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Towards synthesis of Bis -(N,N'-1,8-naphthylene)- 1,8 - Diaminonaphthalene

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TOWARD SYNTHESIS OF
BIS -(N,N'-1,8- NAPHTHYLENE)- 1,8 - DIAMINONAPHTHALENE

by


Billy
William Chiu-sheung Ng UC 1969

Senior Thesis Submitted
in Partial Fulfillment
of the Requirements of Graduation

DEPARTMENT OF CHEMISTRY

UNION COLLEGE

2nd June, 1969



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This Thesis
Submitted by

Willy Ng Chiu-sheung
(William Chiu-sheung Ng)

to the

Department of Chemistry of Union College
in partial fulfillment of the requirements of the degree of
Bachelor of Science with a Major in Chemistry

is approved by

William B. Martin, Jr.
(William B. Martin, Jr.)

TO MY PARENTS

TO BONNIE

ACKNOWLEDGEMENT

The author wishes to express his heartfelt appreciation and gratitude to Professor William B. Martin, Jr. for his inspirational guidance, immense patience and encouragement during the course of this investigation. The author would like to acknowledge the assistance of Mr. B. Adams of Schenectady Chemical Research Laboratory for making available the use of the facilities.

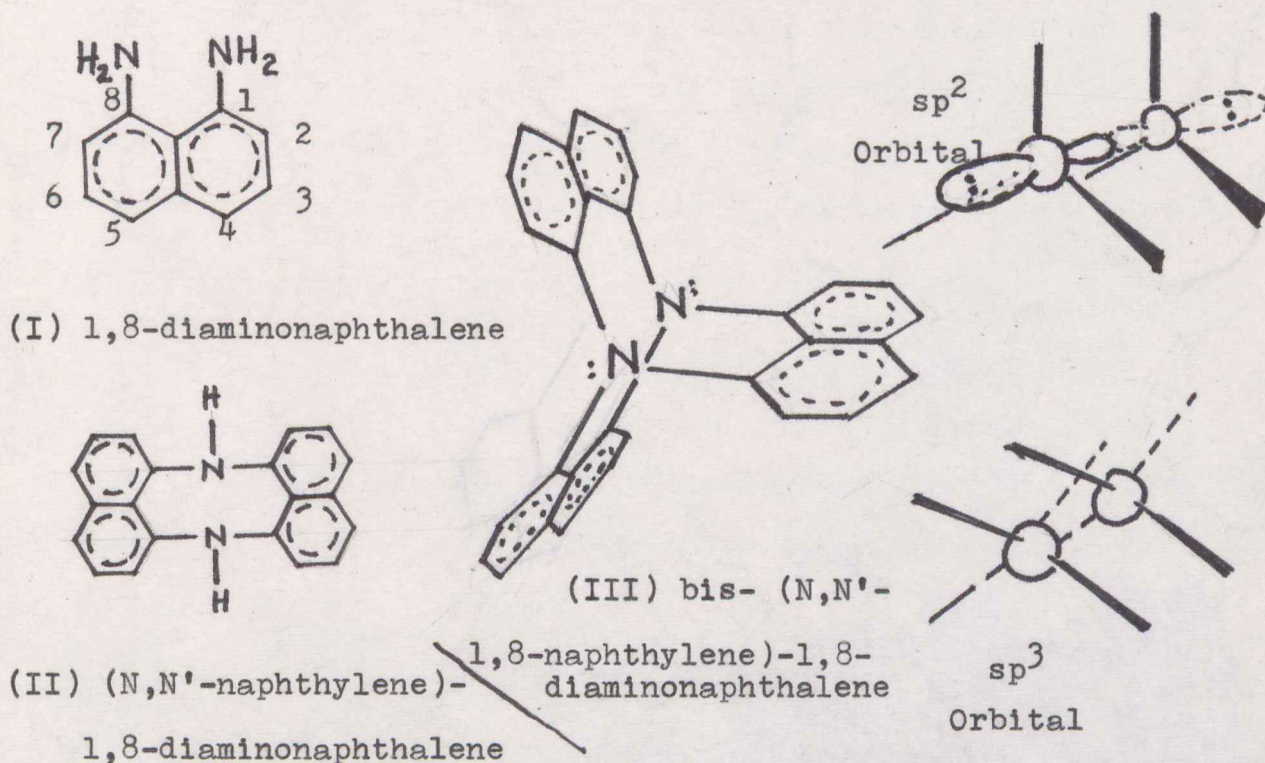
ACKNOWLEDGEMENT

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INTRODUCTION

This project is concerned with attempted synthesis of a special highly symmetrical compound --- the bis-(N,N'-1,8-naphthylene)-1,8-diaminonaphthalene, (III) --- from 1,8-diaminonaphthalene, (I). In the process of synthesis, it is conceivable that an intermediate product (N,N'-naphthylene)-1,8-diaminonaphthalene, (II), will be formed.



At present, to the best of our knowledge, neither (II) nor (III) has been reported to have been produced. The interest in (III) lies in its extreme symmetry, and on the possible interaction of nitrogen orbitals each with a pair of non-bonded electrons in possibly a sp² hybrid system.

The production of (III) relies on the stability of the formation of the 3rd N---C bond. This 3rd N---C bond may require a change in the nitrogen bonding structure from sp^3 to sp^2 hybridization. Otherwise, the third naphthalene group cannot fit in without experiencing bending of the 1,8 bonds of naphthyl systems. As a result, bond strain as well as steric effects occur.

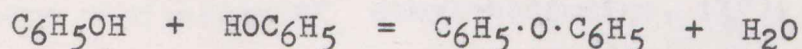
HISTORICAL

There has been no report of any kind concerning the synthesis of similiar highly sterically symmetrical triaryl compounds other than triphenyl amine. It is even¹ rarer for such compounds with naphthalene rings.

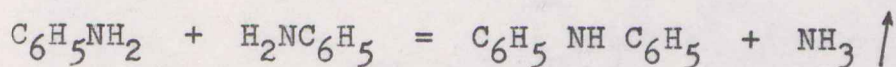
In 1929, Karpuklin reported² :



In July 1931, Dr. Schöllkopf of Germany reported a method of producing a 15% yield of diphenyl ether from phenols by heating the latter to 350°C. in an autoclave with activated fuller's earth³.



He suggested that treating aniline similarly, diphenylamine could be produced on the liberation of ammonia⁴.



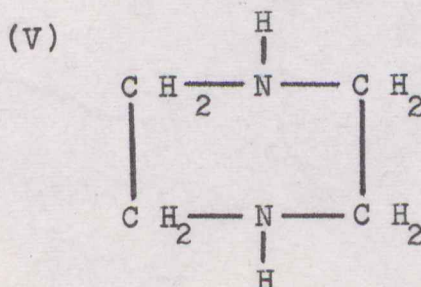
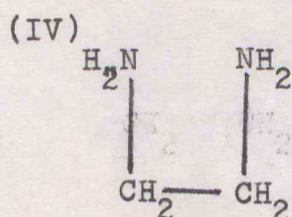
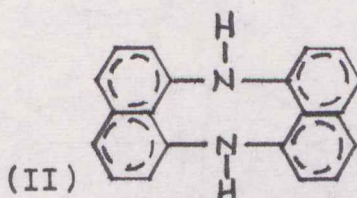
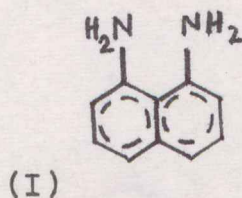
He also suggested that treating aromatic amines with phenol similarly as above, diarylamine could be produced accordingly :



Furthermore, in analogy, he said that naphthylamine could yield dinaphthylamine under similar conditions. No actual laboratory preparation was given in Schöllkopf's report. There is no simple way to find out whether Dr. Schöllkopf had actually carried out any experimental investigation on his proposal.

