ANALYTICAL REAGENTS FOR NITROGEN DIOXIDE

by

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CHAPTER I

INTRODUCTION

Nitrogen dioxide, NO_2, has a boiling point of 21.15°C. In gas form it is reddish-brown. The commercial brown liquid under pressure is called "Nitrogen Tetroxide". Actually this is an equilibrium mixture of NO_2 and the colorless N_2O_4:

$$2NO_2 \rightleftharpoons N_2O_4,$$

where N_2O_4 is the high pressure or low-temperature form, and the NO_2 is its dissociation product at lower pressures or higher temperatures.

The presence of nitrogen oxides (NO_x) in air is very largely derived from internal combustion engines. Dinitrogen trioxide, N_2O_3, exists in a negligible concentration in the atmosphere. Nitrogen monoxide, NO, is rapidly oxidized to NO_2 in the presence of atmospheric oxygen unless at low concentration levels, e.g., 50 parts per million (ppm), where it is considered not harmful to human body. Nitrogen dioxide can be perceived by smell in concentrations as low as 0.1 ppm. However, it is possible to get accustomed to it; by slowly increasing the NO_2 concentration the odor threshold may become as high as 25 ppm. In the human body, at 13 ppm, NO_2 starts to irritate respiratory mucous membrane and at 100-150 ppm after 30-50 minutes it may cause death due to oedema of the larynx (1).

In large amounts, NO_2 is readily recognized by its characteristic red-bown color. It has an absorption band in 390-500 nm region. NO_2 also gives a positive test with Griess reagent due to the presence of nitrite in the solution, which forms the basis of low-concentration colorimetric method of analysis (2).

In the original Griess reaction, sulfanilic acid was diazotized and then coupled with 1-naphthylamine in sulfuric acid solution to give the characteristic azo color. Warington (3) modified the Griess reaction by developing the color in a hydrochloric acid medium. Ilsovay (4) cited the advantages of performing the reactions in acetic acid solution. Weston (5) reported the Ilsovay method to be more rapid. He also stated that an excess of acetic acid affected reaction sensitivity to a lesser extent than an excess of hydrochloric acid.

The goal of this research has been to find a new reagent of better sensitivity and/or stability when used as a solid phase detector, e.g., when applied on filter paper, for NO_2.

It has been pointed out that the first step of the formation of azo dye in the presence of NO_2 involves the formation of a diazonium ion. This diazonium ion is very weakly electrophilic and can only couple with very reactive aromatic rings. A ring-substituted electron-withdrawing group increases electrophilicity of the diazonium ion. A ring-substituted electron-releasing group activates the coupler ring. Thus sulfanilic acid couples with 1-naphthylamine or N-(1-naphthyl)-ethylenediamine while benzenediazonium ion does couple with phenol but not with anisole. This laboratory (6) has succeeded in the synthesis of N-(4-aminophenylsulfonyl)-N'-(1-naphthyl)-ethylenediamine (7) and proved it to be very active toward the analysis of nitrite in solution and NO_2 gas in air. However, as a solid reagent this reagent is not stable in storage. The modification of using a quaternary ammonium group attached to the naphthylamine moeity may hopefully improve its stability while retaining the same electron-withdrawing feature. It was pointed out that the azo dyes formed by (p-aminophenyl)-trimethylammonium chloride have exceptional color stabilities

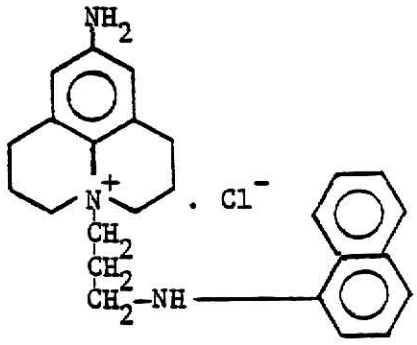
compared to other azo dyes (8, 9). Color stability would be extremely important in a passive monitoring device.

In this paper the author tried to synthesize a new compound that has a quaternary ammonium group serving both as an electron-withdrawing group to the diazo compound and also as a linkage or as part of an ion pair to the coupler moiety, such as: (a) 9-amino-N-(3-(1-naphthylamino)-propyl)-julolidinium chloride, (b) (p-aminophenyl)-dimethyl-(3-(1-naphthylamino)-propyl)-ammonium chloride, (c) (p-aminophenyl)-trimethylammonium 1-naphthyl-aminomethanesulfonate, or (d) (p-aminophenyl)-trimethylammonium 2-(1-naphthylamino)-ethylaminomethanesulfonate and also report a quantitative test for NO_2 using phloroglucinol.

CHAPTER II

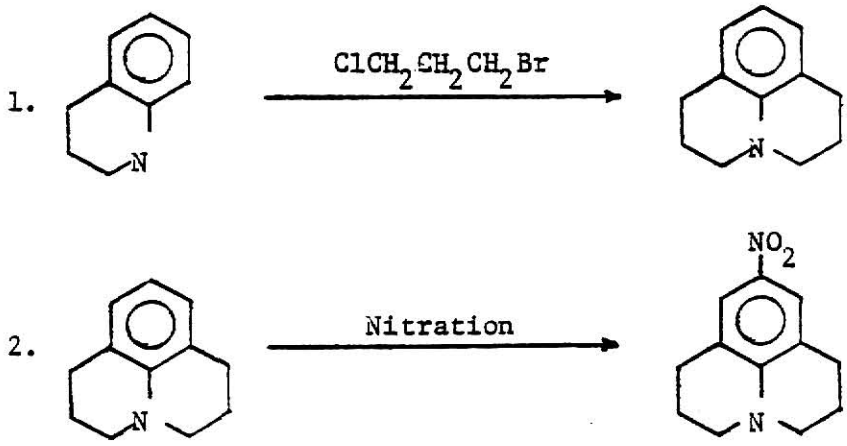
ATTEMPTED SYNTHESIS OF 9-AMINO-N-(3-(1-NAPHTHYLAMINO)-PROPYL)-JULOLIDINIUM CHLORIDE

This chapter describes the attempt to synthesize 9-amino-N-(3-1-naphthylamino)-propyl)-julolidinium chloride,

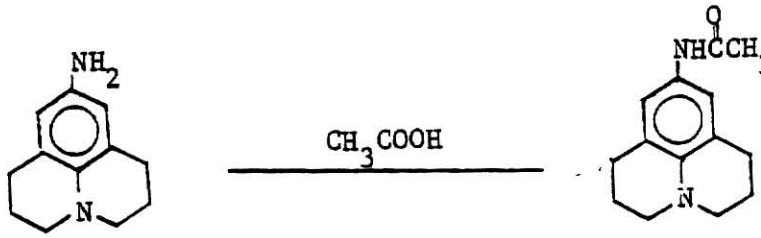


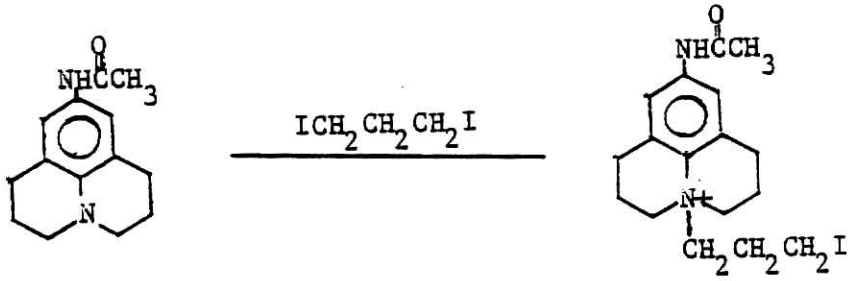
This compound is presumably capable of forming an azo dye by itself with nitrous acid. The 9-position amino group on julolidine skeleton diazotizes in the presence of nitrous acid then intermolecularly couples with the naphthalene moiety at the para position to form a characteristic azo color. The quaternary ammonium group serves to withdraw electrons while the secondary amino group on the naphthalene skeleton serves as an electron donor. Both are capable of facilitating the formation of the azo dye.

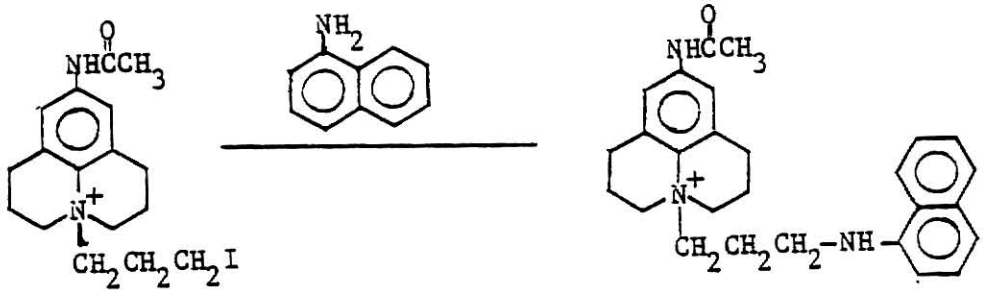
Proposed synthesis route is as follows:

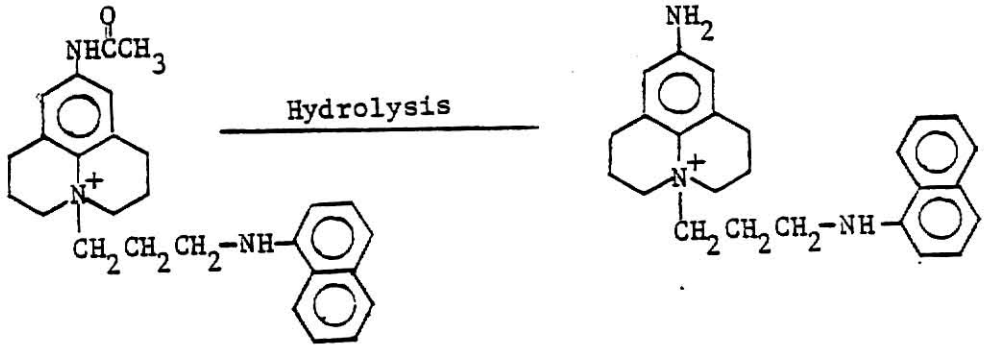


3. 
NO2
N
Reduction
NH2
N

4. 
NH2
N
CH3COOH
O
NHCCH3
N

5. 
O
NHCCH3
N
ICH2CH2CH2I
O
NHCCH3
N+
CH2CH2CH2I

6. 
O
NHCCH3
N+
CH2CH2CH2I
NH2
O
NHCCH3
N+
CH2CH2CH2-NH

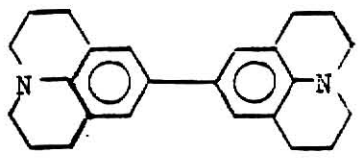
7. 
O
NHCCH3
N+
CH2CH2CH2-NH
Hydrolysis
NH2
N+
CH2CH2CH2-NH

