis-diazobenzene-amide was dissolved in 5 cc. of methyl alcohol. A very small piece of sodium was then dissolved in this solution. One gram of methyl iodide was

added to the solution and the mixture was allowed to stand. After a period of one hour, a precipitate was formed, which was filtered off and dried on a porous plate. The product was recrystallized from ether and melted at 113-114°C.

Goldschmidt and Badl[42], and Dimroth, Eble and Gruhl[44] prepared this same compound from phenyldiazonium chloride and methyl amine. They reported a melting point of 112-113°C. for this product.

Preparation of 3-Methyl-1,5-bis-(p-toyl)-pentazdiene-(1,4)

Reaction.--



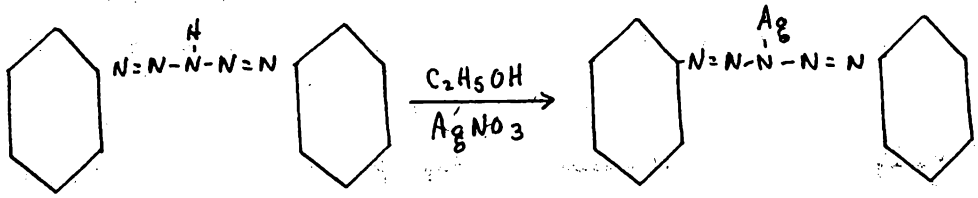
Procedure.--One gram of bis-p-diazotolylamide was dissolved in a solution containing approximately 0.1 gram sodium dissolved in 5 cc. of methyl alcohol. One gram of methyl iodide was added to the solution. After standing for two hours at room temperature, a precipitate was formed in the solution. This precipitate was filtered from the solution and recrystallized from ether. The yield of product was 0.2 gram. The recrystallized

product was yellow in color and melted at 147°C in a melting point bath.

This compound was prepared in the same manner by von Pechmann and Frobenius[38]. Goldschmidt and Badl[43] prepared this compound from p-tolyldiazonium chloride and methyl amine. They reported a melting point of 147°C for this product.

Preparation of the Silver Salt of 1,5-Diphenyl-pentazdiene-(1,4)

Reaction.--



Procedure.--A small quantity of 1,5-diphenyl-pentazdiene-(1,4) was dissolved in cold ethyl alcohol. Addition of an excess of alcoholic silver nitrate solution to this solution gave a yellow precipitate. This precipitate was explosive. It was dried and 0.2012 gram of the silver salt was weighed out and placed in a Parr bomb. The sample was treated in the manner described in Chapter II, page 39 except that the solution of hydrazine sulfate was omitted. The

silver was precipitated by the addition of an excess of a solution of chemically pure sodium chloride. The solution was heated to coagulate the precipitated silver chloride, cooled, and the precipitate was filtered into a prepared Gooch crucible, and dried at 110-115°C for one hour. The silver chloride weighed 0.0874 gram giving a percentage of silver in the original sample equal to 32.7% . The calculated percentage of silver in the silver salt is equal to 32.5%.

Lifschitz[46] prepared the pure silver salts of pentazo compounds by acidifying a solution of the pentazo compound with nitric acid and treating with silver nitrate. The salt was filtered off and dissolved in boiling pyridine containing a small quantity of alcohol. The solution was cooled and ether was added which precipitated the silver pentazo compound. This method was tried in this investigation but the heat necessary to dissolve the compound in pyridine caused some decomposition of the pentazo compound.

CHAPTER IV

SUMMARY

Summary

1. The reduction of a number of diazonium salts with alkaline formaldehyde has been found to produce good yields of hydrocarbons. The best yields of hydrocarbons were obtained from those diazonium salts which contained an electron donor group substituted in the aromatic nucleus. Poorer yields of hydrocarbon were obtained from diazonium salts containing an electron acceptor group substituted in the aromatic nucleus. This method of reduction often gave the best yields of hydrocarbons in cases where the classical method of reduction with alcohol gave the poorest yields and vice versa. Hence the two methods supplement each other.

2. Twelve triazo derivatives of morpholine have been prepared in yields of 70-90% and the melting points of these derivatives are listed on page 91.

3. Liquid ammonia was found to be unsuitable as a solvent for carrying out the typical diazonium salt reactions due to the formation of

pentazdiene compounds with the diazonium salts. The preparations of some pentazdiene (1,4) compounds was carried out and some of their derivatives were prepared.

α,β-bis-benzoldiazoaminoethane was prepared by a method which is not reported in the literature. This compound had previously been prepared from phenylmagnesium bromide and 1,2-diazoethane.

Table V

Substituted Diazobenzene Derivatives of Morpholine

Triazo Compound	Melting Point
Diazobenzene-morpholine	28°C
Diazobenzene-(4-methyl)-morpholine	48.5°C
Diazobenzene-(2-methyl)-morpholine	18°C
Diazobenzene-(4-chloro)-morpholine	54.5°C
Diazobenzene-(3-chloro)-morpholine	24-25°C
Diazobenzene-(4-bromo)-morpholine	88.5°C
Diazobenzene-(4-nitro)-morpholine	133.5°C
Diazobenzene-(4-acetyl)-morpholine	92°C
Diazobenzene-(4-acetamino)-morpholine	178°C
Diazobenzene-(4-carboxyl)-morpholine	169°C
Diazobenzene-(4-arsinic acid)-morpholine	179°C
Diazobenzene-(4-sulfonic acid)-morpholine	177°C

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