In the Fall of 1968, Professor William B. Martin, Jr. suggested a method of synthesizing bis-(N,N'-1,8-naphthylene)-1,8-diaminonaphthalene, (III), from 1,8-diaminonaphthalene, (I), by catalytic deamination on heating in the presence of an inert solvent and an inert atmosphere, such as passing nitrogen gas through while the reaction is in process.

Professor Martin's suggestion was based on the surprising similarity of ethylenediamine, (IV), with 1,8-diaminonaphthalene, (I) ; and piperazine, (V), with (N,N'-1,8-naphthylene)-1,8-diaminonaphthalene, (II).

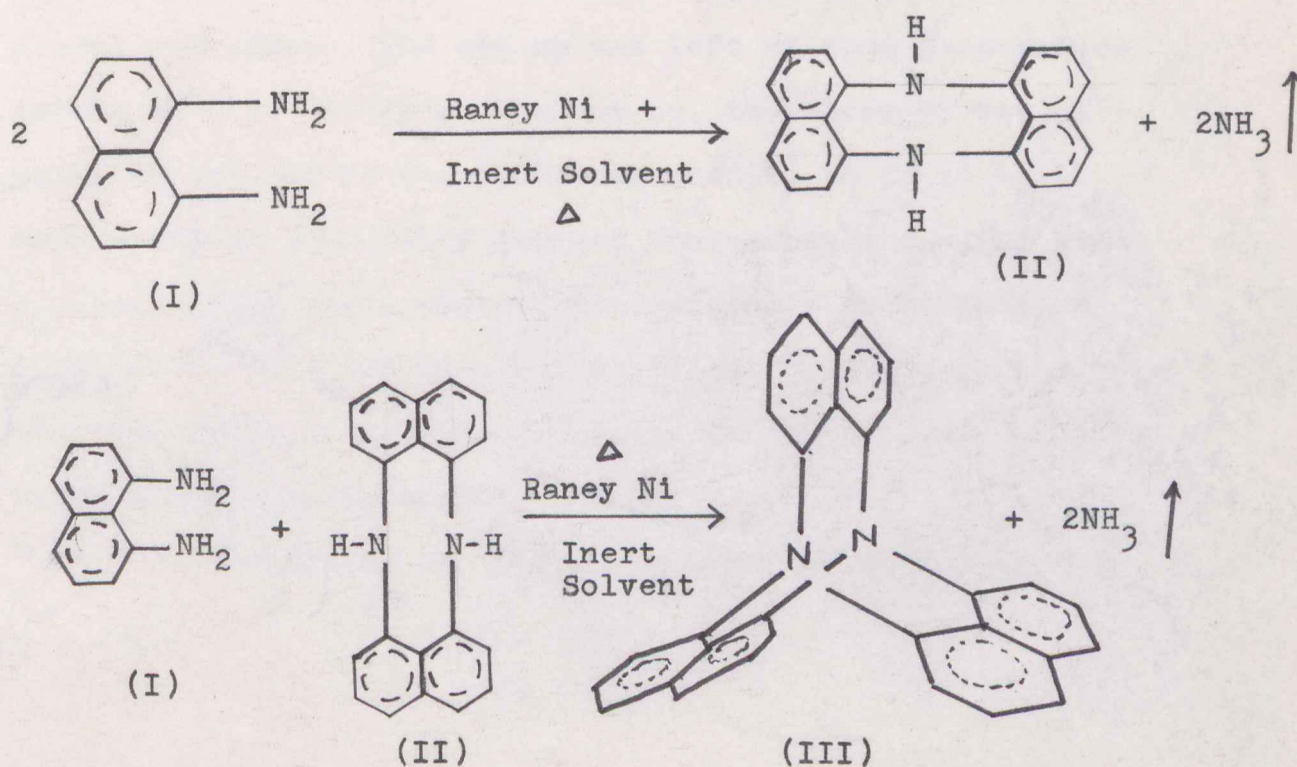


The difference in structure is a naphthalene in (I) and (II) in place of the ethyl groups of (IV) and (V) respectively.

There is a report on the success of preparing piperazine from diethylenetriamine, (VI), with Raney nickel in an inert solvent. In this same literature, it is also reported that piperazine is prepared from heating ethylenediamine, (IV)⁵.

This is a process for preparing aliphatic secondary amines from primary amines by catalytical deamination. Similar conditions for preparing dibenzylamine from benzylamine are also reported by Adkins⁶.

It is on these grounds that the project is carried out with the hope of duplicating the sequence of preparing secondary aliphatic amines from primary amines. In this case, by deamination of primary aryl amines to give secondary, or even tertiary aryl amines on further heating.



EXPERIMENTAL

The catalyst used in the experiment was freshly prepared Raney nickel. The Raney nickel was stored in benzene solution. The solvents used were decalin and xylene.

By looking at the equations, the main indication of whether the catalytic deamination reaction will proceed or not, is whether ammonia is evolved or not. Therefore, the first test was to determine whether the process of synthesis would go or not. This was first done by noticing whether there was a change from low to high pH on a piece of wet pH paper.

The first run was carried out by putting 1 gm. of 1,8-diaminonaphthalene in benzene. The pH of the solution was tested with a piece of wet pH paper. The result was an indication of pH 9 - 10. Then a spatulaful of Raney nickel was added. The set up was left at room temperature (about 25°C.). After an hour or so, the piece of wet pH paper at the rim of the flask had changed to pH 10 - 11. Such a change in acidity implied that ammonia gas had been evolved, since there was no other probable side reaction which could have led to a change of pH. Therefore, the proposed reaction seemed optimistic and the freshly prepared Raney nickel was apparently effective.

A simple set up as in diagram 1 was carried out in

two different procedures, (A) and (B). In (A). 1 gm. of 1,8-diaminonaphthalene was dissolved in 20 ml. of xylene and 2 spatulasful of Raney nickel were added. The wet pH paper changed from pH 1 to 9 after 15 minutes of warming at 60°C. After continuous heating for 4 hours, the temperature was raised to $112 \pm 2^\circ \text{C}$. or so for another 5 hours, making a total of 9 hours of heating.

In (B), the same quantity of the sample was heated for the same period of time with the same amount of Raney nickel, at similar temperature within a range of five degrees without the solvent.

Thin Layer Chromatography (TLC)

Samples from (A) and (B) were taken. A portion of (A) was dissolved in benzene and the rest in ethanol for TLC. The procedure was repeated identically with (B). In such a manner, 4 different samples were obtained.

(A)_B, (B)_B, sample of products from procedure A and B respectively dissolved in benzene,

(A)_E, (B)_E, sample of products from procedure A and B respectively dissolved in ethanol.

In order to ensure a fairly accurate developing process, the following conditions were observed :

(1) Each sample was developed on a strip with 1,8-diaminonaphthalene, (I), dissolved in the corresponding solvent occupying the left of the strip,

(2) The strips (A)_B and (B)_B were developed at the same time in benzene in one jar; (A)_E and (B)_E were run at the same time in ethanol in another jar.