Preparation of Julolidine

A mixture of 13.3 g (0.10 mole) of 1,2,3,4-tetrahydroquinoline and 80 g (0.51 mole) of trimethylene chlorobromide is placed in a 100-ml round-bottomed flask attached to a reflux condenser. Heat at 150-160°C for 20 hours. Cool down. A solution of 10 ml concentrated HCl in 90 ml H_2O is added. Remove excess trimethylene chlorobromide by steam distillation. The acidic residue is made alkaline with 40% NaOH solution (about 25 ml) and extracted with two 30-ml portions of ether. The ethereal solution is washed with 30 ml of water and dried over NaOH pellets. Evaporate the ether and distill the residue under reduced pressure. Collect the portion that boils at 98-108°C (at about 1 mm Hg). The yield is 13 g (75%); m.p. 39-40°C. The n.m.r. spectrum (in $CDCl_3$/TMS) has signals at δ = 2.0 ppm (multiplet, area 4 protons, 2- and 6- position), 2.7 ppm (triplet, area 4 protons, 3- and 5- positions), 3.1 ppm (triplet, area 4 protons, 1- and 7-positions) and 6.15-6.82 ppm (multiplet, area 3 protons, 8-,9- and 10-positions).

Attempted Nitration of Julolidine

Nitration of juoloidine has been tried in different ways by using (a). mixed acid of H_2SO_4 and HNO_3, (b). acetic anhydride and $Cu(NO_3)_2.3H_2O$ and (c). NO_2BF_4 in tetramethylene sulfone, in ice bath. The reaction products are either a tar or a red compound which NMR and MASS show to be a dimer of julolidine,



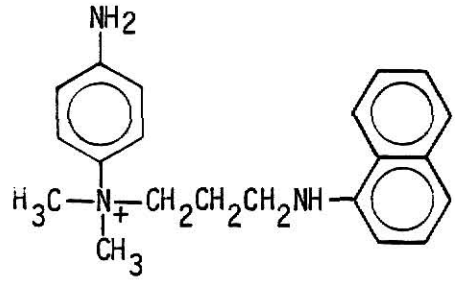
Nitrosation of juololidine produces the same red compound.

Preparation of 9-nitrojulolidine through double ring closure of p-nitroaniline with large excess of trimethylene chlorobromide has also been attempted. But the deactivating group, NO_2, evidently makes it unfeasible.

CHAPTER III

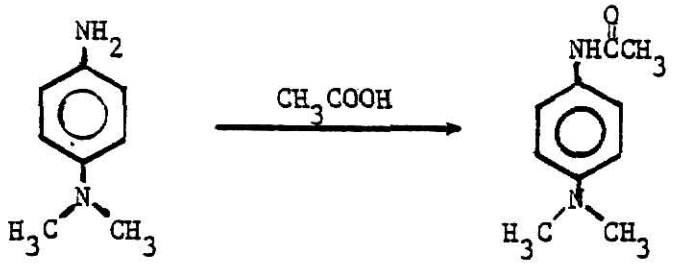
ATTEMPTED SYNTHESIS OF (p-AMINOPHENYL)-DIMETHYL-(3-(1-NAPHTHYLAMINO)-PROPYL)-AMMONIUM CHLORIDE

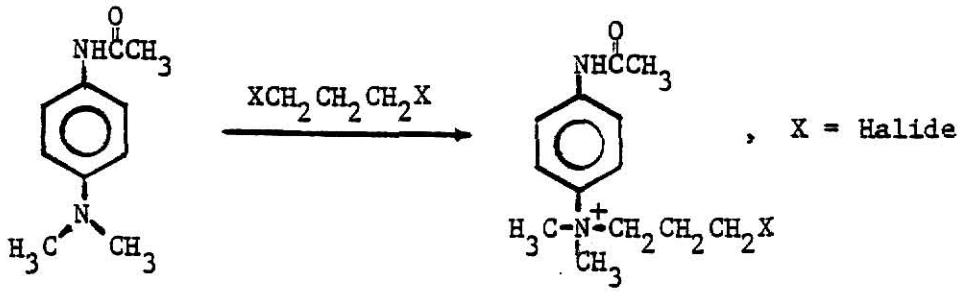
This chapter describes the attempted synthesis of (p-aminophenyl)-dimethyl-(3-(1-naphthylamino)-propyl)-ammonium chloride,

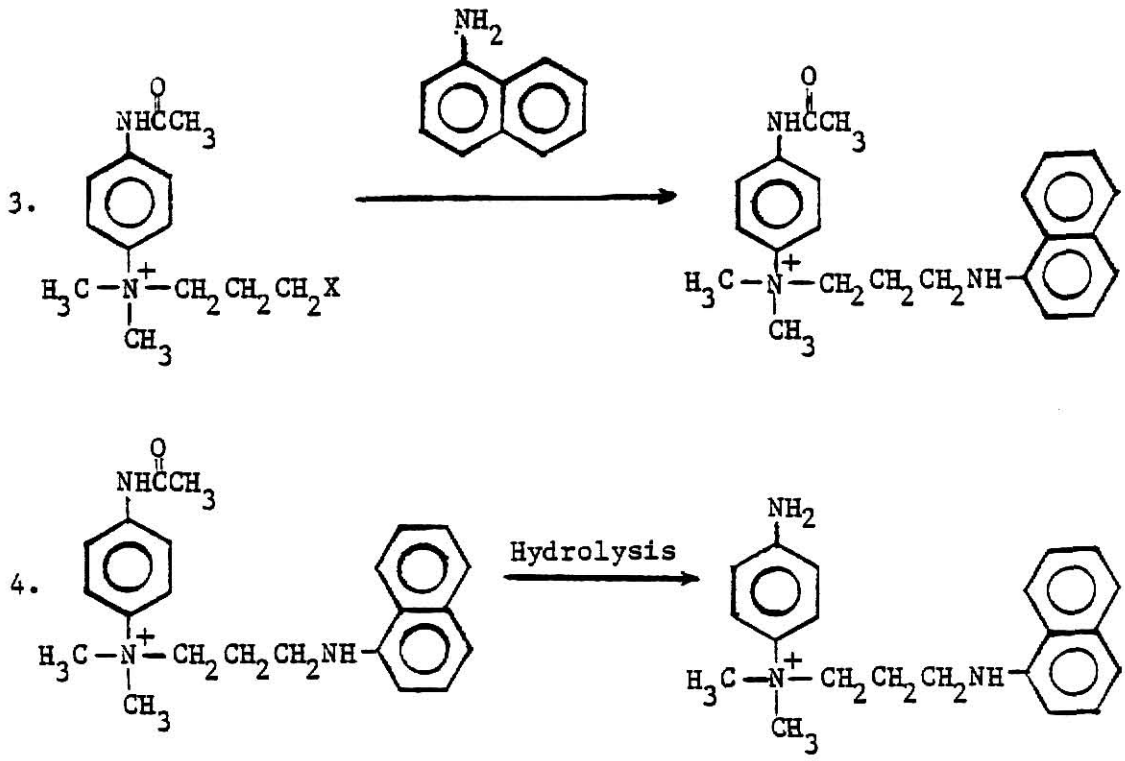


The quaternary ammonium group again is the electron-withdrawing group favoring diazotization and the subsequent coupling reaction of the amino group para to it. The secondary amino group at the other end directs the coupling reaction to occur at 4-position of the naphthalene.

The proposed route starts with N,N-dimethyl-p-phenylenediamine dihydrochloride in a four-step synthesis:

1. 

2. 



Acetylation of N,N-dimethyl-p-phenylenediamine

A mixture of 5 g. (0.0239 mole) of N,N-dimethyl-p-phenylenediamine dihydrochloride, 20 ml of glacial acetic acid and 4 ml of acetic anhydride is heated in a 100-ml round-bottomed flask, equipped with a reflux condenser. The starting material dissolves gradually as the reaction proceeds and is completely gone after 15 minutes of boiling. Let the reaction mixture boil for another 15 minutes. Cool and pour with stirring into 200 ml of water. Neutralize with solid $NaHCO_3$. Approximately 35 g. of $NaHCO_3$ is needed. The product precipitates as a brown solid. Extract with 100-ml portions of ether three times. Combine the ethereal extracts. Wash with 5% NaOH and dry over anhydrous Na_2SO_4. Evaporate the ether to obtain 2.2 g. leaflike white product. The n.m.r. spectrum (in DMSO-d_6) has signals at δ = 2.00 ppm (singlet, area 3 protons, acetyl $-CH_3$), 2.82 ppm (singlet, area 6 protons, 2 methyl groups), 6.43 - 7.50 ppm

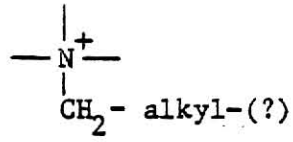
(quartet, area 4 protons, aromatic hydrogens) and 9.50 ppm (singlet, area 1 proton, amide NH). The i.r. spectrum (KBr pellet) has a strong absorption band at 1670 cm^{-1} (C = O stretching).

Freeing the N,N-dimethyl-p-phenylenediamine, by using 40% NaOH, prior to the acetylation gives a slightly higher yield. Neutralization of the amine salt product with 40% NaOH instead of $NaHCO_3$ powder gives substantially the same yield and purity. If a purer product is needed it can be re-crystallized from ethanol or water. The result is white needle-like crystals, but the yield is low.