Results :

Benzene as solvent :

$$\left. \begin{array}{l} (A)_B \quad R_f(I) = 0.41 \\ R_f \text{ product} = 0.43 \end{array} \right\} R_f(I) - R_f \text{ product} = (-0.02)$$

$$\begin{array}{rcl}
 \text{(B)}_B & R_f \text{ (I)} & = 0.41 \\
 & R_f \text{ product} & = 0.46
 \end{array}
 \left. \vphantom{\begin{array}{rcl} \text{(B)}_B & R_f \text{ (I)} & = 0.41 \\ & R_f \text{ product} & = 0.46 \end{array}} \right\} R_f \text{ (I)} - R_f \text{ product} = (-0.05)$$

Ethanol as solvent

$$\begin{array}{rcl}
 \text{(A)}_E & R_f \text{ (I)} & = 0.77 \\
 & R_f \text{ product} & = 0.75
 \end{array}
 \left. \vphantom{\begin{array}{rcl} \text{(A)}_E & R_f \text{ (I)} & = 0.77 \\ & R_f \text{ product} & = 0.75 \end{array}} \right\} R_f \text{ (I)} - R_f \text{ product} = (+0.02)$$

$$\begin{array}{rcl}
 \text{(B)}_E & R_f \text{ (I)} & = 0.81 \\
 & R_f \text{ product} & = 0.76
 \end{array}
 \left. \vphantom{\begin{array}{rcl} \text{(B)}_E & R_f \text{ (I)} & = 0.81 \\ & R_f \text{ product} & = 0.76 \end{array}} \right\} R_f \text{ (I)} - R_f \text{ product} = (+0.05)$$

Two major conclusions can be drawn from the above results :

(a) With benzene as solvent, the products travelled farther than the reactant, (I). With ethanol as solvent, the products travelled not as far as the starting material, (I). In TLC, the rate of migration of a compound is dependent upon the choice of solvent⁷. Benzene is comparatively less polar than ethanol, and the products travelled farther than (I) in benzene, and the reverse was true in ethanol. This evidence implied compound (I) to be more polar than the products, whatever they might be. At the same time, if (I) is compared with either (II) or (III) structurally, (I) is conceivably more polar because (I) has more amino hydrogens.

(b) The difference of R_f values of (A) and (B) in each solvent shows that the (B) product gives a wider difference in distance migrated from that of (I). This might be interpreted that there was a mixture of more highly condensed amines in (B) which were not yet separated but made the 'single' spot appeared to move at a different rate. In other words, the (B) condition was more effective in condensation than (A). Since the only difference in the set up of (B) from (A) was that (B) was carried out concentrated while (A) had a solvent. This is to say, the presence of solvent does not help the reaction.

Even though the components present in the products have not been identified, there was another striking feature of analysis with TLC when samples were developed with 2/3 by volume of petroleum ether and 1/3 by volume of ethanol. The sample from (A), i.e. with xylene as solvent, showed 3 distinct spots while the TLC result of (B) showed only 2 spots.

Infra-Red Spectrum (Perkin - Elmer 237)

Upon running the Infra-Red instrument, the spectra are not as informative as hoped. This might be explained by the fact that primary and secondary amines absorb around similar range of wavelengths, (see Plate I). The overlapping in absorption makes it difficult to distinguish primary from secondary amines. Tertiary amines absorbs strongly around 7.4 microns, and mediumly at 8.5 microns. In the vicinity of these two regions, both primary and secondary amines absorb strongly too. Besides, there is far from 100% yield of any compound. This implies a superimposed spectrum is inevitable. The only possible way to manage a clear recognition of the presence of secondary amine would be by comparing the difference in intensity of the absorption by the primary amine on a spectrum of (I). This method of identification is far from valid.

Vapor Phase Chromatography (VPC)

Perkin Elmer 154-C (Vapor Phase Fractometer with
Speedomax G Recorder)

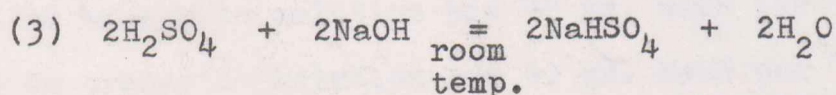
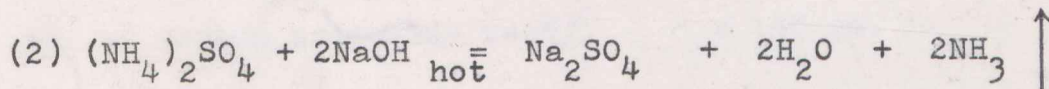
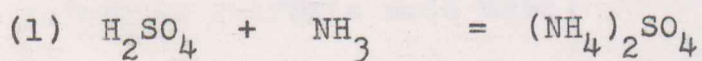
VPC was run in the Schenectady Chemical Research Laboratory through the help of Mr. Beverly Adams for the reason that the school did not have the appropriate column available. The boiling point of the product has not been discovered. It might be very high. The highest temperature the VPC instruments in school can reach is around 260° C.

The results obtained from the Schenectady Chemical Research Laboratory indicated the optimum temperature required was around 240° C. This data assured the author that runs could be done in school provided an appropriate column were available. A suggested column (Silanized, acid-washed Chromosorb W with D.C. Silicone oil 200) was prepared under the supervision of Professor Lanese. But the column did not seem to work the way it was designed to. Upon the injection of any sample in a solvent (chloroform), only the solvent came through. The temperature range had been varied from 190° C. to 250° C. at 10° intervals. The charts all looked the same regardless of temperature.

Kjeldahl-like Trapping of Evolved Ammonia

In conjunction with the VPC process, a set up as shown in diagram 2 was carried out. Nitrogen gas was passed through slowly to preserve the amine samples from atmospheric oxidation. At the same time, the nitrogen stream would help in pushing the liberated ammonia out of the flask and enhance any equilibrium toward desired products.

Standardized concentrated sulfuric acid was set up to absorb any liberated ammonia.



The sodium hydroxide used was of known normality. Combining equations (1) and (3) above, the quantity of ammonia evolved was calculated. This in turn would indicate to what extent the reaction had proceeded.

Phenolphthalein was used as the indicator for this strong acid - strong base titration because of the sharp change in color from intense purple to colorless.

First sample of sulfuric acid (2 ml.) was taken after 6 hours heating at $165 \pm 5^{\circ}\text{C}$. Then, samples of 2 ml. sulfuric acid at a time were withdrawn for titration against the sodium hydroxide of known normality at half hour intervals until the titration results showed a definite value.

Experimental Data

Wt. of 1,8-diaminonaphthalene used = 1 gm.

Volume of sulfuric acid used = 90 ml.

Wt. of sodium hydroxide used = 40 gm.

1N sodium hydroxide solution has 40 gm. NaOH per 1,000 ml. soln.,

2N sodium hydroxide solution has 40 gm. NaOH per 500 ml. soln.

Standardizing Sulfuric Acid

	(1)	(2)	(3)
Vol. of NaOH used =	50 ml.	50 ml.	50 ml.
Vol. of H_2SO_4 used =	2.73	2.80	2.80
Average vol. of H_2SO_4 used =	2.78 ml.		