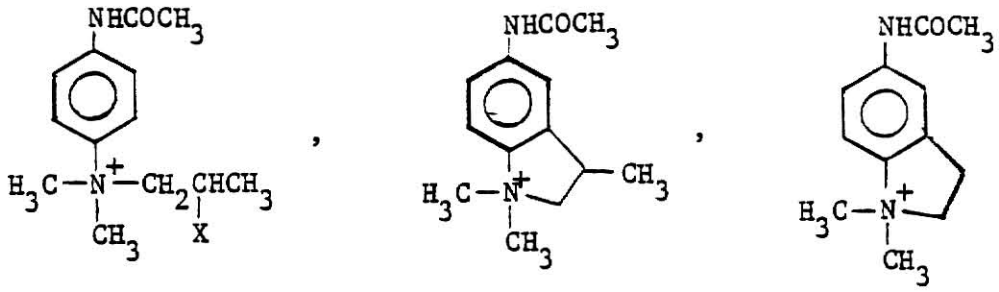
Attempted Synthesis of (p-Acetylaminophenyl)-dimethyl-3-iodopropylammonium halide

The reaction of p-(N,N-dimethyl)-acetanilide with dihalopropane is a complicated case. To avoid the dihalide from reacting on both sides with a tertiary amine different mole ratios of dihalide (ranging from a 20% excess to a 300% excess), different reaction time and temperature (ranging from room temperature up to a 16-day reflux) in different solvents (EtOH, EtOH + ether, and benzene) have been tried. The dihalide is added all at once or dropwise through a dropping funnel. 1,3-Diiodopropane and 1,3-dibromopropane have both been tried. The results are either unreacted starting material, if the reaction condition is mild, or a white gummy unidentifiable product, if stronger condition is used. Upon study of the n.m.r. spectra of the white gummy products, they all give signals at δ = 7.6 - 8.0 ppm, either singlet or doublet (aromatics), 2.1 ppm singlet (acetyl $-CH_3$), 3.6 ppm singlet ($N-CH_3$'s) and several methylene groups at 3.2 - 4.4 ppm and/or 1.7 - 2.2 ppm. This information suggests that alkyl

has attached to the desired nitrogen forming a quaternary ammonium salt on one end. The characteristic quartet pattern of the para-disubstituted benzene disappears as a result of the quaternary ammonium electron-withdrawal, but the other end of the alkyl halide also has some unknown and undesirable changes.

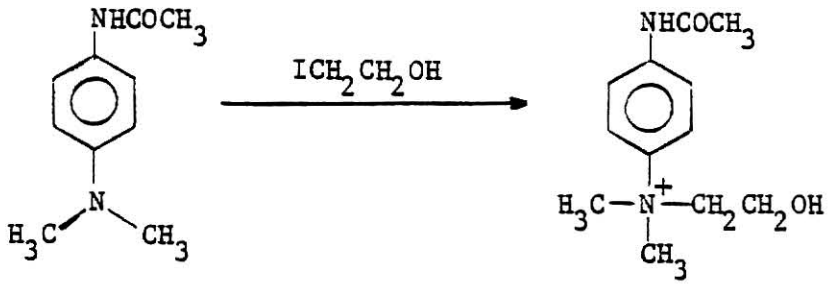


This compound does not react with either 1-naphthylamine or N-(1-naphthyl)-ethylenediamine. Also, it does not pick up the much more reactive morpholine or pyrrolidine which have characteristic n.m.r. spectra. We conclude the unknown product to be one, or more likely a mixture, of the following undesirable compounds:



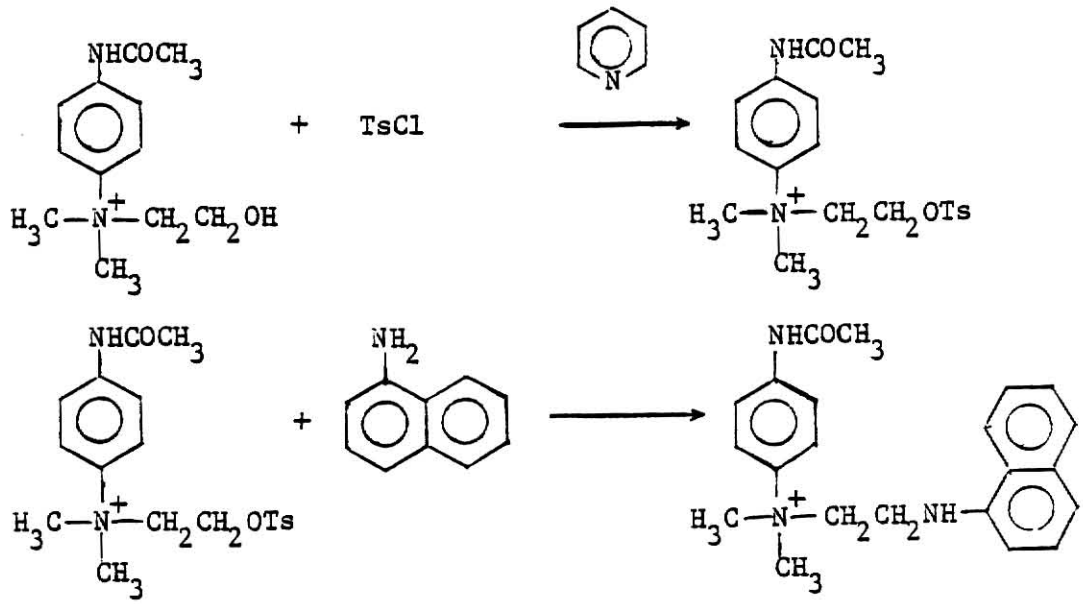
Preparation of (p-Acetylaminophenyl)-dimethyl-(2-ethoxy)-ammonium Iodide

Since the dihalopropane cannot serve as a linkage between N,N-dimethyl-amino-p-anilide and 1-naphthylamine, monohaloalkane is proposed to react with N,N-dimethyl-p-anilide first. After a quaternary ammonium salt is formed the other end of the alkane can be modified then further reactions may hopefully be done. Therefore 2-iodoethanol was proposed.



Dissolve 2.90 g. (0.0163 mole) of N,N-dimethylamino-p-anilide in 25 ml ethanol in a 100-ml round-bottomed flask fitted with a reflux condenser on top of which is mounted a Drierite tube. Add 3.52 g (0.0205 mole) of 2-iodoethanol and reflux for 20 hours. Transfer the deep red solution into a 150-ml beaker. After cooling to room temperature, 75 ml of ether is added. A white milky precipitate forms at once and soon turns into glass precipitated at the bottom. Allow it to stand in an ice bath for two hours. Decant the supernatant liquid. Scratch and break up the glass, pulverize with a small amount of ether. Repeat several times. The crude product weighs 3.00 g. Recrystallize from 15 ml hot ethanol, yield 2.38 g. of white solid. M.P. 156 - 158°C. The n.m.r. spectrum (in DMSO-d_6) has signals at δ = 2.06 ppm (singlet, area 3 protons, $COCH_3$), 3.46 ppm (triplet, area 2 protons, N^+CH_2), 3.65 ppm (singlet, area 6 protons, $N^+(CH_3)_2$), 4.00 ppm (triplet, area 2 protons, CH_2), 4.77 ppm (singlet, area 1 proton, OH), 7.80 ppm (singlet, area 4 protons, aromatic hydrogens) and 10.20 ppm (singlet, area 1 proton, NH).

Attempted Synthesis of (p-Acetylaminophenyl)-dimethyl-(2-(1-naphthylamino)-ethyl)-ammonium Iodide



Purification of p-Toluenesulfonyl Chloride (10): 10 Grams of impure tosyl chloride is dissolved in the minimum amount of chloroform (about 25 ml) and the solution is diluted with 5 volumes of petroleum ether to precipitate impurities (largely tosic acid). The solution is separated, treated with active charcoal and filtered again. Evaporate under reduced pressure to give 6.34 g. of fine white crystals of tosyl chloride.

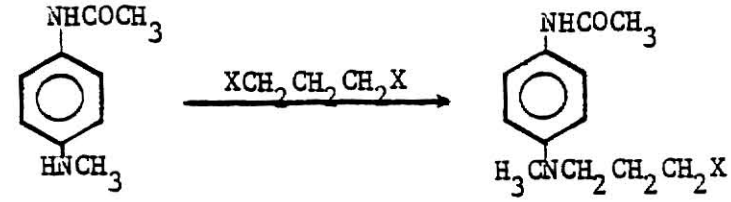
Purification of Pyridine: 150 mL technical grade pyridine is refluxed with 10 g. of BaO powder for one hour. Distill and collect the fraction at temperature higher than 50° C. Store in a brown bottle over 4A molecular sieve. Filter before use.

The reaction between alcohols and sulfonyl chlorides to form alkyl sulfonates is known. The sulfonate ion, being a good leaving group in nucleophilic substitution, can be replaced by an amine. In the case of (p-acetylaminophenyl)-dimethyl-(2-ethoxy)-ammonium iodide, which bears both a hydroxyl group and a quaternary ammonium moiety, we tried many different reaction conditions but the desired reactions could not be obtained. First

the side product, HCl in the first reaction, could not be separated as the pyridine hydrochloride salt. It is presumably due to ion exchange between iodide and chloride. Second, the β-elimination occurs with the breaking of the quaternary ammonium structure. There is evidently no linkage between naphthylamine and the quaternary ammonium salt. Finally, compare the structures of $^{+}N\text{-}CH_2CH_2OTs$ and $^{+}CH_2CH_2CH_2X$ from the previous chapter, probably the same situations might have also been encountered since OTs is an even better leaving group than a halide. We assume the said compound, or more specific, the quaternary ammonium ion that bears both a benzene ring and an alkyl-Y (where Y = leaving group) group, cannot exist even for a short time. N-(1-Naphthyl)-ethylenediamine was also tried in addition of 1-naphthylamine, but the result was the same.