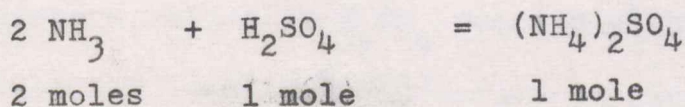
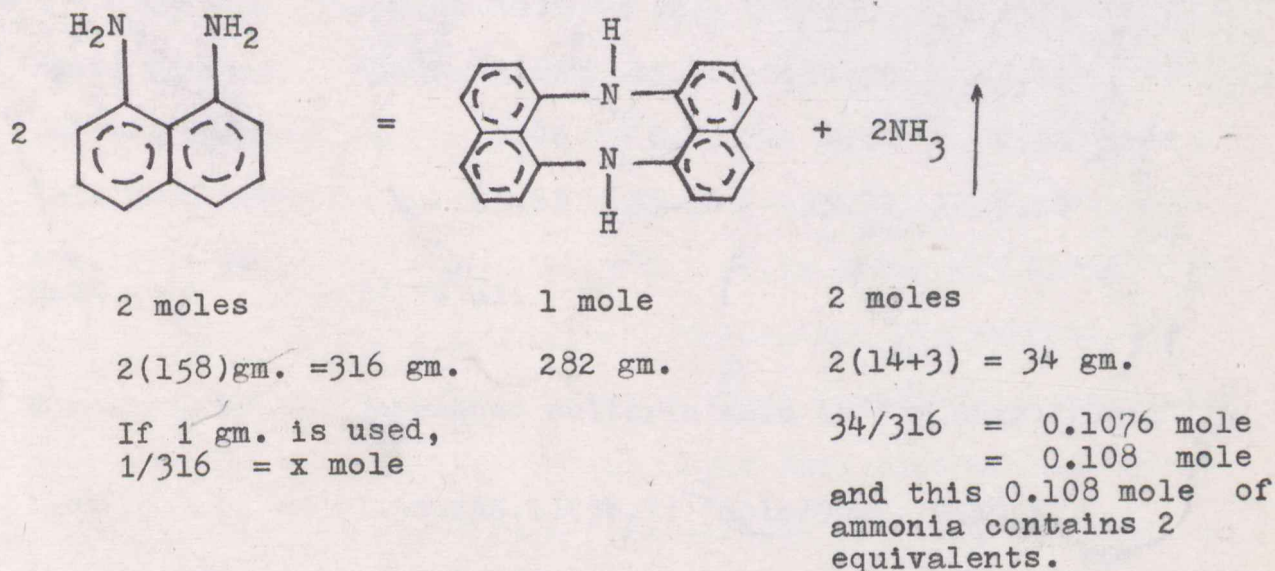
$$N_1 V_1 = N_2 V_2$$

$$N_{\text{H}_2\text{SO}_4} = (2 \times 50) / 2.78$$

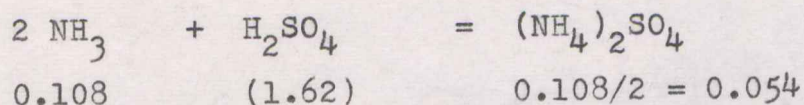
$$= 36.03$$

$$= 36.0$$

36N H_2SO_4 contains $(36 \times 49) \text{ gm.} = 1764 \text{ gm.}$ of H_2SO_4 in 1,000 ml. soln.,
 i.e. $(1764 \times 90/1000) \text{ gm.}$ of H_2SO_4 in 90ml. of H_2SO_4 solution, or
 158.76 gm. or 1.62 mole.



Assuming 100% complete reaction,



$$\begin{aligned}
 \text{moles of unreacted } \text{H}_2\text{SO}_4 &= 1.62 - 0.054 \\
 &= 1.566
 \end{aligned}$$

18 moles per 1,000 ml. of H_2SO_4 solution is 36N H_2SO_4
 1.566 moles per 1,000ml. of H_2SO_4 solution is $(36 \times 1.566)(18)^{-1} \text{ N}$
 1.566 moles per 90ml. of H_2SO_4 soln. is $(36 \times 1.566 \times 1000)(18 \times 90)^{-1}$
 i.e. 34.804 N
 or 34.80 N

On titration the volume of NaOH required,

$$= (2 \text{ ml} \times 34.8 \text{ N}) (2.01\text{N})$$

$$= 34.7 \text{ ml.}$$

Titration of reacted H_2SO_4 against 2.01N NaOH

	(1)	(2)	(3)	(4)
Final reading	42.65	35.40	39.30	45.00
Initial reading	7.40	0.10	4.00	9.80
Vol. NaOH used	35.25	35.30	35.30	35.20
Ave. vol. of NaOH used	= 35.26 ml.			

Normality of the unreacted sulfuric acid is $(35.26 \times 2)(2.01)^{-1} \text{ N}$,

i.e. 35.1 N, or $(1.566 \times 35.1)(34.7)^{-1} \text{ mole/90ml. H}_2\text{SO}_4$;

i.e. 1.5867 mole, or 1.587 moles.

Therefore, moles of H_2SO_4 reacted with NH_3 liberated from reaction = $(1.62 - 1.587)$

$$= 0.033$$

Therefore, number of moles of NH_3 liberated from the reaction

$$= 2(0.033)$$

$$= 0.066$$

Assuming this represents the extend of the reaction, then,

$$\begin{aligned} & (0.066/0.108) \times 100\% \\ & = 61.34 \% \end{aligned}$$

Effort was made to obtain a pure sample of the product. The apparatus was allowed to stand undisturbed for a few days. In doing so, the product could all settle down. The decalin was decanted. The remaining decalin was evaporated by warming over a heating mantle. As the boiling point of decalin is $195^{\circ}\text{C}.$, and 1,8-diaminonaphthalene sublimes at $205^{\circ}\text{C}.$, the temperature was set at $200 \pm 5^{\circ}\text{C}.$ While doing all these, the fact that the boiling point of the product was unknown was disregarded carelessly. After all the decalin was evaporated in the open atmosphere, it was found that most of the remain reddish brown compound was very soluble in acetone⁹, but not in either ether or chloroform. A clean beaker was dried and weighed. It was hoped that if the acetone were evaporated from the compound, the weight of the compound could be found. This turned out to be 0.0437 gm. (i.e. if all this were either product (II) or (III), it would be 4.37 % yield.) In comparison to the quantity of ammonia liberated, which is 61 %, the yield was extremely low.

Trying to explain this low yield, the recovering procedure was revised. Thus it was conceived that the compound might have decomposed on the $200^{\circ}\text{C}.$ heating; also the atmospheric oxidation might have taken place. It was also possible that reaction occurred between acetone and 1,8-diaminonaphthalene⁹.

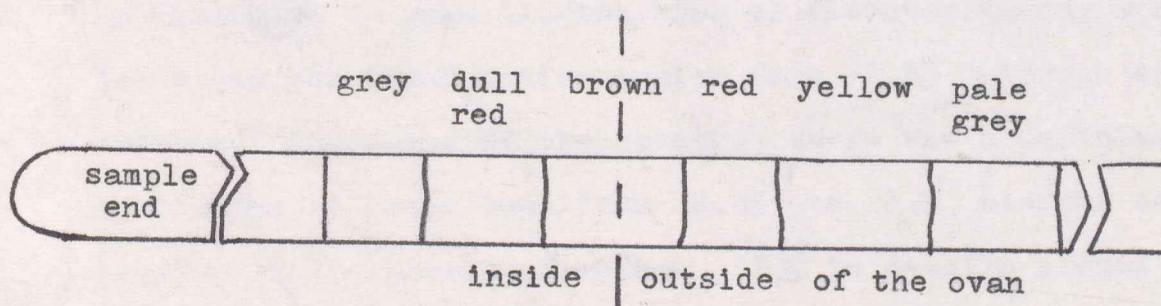
It was conceivable that the Raney nickel retained some weight of products.