The assumption that the mid-product, $^{+}N\text{-}CH_2CH_2Y$, can not exist does not imply the final product can not be synthesized. Connecting the (p-acetylaminophenyl)-methylamine and the 1-naphthylamine by a $XCH_2CH_2CH_2X$ then making it a quaternary ammonium salt might work. A suggested synthesis route for continuation would be as follows:

1.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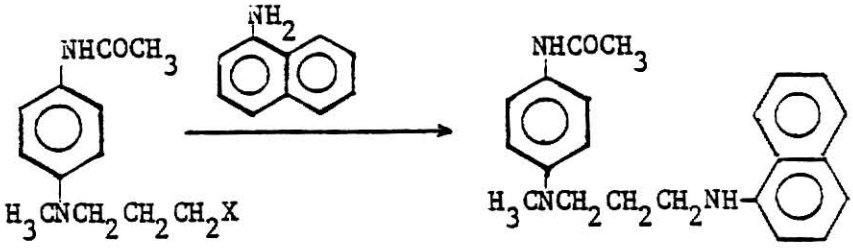
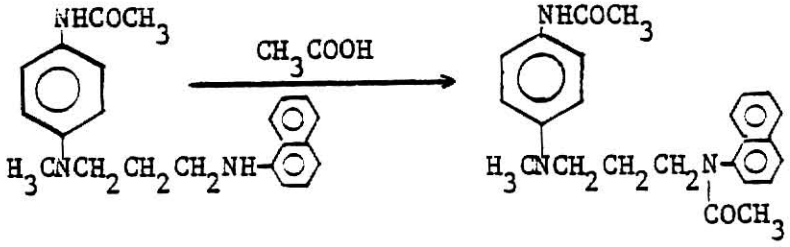
HNCH3
XCH2 CH2 CH2X
NHCOCH3
H3CNCH2 CH2 CH2X

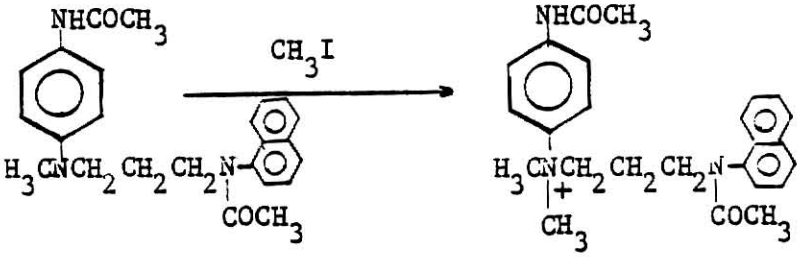
2.


NH2
NHCOCH3
H3CNCH2 CH2 CH2X
NHCOCH3
H3CNCH2 CH2 CH2NH

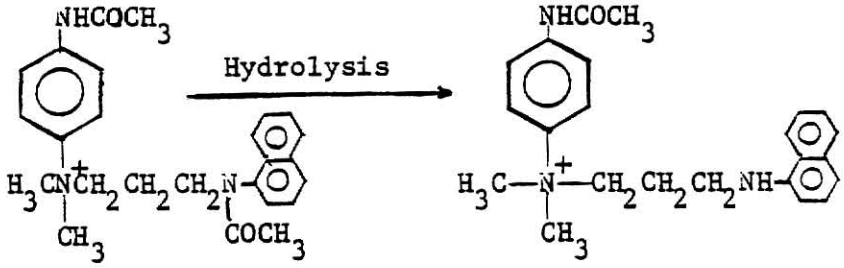
3.


NHCOCH3
CH3COOH
H3CNCH2 CH2 CH2NH
NHCOCH3
H3CNCH2 CH2 CH2N
COCH3

4.


NHCOCH3
CH3I
H3CNCH2 CH2 CH2N
COCH3
NHCOCH3
H3CNCH2 CH2 CH2N
CH3
COCH3

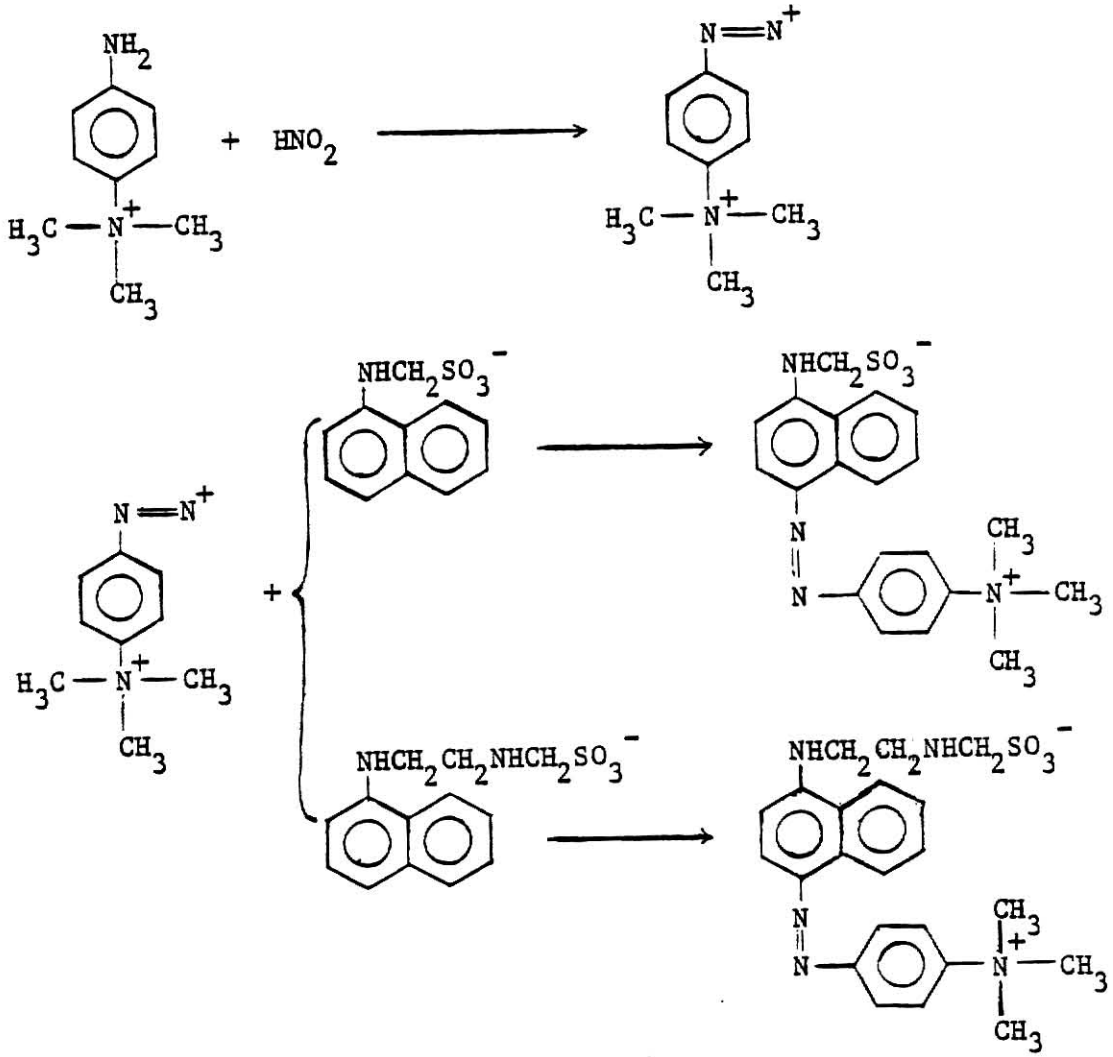
5.


NHCOCH3
Hydrolysis
H3CNCH2 CH2 CH2N
CH3
COCH3
NHCOCH3
H3C—N—CH2 CH2 CH2NH
CH3

CHAPTER IV

SYNTHESIS OF SODIUM 1-NAPHTHYLAMINOMETHANESULFONATE AND SODIUM 2-(1-NAPHTHYLAMINO)-ETHYLAMINOMETHANESULFONATE AND THEIR COUPLING ACTIVITIES

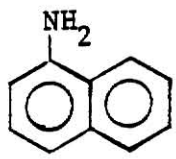
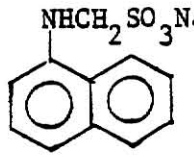
Sodium 1-naphthylaminomethanesulfonate and sodium 2-(1-naphthylamino)-ethylaminomethanesulfonate both have an amino substituent at 1-position on naphthalene which favors the diazo coupling reaction at 4-position. The diazo component compound to be used is (p-aminophenyl)-trimethylammonium chloride. The expected reactions leading to the formation of azo dyes are:



PART I. SYNTHESIS

Preparation of Sodium 1-Naphthylaminomethanesulfonate

1. $HCHO + NaHSO_3 + H_2O \longrightarrow HOCH_2SO_3Na \cdot H_2O$

2. $HOCH_2SO_3Na \cdot H_2O +$   $\cdot H_2O$

Three grams (0.0288 mole) of $NaHSO_3$ is dissolved in a solution of 2.2 ml 37% HCHO (technical grade, approximately 0.03 mole) in 7.8 ml H_2O. With stirring, heat the reaction mixture to 70° C. Sodium bicarbonate reacts with formaldehyde at room temperature with moderate release of heat, but the reaction is still incomplete even after 24 hours. The unreacted $NaHSO_3$ can decompose the latter-added 1-naphthylamine to 1-naphthol or undesired sulfonation biproduct (11, 12). Fortunately the complete reaction can be achieved at 60 - 70°C in a few minutes. Evaporate to dryness to obtain 4.15 g. $HOCH_2SO_3Na.H_2O$ as a white solid. The n.m.r. spectrum has sharp signals at δ = 4.4 ppm (singlet, CH_2) and 4.5 ppm (singlet, OH).

Purification of 1-naphthylamine is done by sublimation of the impure black material in a stream of nitrogen. Pure white crystaline 1-naphthylamine can be obtained easily in this way.

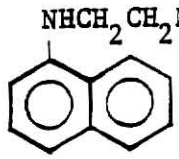
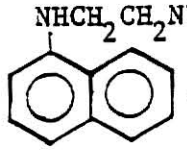
In a 50-ml round-bottomed flask is placed a solution of 1.16 g. (0.00811 mole) of purified 1-naphthylamine in 20 ml of $EtOH/H_2O$ (1:1). With stirring, 1.08 g (0.00711 mole) of $HOCH_2SO_3Na.H_2O$ is added. 1-Naphthylamine is not soluble in water while the latter is not soluble in ethanol. But both are soluble in 50% ethanol. Stirring is continued at room temperature

for 14 hours then at 50°C for another 20 hours (attempted reaction at higher temperatures for a shorter time has been tried but the reaction mixture turns black). Evaporate to dryness. Pulverize with two 45-ml portions of 95% EtOH. 0.87 g. product is obtained as white fine solid. The n.m.r. spectrum (in DMSO-d_6), Fig. 1. has signals at δ = 4.25 ppm (doublet, coalesced to singlet upon treatment with D_2O, area 2 protons, CH_2), 6.40 ppm (triplet, merged with H_2O peak into a sharp singlet upon treatment with D_2O, area 1 proton, NH) and 6.77 - 8.50 ppm (multiplet, area 7 protons, aromatics).