Despite of the low yield, an attempt was made to find the melting point of the remain compound, in case this contained the desired products. This remain compound was fine powder and had a shinny surface.

- (1) At 140° C. ----- this had a fibrous structure
- (2) At 150° C. ----- broke-down of fiber structure to
small, fine crystals occurred
- (3) At 235° C. ----- part of this melted, and some remained
- 94) At 330° C. ----- the residual part of (3) remained
unchange.

Vacuum Distillation

Owing to the minute quantity of product available, vacuum distillation was suggested for identifying the components in product. A modified set up was illustrated in diagram 3. Sargent Catalog No. s-36517 type of ovan was used. At 215°C ., first sign of noticable orange condensation was noted. The result is shown below --



After the temperature has reached 380°C ., the process was stopped. It was discovered that there was a lot of loose, fine dark brown powder left at the sample end of the tube. Upon testing physically, this was found to be largely carbon. Apparently, there was over heating at a certain stage. How the naphthalene ring, or the decalin ring could be oxidized to carbon was unknown.¹⁰

Another ammonia trapping experiment without Raney nickel was run again. The scheme for this run was step-wise heating. Sample was extrated from the reaction flask each morning for IR spectra. Then the reaction flask was heated for a certain periods in the afternoon at a recorded temperature. The set up was allowed to cool and materials solidified at night. The IR (KBr) spectra were compared on a day-to-day basis. As discussed on page 11, the hope of discovering any secondary amine was the broad medium region from 2.85 microns to 3.2 microns. According to the spectra, there was a definite appearance of broad band from 2.85 to 3.2 microns after heating 1,8-diaminonaphthalene, (I), in decalin around 150° C. for 5 hours without Raney nickel. On dividing the reactants at this stage into 2 portions, (X) and (Y), with Raney nickel presented in (X), the result of comparing the IR spcetra on further heating showed Raney nickel helped the reaction forming secondary amine faster.

As far as determining the presence of tertiary amine from the spectra was concern, it was too difficult.

Thin Layer Chromatography on (X) and (Y)

X with Raney nickel and was heated	---	140° C.	2 1/2 hours	
		152° C.	2	"
		160° C.	6	"
		100° C.	1	"
		120° C.	2	"
Y without Raney nickel and was heated	---	140° C.	2 1/2	"
		152° C.	2	"
		160° C.	1 1/2	"
		170° C.	2	"
		190° C.	6	"

TLC Results --Benzene as solvent

$$(X)_B \quad R_f (I) = 0.39$$

$$R_f \text{ product} = 0.47$$

$$(Y)_B \quad R_f (I) = 0.43$$

$$R_f \text{ product} = 0.53$$

2/3 Ligroin & 1/3 Ethanol as solvent

$$(X)_L \quad R_f (I) = 0.50$$

$$R_f \text{ product} = 0.50$$

$$(Y)_L \quad R_f (I) = 0.38$$

$$R_f \text{ product} = 0.36$$

The main interest towards these results was not that of concern with the physical measurements, but the successful separation of the three distinct spots in $(X)_L$ and not in $(Y)_L$. (see Plate 2). On comparing the results of $(X)_L$ and $(A)_L$, there were similarities in the manner the spots were distributed. This tended to make one wonder whether Raney nickel was favorable for the reaction?

DISCUSSION

Not many organic reactions under go to completion giving an over all yield of a sole product only. There is almost always a mixture of products -- desired or not. This synthesis is more likely than not to be one of them. There is a possibility that undesired products arising from side reactions as well as uncompleted mechanisms might be present in large quantity ¹⁰. However, the main concern is that the desired products, i.e. (II) and (III), are likely being produced. The most difficult problem of identitying the products is that, assuming reactions mostly occur around the amino-groups, the products differ from each other by 2, 4 or 6 hydrogens around the nitrogens. As described on pages 11 and 20, IR spectra do not help as much. The diminishing in absorption in 2.9 to 3.1 microns on the spectra, nevertheless, implies a diminishing in free N---H vibration. This result corresponds to the formation of secondary, or even tertiary amines may have been formed.

The results from all the TLC runs on pages 8 and 21 might be interpreted as follows -

(1) Presence of solvent hinders the reaction :

This is shown from the results of developing samples from (A) and (B) in benzene and ethanol. Also, the results from developing (B) in 2/3 Ligroin & 1/3 ethanol might give an inference that most of the product was (III), and the quantity of (II) presence was minute. This

is possibly why there were only 2 spots. The result of having 3 spots from developing (A) in 2/3 ligroin & 1/3 ethanol represented there was an intermediate product.

(2) Presence of solvent is essential :

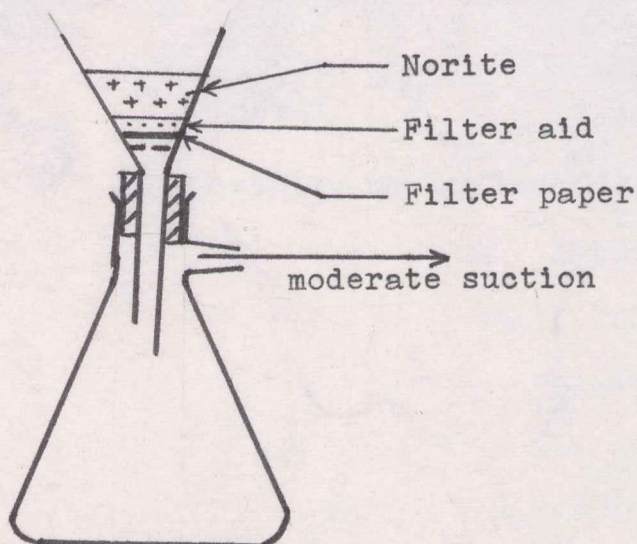
The mixture of 2/3 ligroin & 1/3 ethanol was a better developing solvent than either benzene or ethanol alone. The 3 spots might showed that (a) the presence of solvent had aided the reaction to go further giving (III) from (II) in the two step mechanism, or from (I) directly, (b) the absence of solvent had hindered the reaction from going further after forming (II).

(3) A better developing solvent for these amines using TLC has yet to be found.

If this experient is carried out again, the following steps might be helpful.

- (1) Purification of 1,8-diaminonaphthalene, (I),
The mp of (I) given in the Handbook of Chemistry & Physics is 66.5°C. But the observed was 55-68°C. for the sample provided. Purification could be done by dissolving (I) in benzene. Before recrystallization, the solution is passed through a norite filter set up as shown. The suction has to be moderate in order to prevent

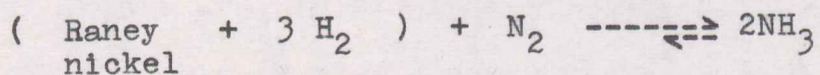
the norite from being dried up. A trap should be set up to prevent water contaminating the filtrate by sucking back. A few drops of ligroin would added to the filtrate to help crystallizing. The filtrate should be colorless. The crystals to be obtained thus have a mp of 65°C .



- (2) Benzene as the inert solvent,
On the first run as reported on page 6, (I) liberated ammonia at room temperature at the present of Raney nickel. Thus, it might be worthwhile to run the reaction once in benzene.
- (3) TLC seems to be the best tool to identify how far the reaction has gone in conjunction with IR spectra, and NMR spectra. TLC is fast and rewarding.
- (4) An appropriate column for VPC is definitely essential.
- (5) Column chromatography is necessary to separate

the components in the mixture product for further indentifications.

- (6) Helium gas (He) is used in place of nitrogen gas. Though there is no confirmation that the passing stream of 'inert' nitrogen does take part in the reaction, it is suspected that the reaction



is possible, though not likely.

SUMMARY

This project works toward synthesizing aryl secondary or tertiary amine by heating primary aryl amine by catalytic deamination in the presence of an inert solvent. The primary aryl amine is 1,8-diaminonaphthalene, and the secondary and tertiary aryl amines are (N,N'-naphthylene)-1,8-diaminonaphthalene and bis-(N,N'-1,8-naphthylene)-1,8-diaminonaphthalene respectively. This project is done in the light that Martell and Martin⁵ have been able to prepare piperazine by heating ethylenediamine with Raney nickel in an inert solvent. Unfortunately, the product has not been identified to the extent that a conclusion can be drawn saying whether the proposed reaction is practicable or not. However, there are favorable evidence supporting the theory that new products are produced.

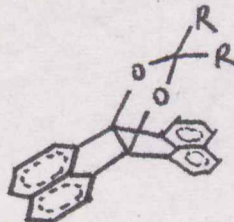
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J. Am. Chem. Soc., 89:14, 3505-10, (1967)

From the Laboratories of
the Rockefeller University
reported the study of

$R = CH_3, O.$



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3. Schollkopf, Karl, Deutsches Reich Patentschrift, No. 530 736.
Chem. Abs., 26, 152, (1932).
4. Frei, J., U.S.P. 1840576, Chem. Abs., 26, 1625, (1932).
5. Martell, A.E., & Martin, W.B.,
J. Am. Chem. Soc., 70:1817 (1948).
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Wisconsin Press, Madison, Wisconsin, (1937), pg. 55.
7. Randerath, Kurt, Thin-Layer Chromatography,
Verlag Chemie. Gmb , H. Weinheim Bergster, (1963)
Translated by D.D. Libman.

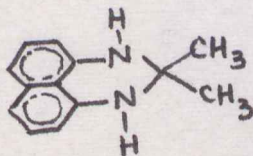
The rate of migration may also be affected by adsorption,
partition or ion-exchange processes, and more often by
a combination of these.

8. Wertheim, E. " Textbook of Org. Chem. "

The Blakiston Co., Philadelphia, (1939), pg.9.

Kjeldahl Method of trapping evolved ammonia usually uses
boric acid. The effectiveness of any mineral acid is the
same.

9. The solubility with acetone is possibly enhanced by the
possible reaction of 1,8-diaminonaphthalene with acetone
giving



10. Fieser & Fieser, " Reagents for Org. Synthesis "

John Wiley & Sons, Inc., (1967), pg. 228.

DIAGRAM 2

(see text pg. 13)