The attempted synthesis of the similar compound, 2-(1-naphthylamino)-ethanesulfonate, was tried through the reaction of 1-naphthylamine with $BrCH_2CH_2SO_3Na$. Various reaction conditions were used including the use of $AgBF_4$ in EtOH or DMF (dimethylformamide). However, the desired reaction was not observed.

Preparation of Sodium 2-(1-Naphthylamino)-ethylaminomethanesulfonate

1. $HCHO + NaHSO_3 + H_2O \longrightarrow HOCH_2SO_3Na \cdot H_2O$

2. $HOCH_2SO_3Na \cdot H_2O +$  $\longrightarrow$  $\cdot H_2O + H_2O$

Dissolve 3.89 g. (0.0150 mole) of N-(1-naphthyl)-ethylenediamine dihydrochloride in 30 ml hot water. Free the amine by adding 40% NaOH solution until pH approximately 11. Cool down and extract with three 100-ml portions of ether. Wash the combined ethereal extracts with three 50-ml portions of water. Evaporate under reduced pressure to obtain 2.55 g. (91% theoretical yield) of yellow liquid.

Technical grade 37% HCHO solution is diluted ten-fold with water. One hundred mililitres of this solution after dilution contains about 4 g. of HCHO. A solution of 1.04 g (0.0100 mole) of $NaHSO_3$ in 10 ml diluted HCHO solution is heated to 70°C then cooled to room temperature. Add this formaldehyde-bisulfite solution through a dropping funnel to the above N-(1-naphthyl)-ethylenediamine in 10 ml of EtOH while stirring. Addition takes about 20 - 30 minutes. Stir at room temperature for another one hour. Evaporate the ethanol and biproduct water under reduced pressure. The residue is an oily yellow semisolid. Wash several times with ether to remove the excess amine. The product remains as white solid which weighs 2.95 g. (92% of theoretical yield based on the amount of $NaHSO_3$ used). The n.m.r. spectrum (in DMSO-d_6), Fig. 2, has signals at δ = 3.20 ppm (multiplet, area 4 protons, NCH_2CH_2N), 3.40 - 3.67 ppm (broad singlet, upon treatment with D_2O this broad signal splits into two sharp peaks, 3.58 ppm, area 2 protons, NCH_2S, and 3.90 ppm, HOD and NH's), 6.10 ppm (broad, merged into 3.90 ppm sharp peak after treatment with D_2O, area 1 proton, aromatic NH) and 6.40 - 8.40 ppm (multiplet, area 7 protons, aromatic hydrogens).

The formation of the formaldehyde-bisulfite addition product must go to completeness before reacting with N-(1-naphthyl)-ethylenediamine. Presumably this is also due to the sulfonation on naphthalene as a result of Bucherer reaction (11, 12).

Attempted synthesis of the similar compound, sodium 2-(1-naphthyl-amino)-ethylaminoethanesulfonate, through the route of $BrCH_2CH_2SO_3Na$ failed. Both ethanol and pyridine were tried as solvents. The product presumably was the amine sulfonic acid salt.

Fig. 1. NMR spectrum of sodium 1-naphthylaminomethanesulfonate (DMSO-d_6, TMS)

a. 3.4 ppm, H_2O

b. 4.25 ppm, CH_2

c. 6.40 ppm, NH

d. 6.77 - 8.50 ppm, Aromatic Hydrogens

Upon treatment with 2 drops of D_2O, NH and H_2O merged into 3.65 ppm and CH_2 coalesced into singlet (top figure).

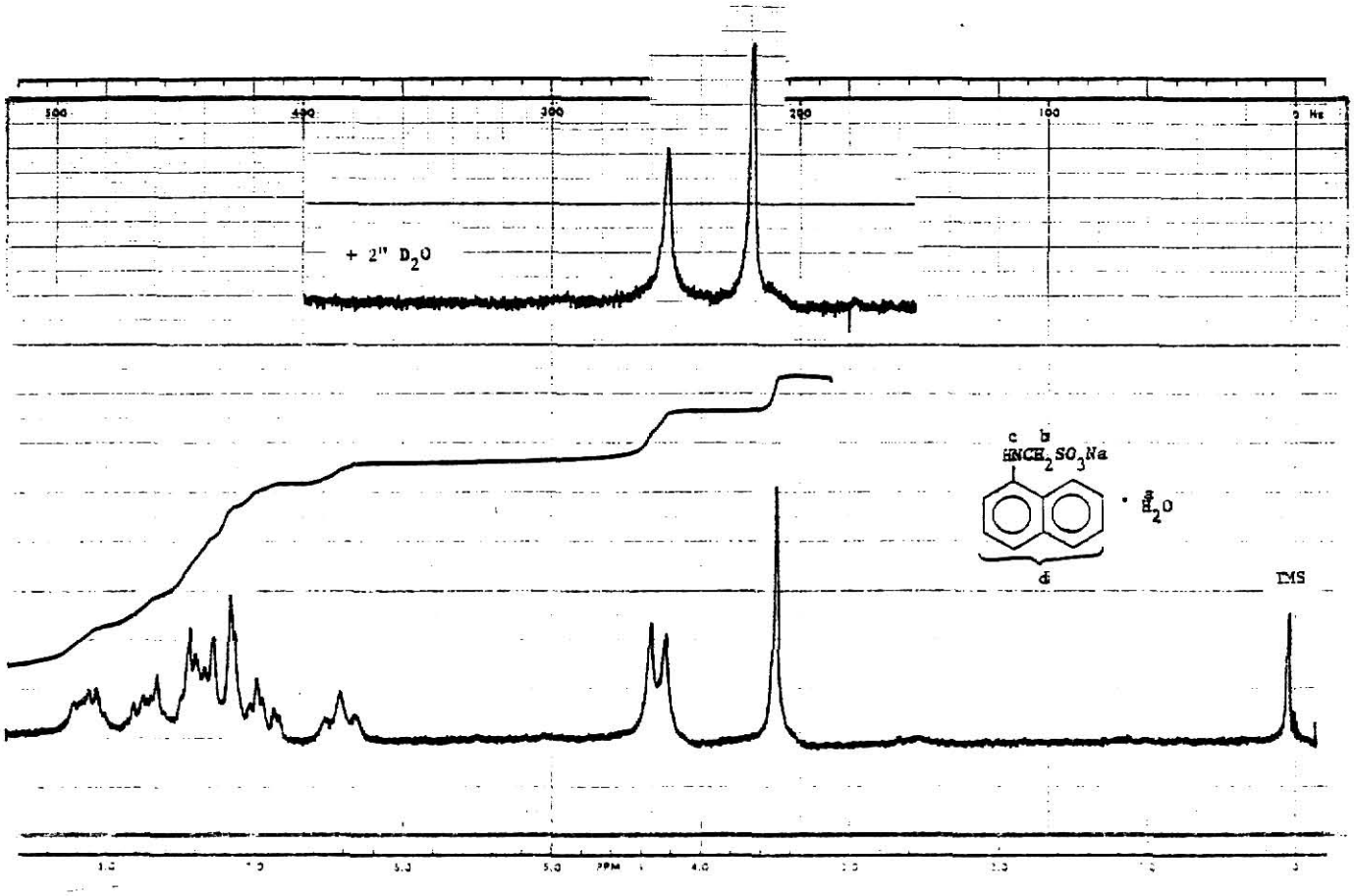

+ 2" D_2O
c b
$HNCH_2SO_3Na$
a
H_2O
d
TMS
PPM

Fig. 2. NMR spectrum of sodium 2-(1-naphthylamino)-ethyl-methanesulfonate

Top: in DMSO-d_6, TMS

a. 3.20 ppm, NCH_2CH_2N

b. 3.55 ppm, CNHC, NCH_2S and H_2O

c. 6.0 ppm, Aromatic NH

d. 6.40 - 8.40 ppm, Aromatic Hydrogens

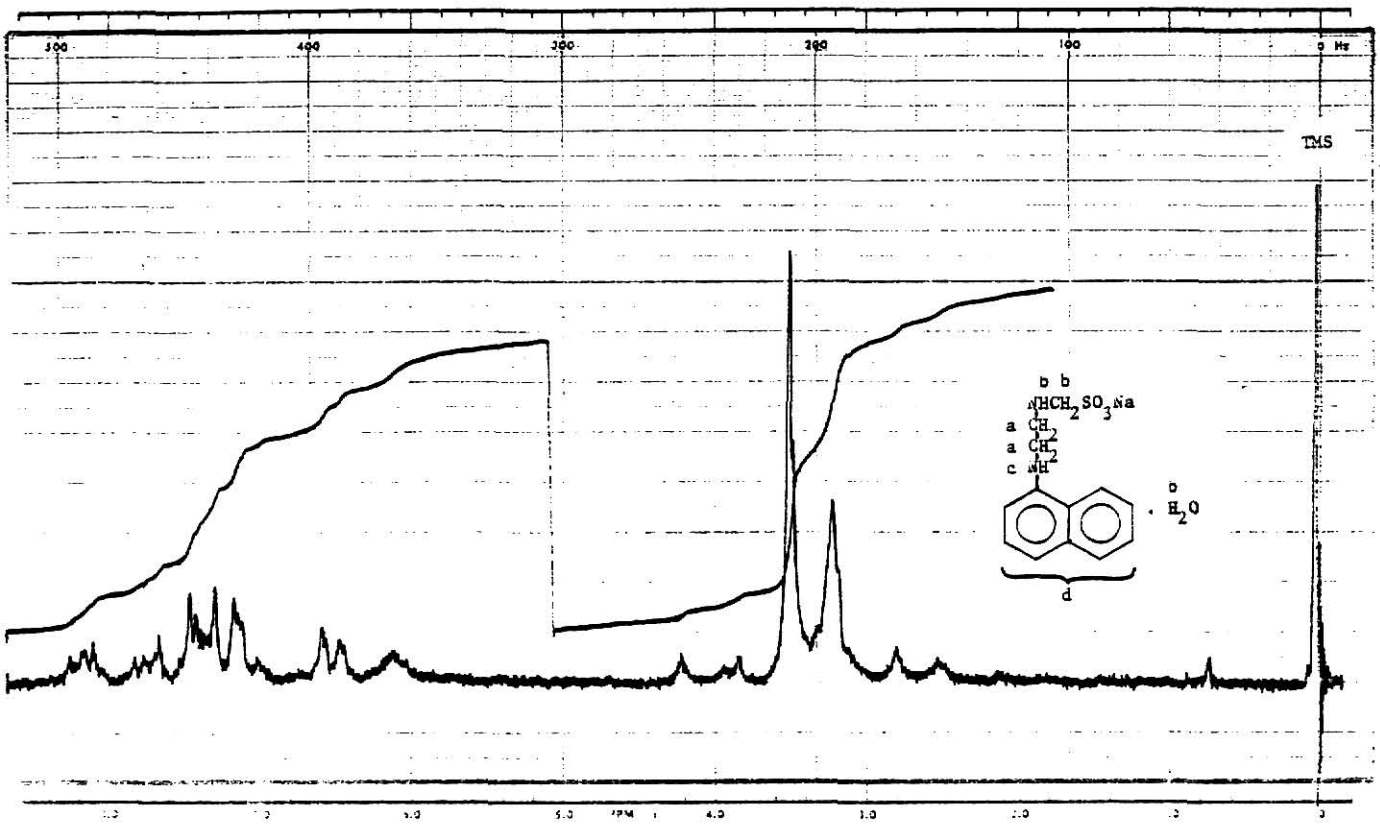
Bottom: in DMSO-d_6 + 6 drops of D_2O, TMS

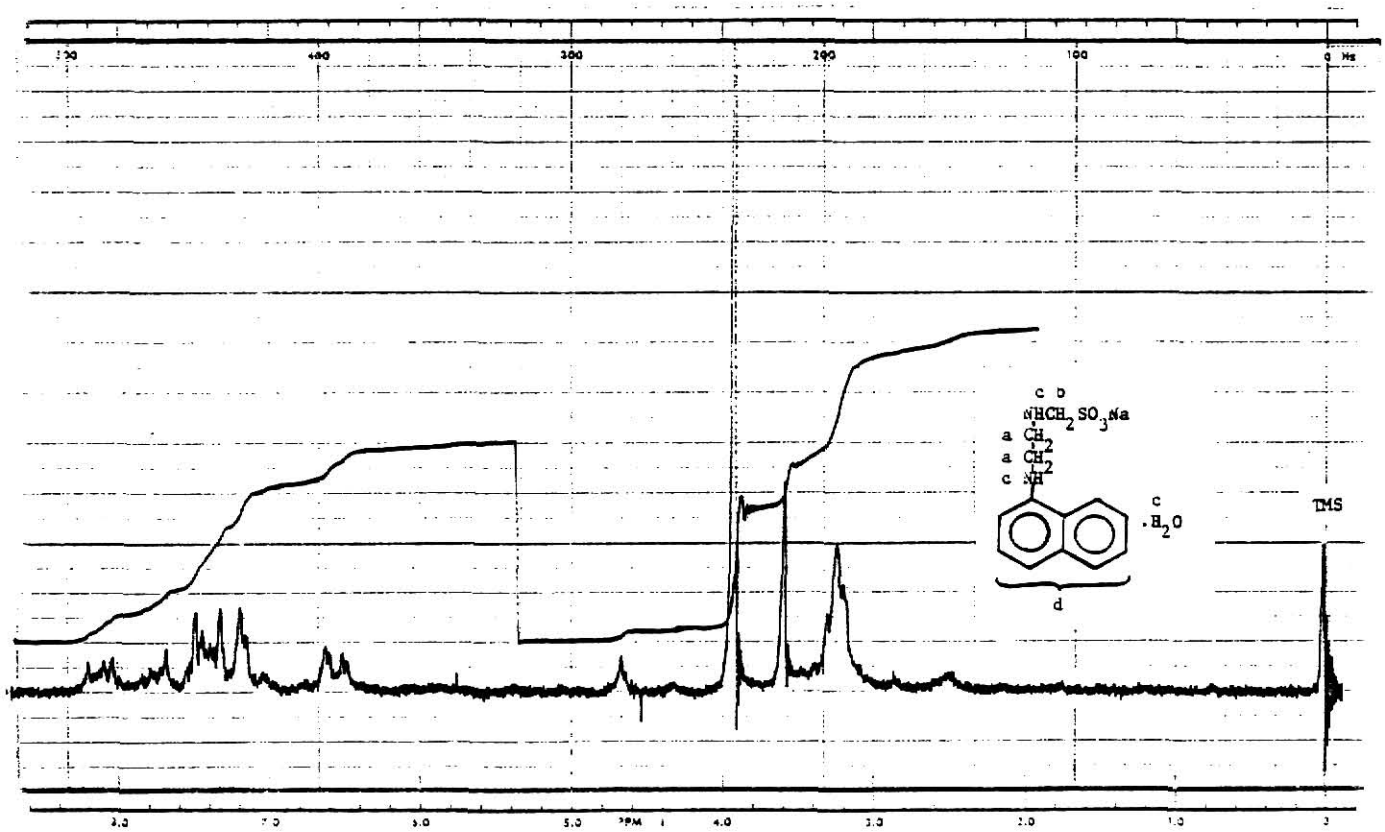
a. 3.20 ppm, NCH_2CH_2N

b. 3.58 ppm, NCH_2S

c. 3.90 ppm, HOD and NH's

d. 6.40 - 8.40 ppm, Aromatic Hydrogens


TMS
b b
NHCH2SO3Na
a CH2
a CH2
c NH
b
· H2O
d


c b
NHCH2SO3Na
a CH2
a CH2
c NH
c
· H2O
d
TMS

PART II. TEST FOR NITRITE IN SOLUTION

Reagents and Equipment

Chemicals used are all the best commercially available grade. Deionized water is used for preparing the reagents unless otherwise noted.

Standard nitrite solution, 250 ppm nitrite nitrogen, 1.232 g. of sodium nitrite and 1 ml chloroform in one liter solution.

(p-Aminophenyl)-trimethylammonium chloride, obtained and purified from the previous work of this laboratory (8).

Colorimetric reagents, 2.16×10^{-2}M., 0.1007 g. of (p-aminophenyl)-trimethylammonium chloride and 0.1496 g. of sodium 1-naphthylaminomethanesulfonate in 25 ml aqueous solution, and 0.1007 g. (p-aminophenyl)-trimethylammonium chloride and 0.1728 g. of sodium 2-(1-naphthylamino)-ethylaminomethanesulfonate in 25 ml spectrograde methanol.

UV Spectrophotometer, Perkin-Elmer model 124 Double-Beam Grating Spectrophotometer with 1-cm light path cells.

Nitrite Color Development

The azo-dye color development is made by mixing the colorimetric reagent, standard nitrite solution and hydrochloric acid. Various ratios of these three were examined and their color stability, time needed for color development and whether precipitates formed or not were compared. The behavior of sodium 1-naphthylaminomethanesulfonate as coupling component is listed in Table 1 and that of sodium 2-(1-naphthylamino)-ethylaminomethanesulfonate in Table 2.

As shown from Table 1, the formation of the azo dye and the color stability depend on the relative amount of the colorimetric reagent, nitrite

concentration and hydrochloric acid present. At relatively high concentrations of the acid, red-purple azo dye forms at the instant hydrochloric acid is added, but it also fades away almost instantly. On the other hand if the acidity is too low there is no azo dye formed but a nitroso yellow color forms. Between these two extreme cases the azo dye is fairly stable which allows the absorption spectrum to be taken, as shown in Fig. 3. Peak absorption wavelength is at 564 nm. Unfortunately, even with the best ratio the color is not stable for longer than 10 minutes. A color development was made directly in the 1-cm light path cuvette and color intensities were taken intermittently as shown in curve 1. of Fig. 3. Evidently since the color is formed (almost instantly) it starts to deteriorate. The deterioration rate is a non-linear curve, curve 1. of Fig. 5. Forty minutes later it becomes a pale reddish yellow color, curve 2 of Fig. 3. The final yellow color is presumably a decomposition product of the azo dye as a result of the formation of the nitroso compound,

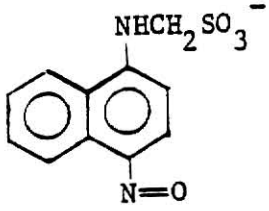


Table 2. is a comparison of 2-(1-naphthylamino)-ethylaminomethanesulfonate as a coupling component with different ratio of nitrite concentrations and acidities. Relatively it takes a higher acidity in order to have color developed than 1-naphthylaminomethanesulfonate. Since it is more basic than the latter. But again this azo dye gradually decomposes to the final stable nitroso compound. Fig. 4. shows the spectra taken right after color development and that of 40 minutes later. The azo dye has maximum

absorption wavelength at 530 nm. Fig. 5, curve 2, shows the deterioration of the azo dye with respect to time.

Table 1. Comparison of Azo Dyes* in Various Conditions

Colorimetric reagent	Nitrite Nitrogen 250 ppm	Nitrite Nitrogen 2.5 ppm	HCl 12M	HCl 1.2M	HCl 0.12M	H_2O	Precipitation	Results Development	Stability**
1	1		1				yes	instant	5 sec
1		120	1				no	instant	5 min
1	1			1			yes	instant	3 min
3	1			1			yes	instant	5 sec
5	1			1			yes	no color***	
3	3			1			less ppt.	instant	5 min
5	5			1			less ppt.	instant	7 min
1	1				1		no	instant	3 min
1	1				3		no	instant	10 min
1		60			3		no	no color***	
1		120			3		no	no color***	
1		120		1			no	1 min	10 min
1		120		2			no	instant	10 min
1		120		3			no	instant	10 min
1	1			2		120	no	15 sec	10 min****
2	1			2		120	no	1 min	7 min
3	1			2		120	no	3 min	greenish
1		100		2			no	20 sec	10 min
1		80		2		20	no	40 sec	10 min
1		60		2		40	no	90 sec	10 min

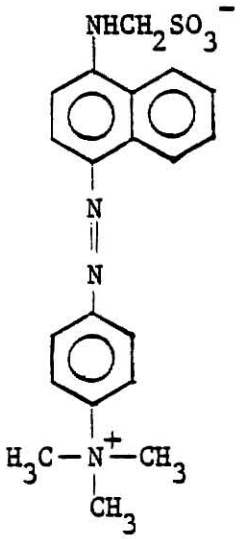
* Formed by 1-naphthylaminomethanesulfonate
** Red-Purple color
*** Yellow
**** This was chosen as the best condition.