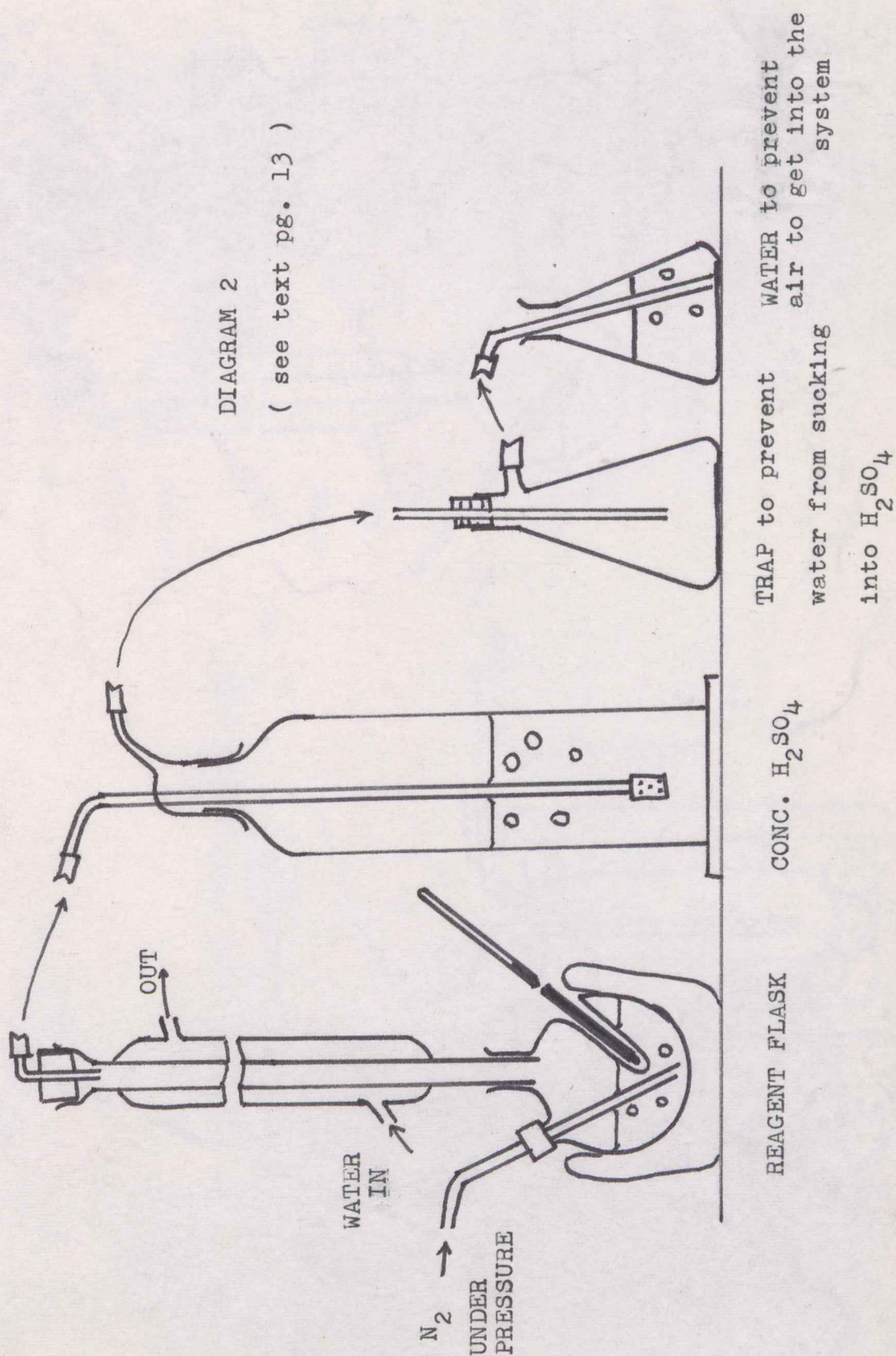
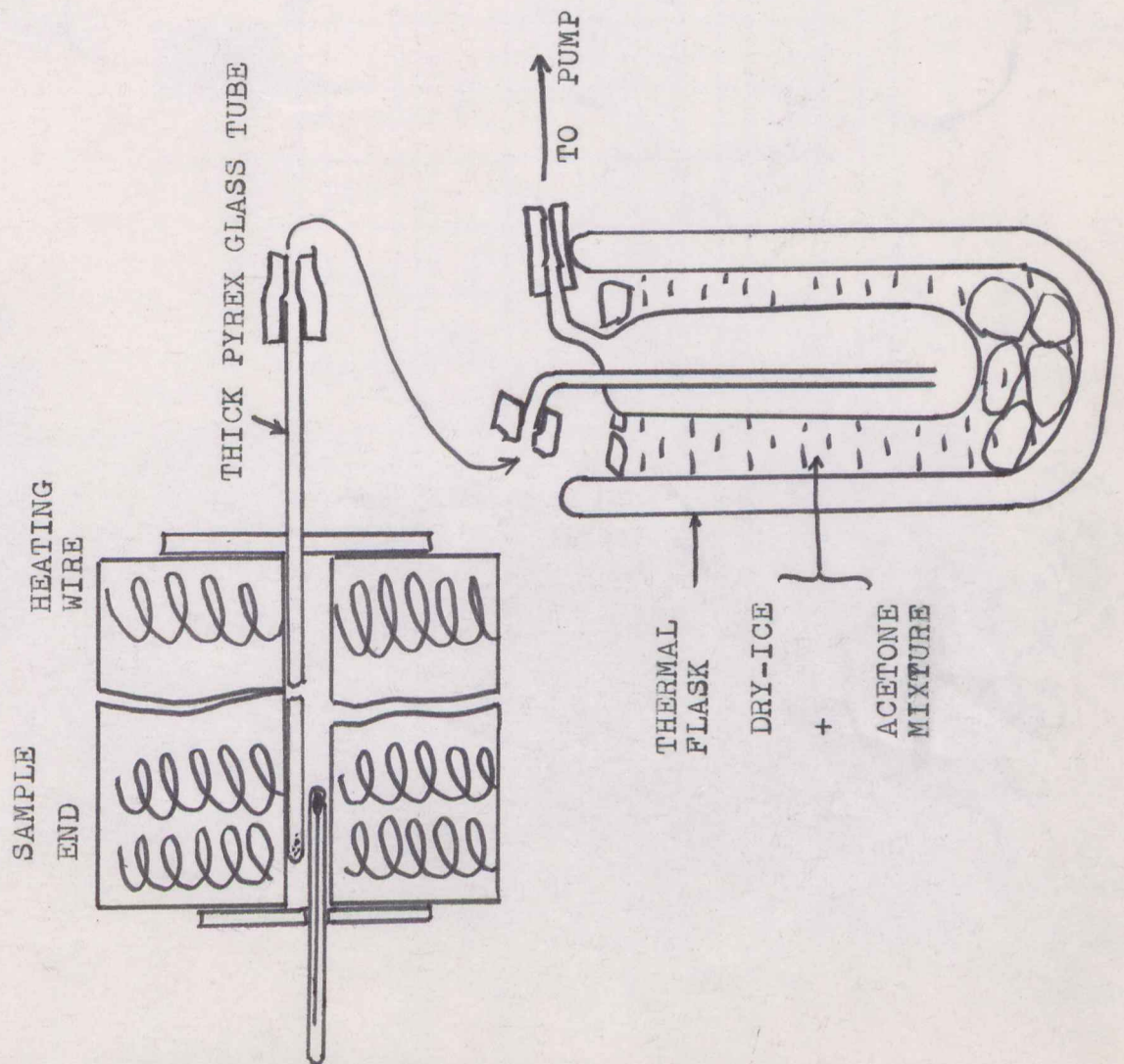
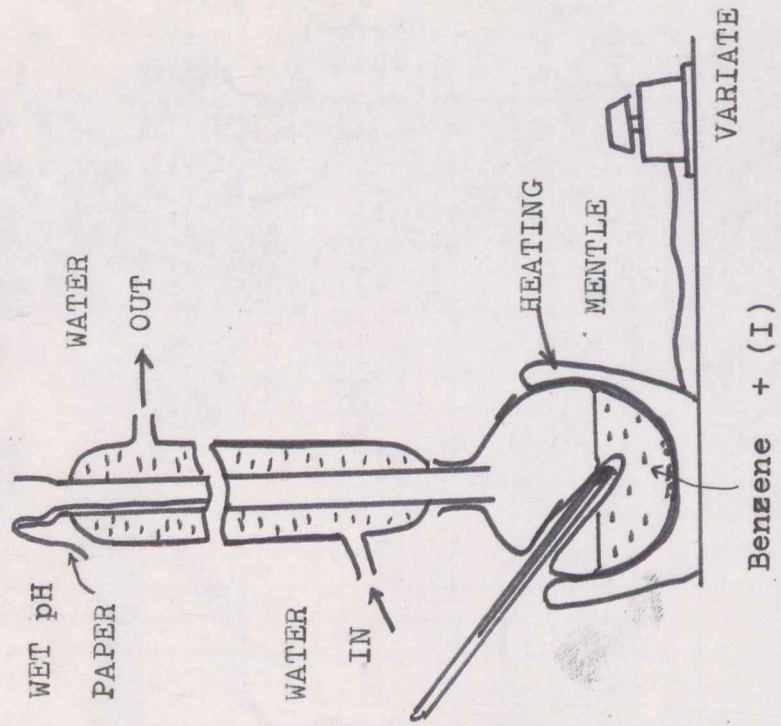