Table 2. Comparison of Azo Dyes* in Various Conditions

Colorimetric reagent	Nitrite Nitrogen 250 ppm	Nitrite Nitrogen 2.5 ppm	HCl 12M	HCl 1.2M	HCl 0.12M	H_2O	Precipitation	Results Development	Stability**
1	1		1				yes	instant	2 min
5	5		1				yes	instant	green
5	5		3				less ppt.	instant	2 min
1		100	3				no	instant	5 min
1		100	2				no	instant	5 min
1		100	1				no	instant***	5 min
1		100		5			no	instant***	5 min
1		100		2			no	3 sec***	5 min
1		100	2				no	instant	5 min
2		100	2				no	instant	5 min
3		100	2				no	brown	
5		100	2				no	brown	
5		100	5				no	instant	turn brown
1		33	2			67	no	instant****	5 min
1		66				34	no	instant****	5 min
1		100	2				no	instant****	5 min

* Formed by 2-(1-naphthylamino)-ethylaminomethanesulfonate
** Red-Purple color
*** Color intensity decreases in less acidic solution
**** Color intensity increases in more concentrated nitrite

Fig. 3. Absorption Spectrum of the azo dye,



, 2.16×10^{-2} M.

Nitrite Nitrogen = 2.0 ppm

Curve 1: Right after mixing

Curve 2: 40 minutes later

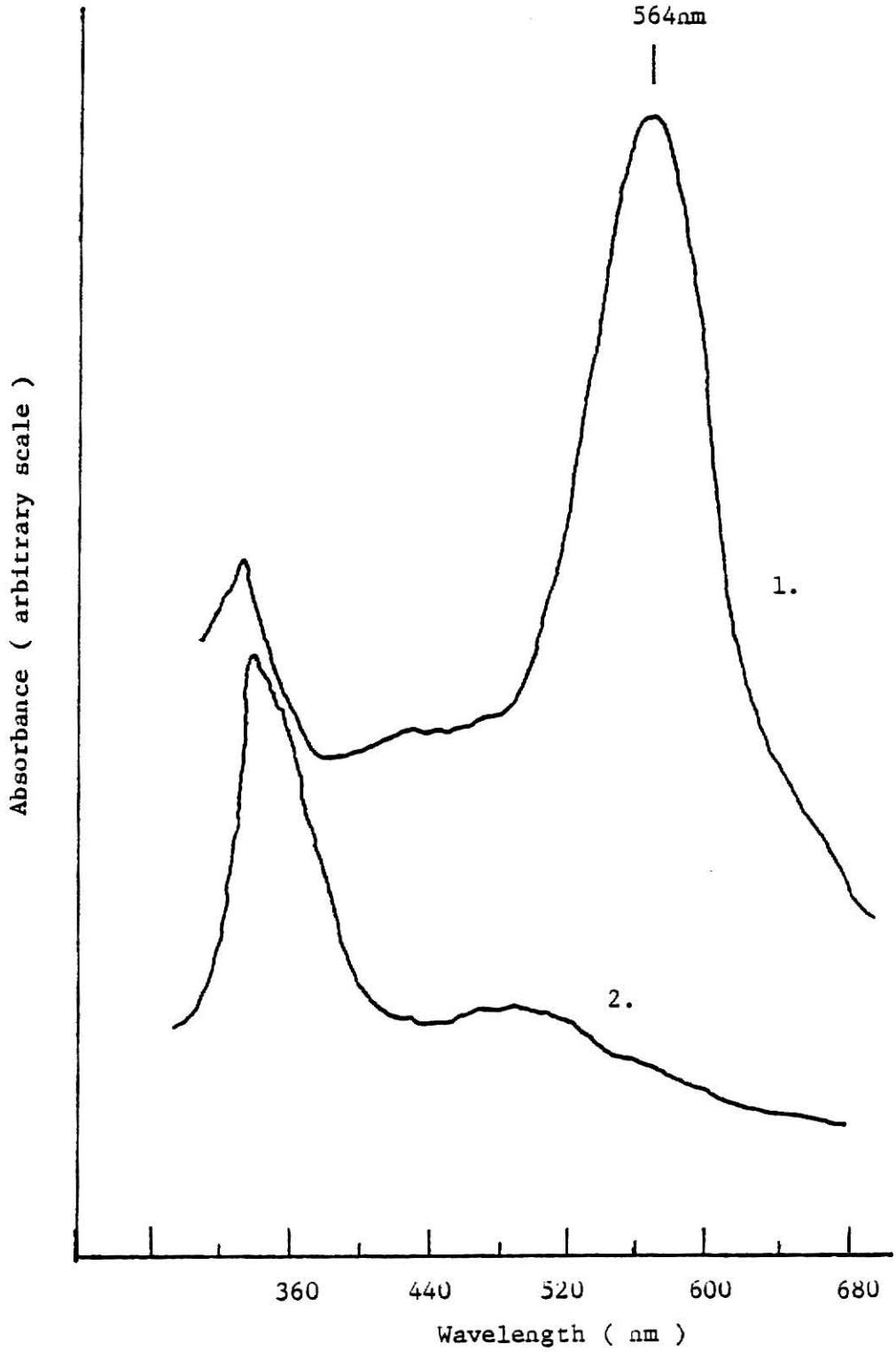
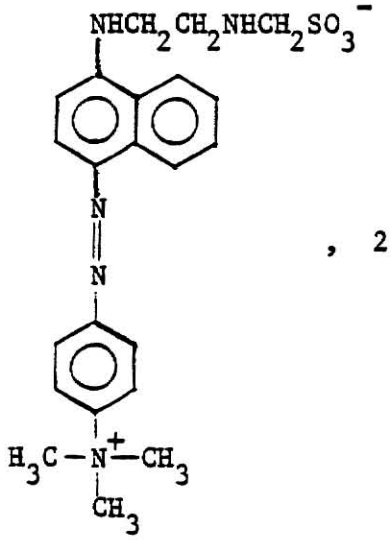

564nm
Absorbance (arbitrary scale)
1.
2.
360
440
520
600
680
Wavelength (nm)

Fig. 4. Absorption spectrum of the azo dye,



, 2.16×10^{-2} M.

Nitrite Nitrogen = 2.4 ppm

Curve 1: Right after mixing

Curve 2: 40 minutes later

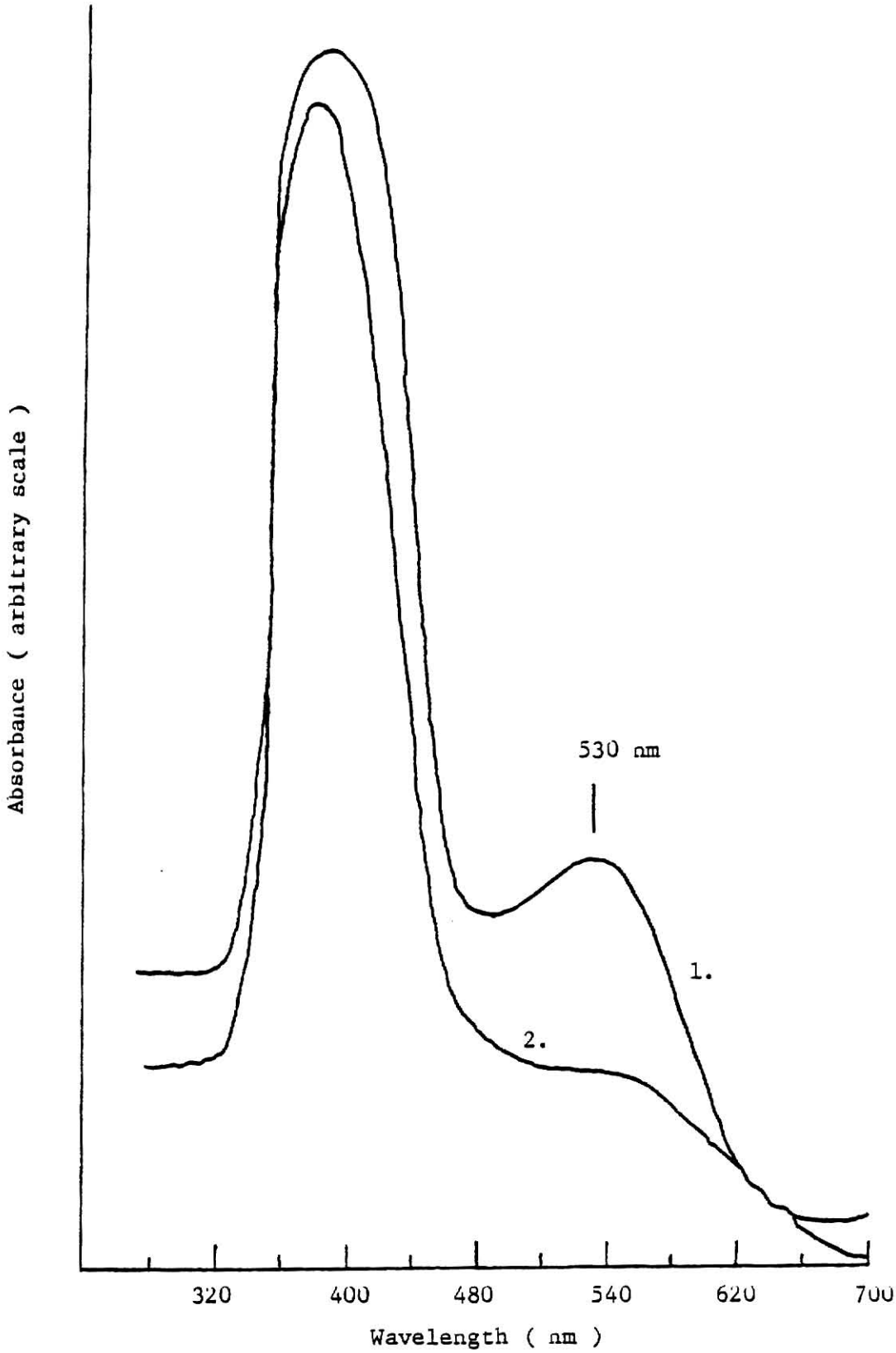
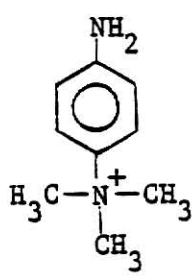
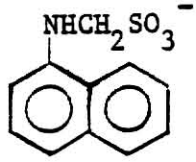
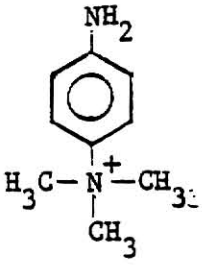
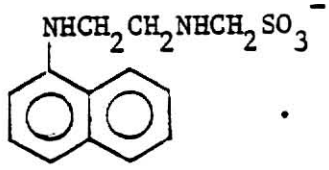
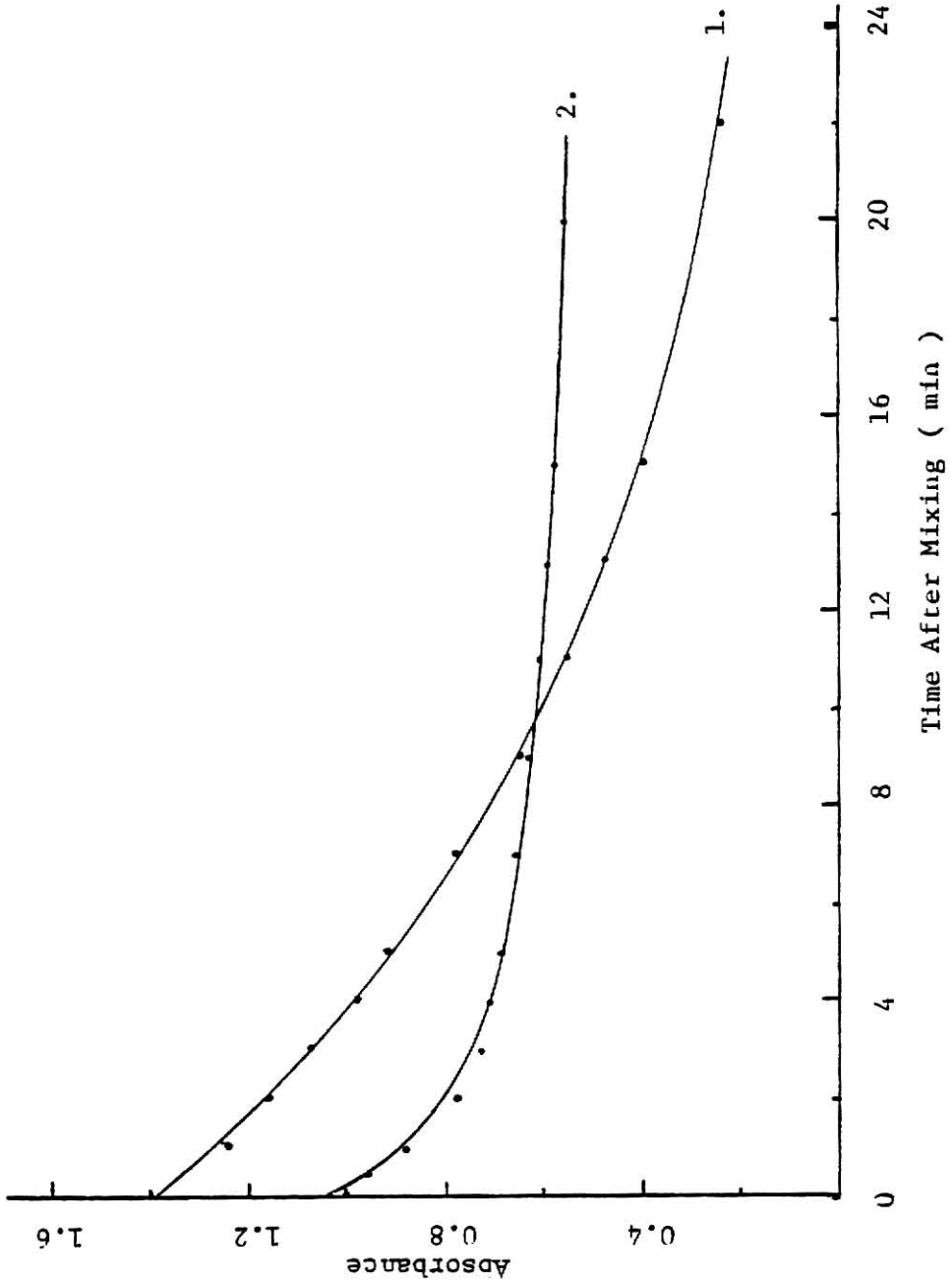