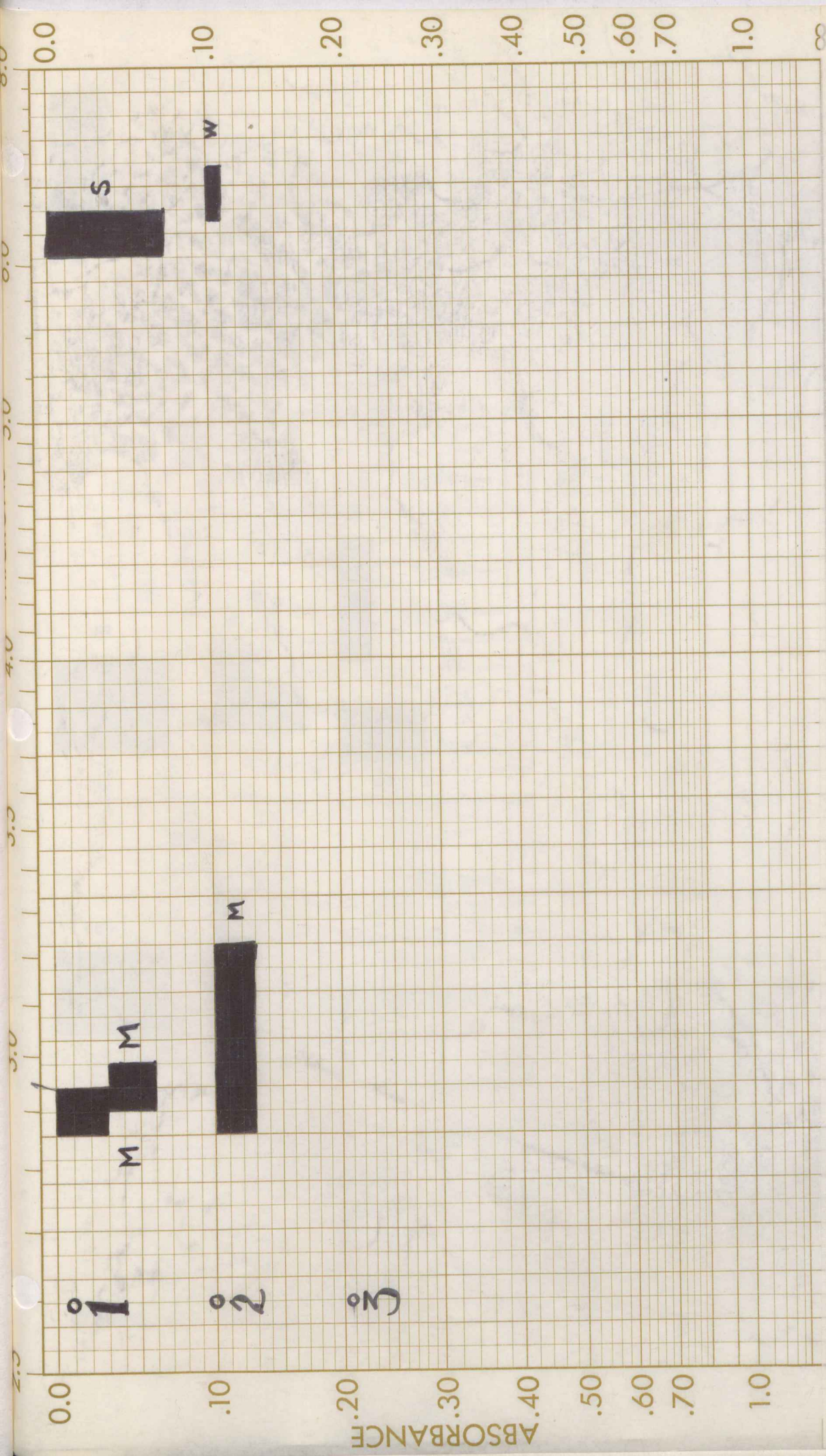
DIAGRAM 3

(see text pg. 19)

DIAGRAM I

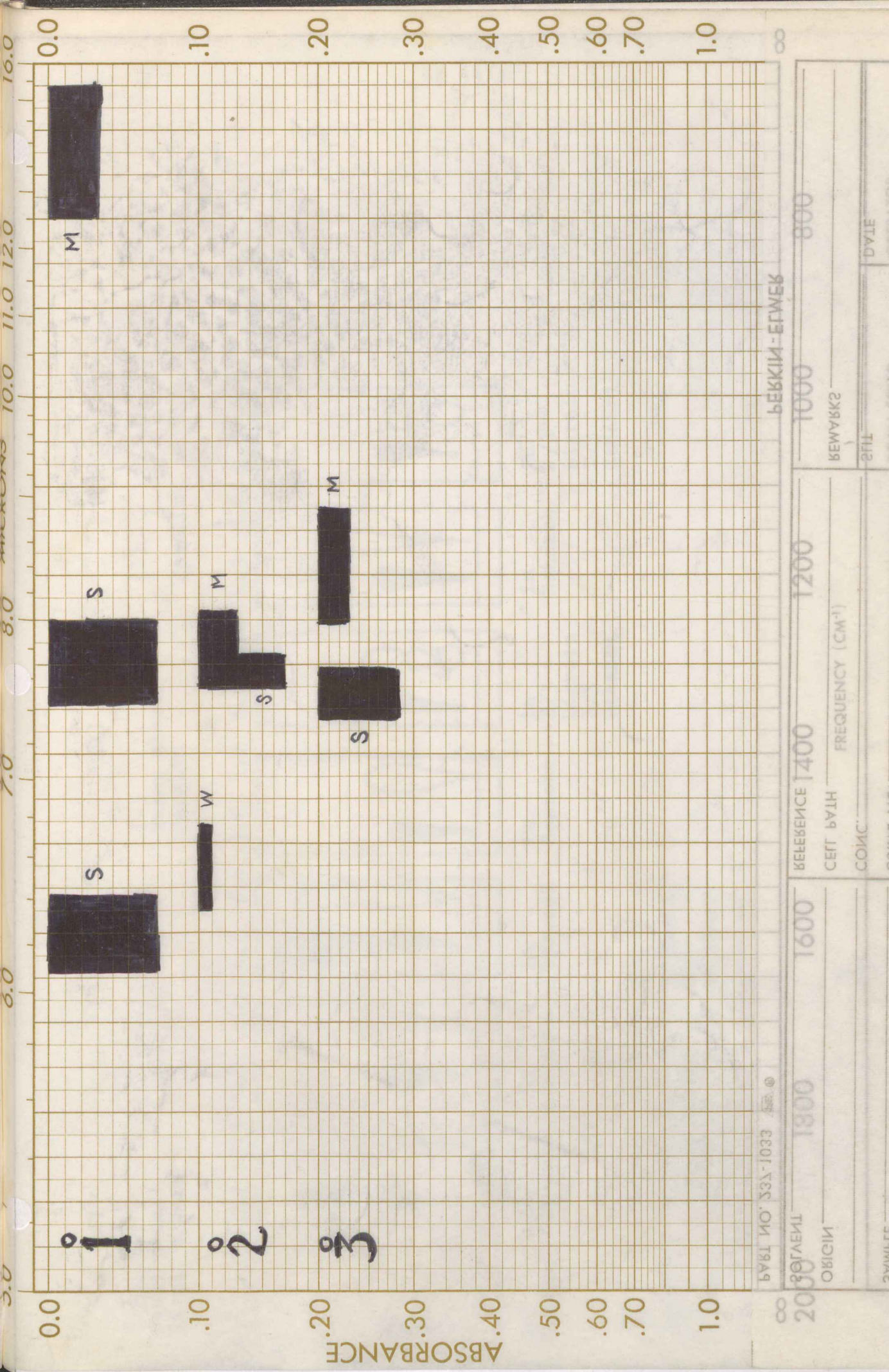
(see text pg. 6)

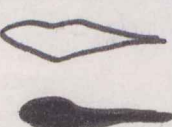

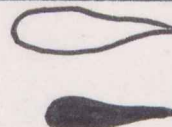
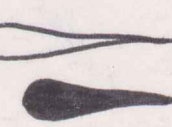
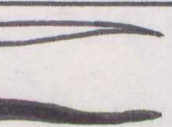

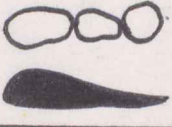
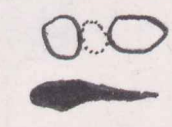




4000 3500 3000 2500 1500 800
 Wavenumber (cm⁻¹)

REFERENCE: PERKIN-ELMER
 SAMPLE: 2014E11
 ORIGIN: 2014E11
 CONIC: 2014E11
 SCAN SPEED: 2014E11
 DATE: 2014E11



(A)	(B)	(X)	(Y)
1 gm. (I) Raney nickel 20 ml. xylene	1 gm. (I) Raney nickel	(I) Raney nickel Decalin	(I) Decalin
4.1 4.3	4.1 4.6	3.9 4.7	4.3 5.8
			
in Benzene	in Benzene	in Benzene	in Benzene
7.7 7.5	8.1 7.6	5.0 5.0	3.8 3.6
			
in Ethanol	in Ethanol	in Ligroin 2/3 Ethanol	in Ligroin 2/3 Ethanol

in
2/3
Ligroin
1/3
Ethanol

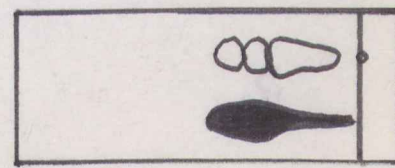
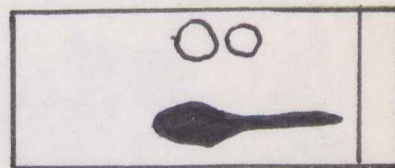


Plate 2

Key :

1,8-diaminonaphthalene as reference
is placed on the left represented
in solid color