Absorbance (arbitrary scale)
530 nm
1.
2.
320
400
480
540
620
700
Wavelength (nm)

Fig. 5. Degradation of the color formed by:

Curve 1 :  +  ,

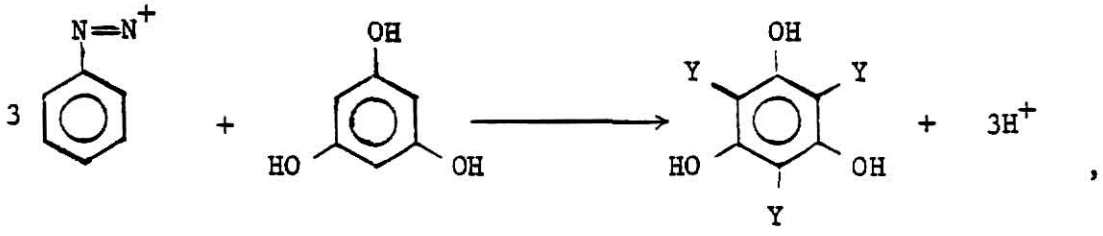
Curve 2 :  +  .

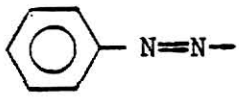

Absorbance
0.4
0.8
1.2
1.6
0
4
8
12
16
20
24
Time After Mixing (min)
1.
2.

CHAPTER V

ADSORPTION OF NO_2 ON PHLOROGLUCINOL IN SOLID PHASE

Phloroglucinol, or 1,3,5-benzenetriol, is an important fine chemical, some 200 tons of which are manufactured annually (13). It is used widely throughout the chemical and allied industries, such as diazotype duplicating and copying process. Phloroglucinol is used as a coupling component to couple with a diazo compound, e.g., benzenediazonium salt, forming the azo dye (14);



where Y = 

By accident it was found in this laboratory that phloroglucinol, by itself, gives a brown color (presumably just a deep yellow color) when moist with acetone on filter paper with high concentrations of nitrogen dioxide. Other ketones work except diaryl-ketones. This reaction was of great interest to us, since when applied on filter paper with a solid, non-evaporating ketone (or combination of ketones) the same reaction may occur which might lead to a new method of NO_2 determination. We are not concerned, at this time, with the mechanism of the reaction between the reagents and NO_2, but are interested in investigating the sensitivity of

this reagent toward NO_2 under various conditions. This chapter reports a quantitative study of color intensity produced by phloroglucinol in the presence of different ratios of p-aminoacetophenone and 4-phenylcyclohexanone.

Reagents and Equipment

Spectrograde acetone is used as the solvent.

Phloroglucinol solution, 0.400 M, 1.6214 g. phloroglucinol, Eastman Organic Chemicals, in 25 ml acetone.

p-Aminoacetophenone solution, 0.400 M, 1.3517 g. p-aminoacetophenone, Aldrich, in 25 ml acetone.

4-Phenylcyclohexanone solution, 0.400 M, 1.7424 g. 4-phenylcyclohexanone, Aldrich, in 25 ml acetone.

Perkin-Elmer Model 124 Double-Beam Grating Spectrophotometer with reflectance sample holder.

Test paper, glass microfiber filters, 4.25 cm diameter, GF/C grade Whatman Co.

Exposure vessel, Kimble low form, cap-style weighing bottle (15).

NO_2 flow system, Appendix.

Permeation tube, PTFE, approximately 6 cm effective length. NO_2, Union Carbide Corp., is condensed into this teflon tube in liquid nitrogen and is then sealed on both ends. The NO_2 gas that permeates out is calculated from the weight loss of the permeation tube. Over 14 days measurement the permeation rate was found to be 2.69 micrograms/minute, Fig. 6. The concentration of NO_2 gas at a given flow is calculated by

$$C\ (ppm) = P / F$$

where F is the total flow rate in liter min^{-1} and P is the permeation rate in microliter min^{-1}, both corrected to 760 torr and 25° C. Thus, at a

fixed permeation rate the NO_2 concentrations can be controlled by varying the flow rate.

Preparation of the Impregnated Test Paper

Different volume ratios of phloroglucinol solution, p-aminoacetophenone solution and 4-phenylcyclohexanone solution are mixed. A package of 12 pieces of test paper was immersed in the solution for 15 minutes and air dried.

Absorption of NO_2 on Test Paper

Impregnated test paper is exposed in the exposure vessel in a stream of NO_2 gas with known concentration. Yellow-brown color starts to form. The UV spectrum (reflectance absorption mode), Fig. 7, shows a broad absorption band that starts at 540 nm and reaches a maximum at 420 nm. A plot of the absorption intensity at 420 nm vs. exposure time was made for phloroglucinol with different ratios of p-aminoacetophenone and 4-phenylcyclohexanone and is shown in Fig. 8. Each curve shows a different response toward NO_2 but they all share a common behavior -- an almost linear increase in their color intensities for the first several hours after which the curve levels off. Several explanations can be made for the color reaching a saturation. They are: (a). a penetration limit of NO_2, (b). a penetration limit of the light source of spectrophotometer and/or (c). the reagent being depleted. Curve 1 and curve 2 probably have no significant difference. The improved sensitivity with the increasing of 4-aminoacetophenone is interesting (as shown by curve 4). However, a mole ratio of 1:3:1 (phloroglucinol, p-aminoacetophenone, 4-phenylcyclohexanone, respectively) and 1:4:1 at the first several hours exposure

shows an identical sensitivity compared to that of 1:2:1. An absorbance vs. NO_2 concentration curve at fixed exposure time (75 min.) shows the same trend, see Fig. 9.

The reaction of NO_2 with phloroglucinol is still unknown. We found ozone does not turn the phloroglucinol yellow. This suggests that the yellow color caused by NO_2 is not as a result of oxidation. The role of ketones in the color development is also ambiguous. This needs a further investigation before a conclusion can be made.

Fig. 6. Weight Loss of Permeation Tube vs. Time

$Y = (-0.00388)X + 6.3890$

Slope = -0.00388 g/day (or -2.69 microgram/min)

99% Confidence Interval about the slope is

(-0.00389 g/day, -0.00387 g/day)

$R^2 = 99.83\%$

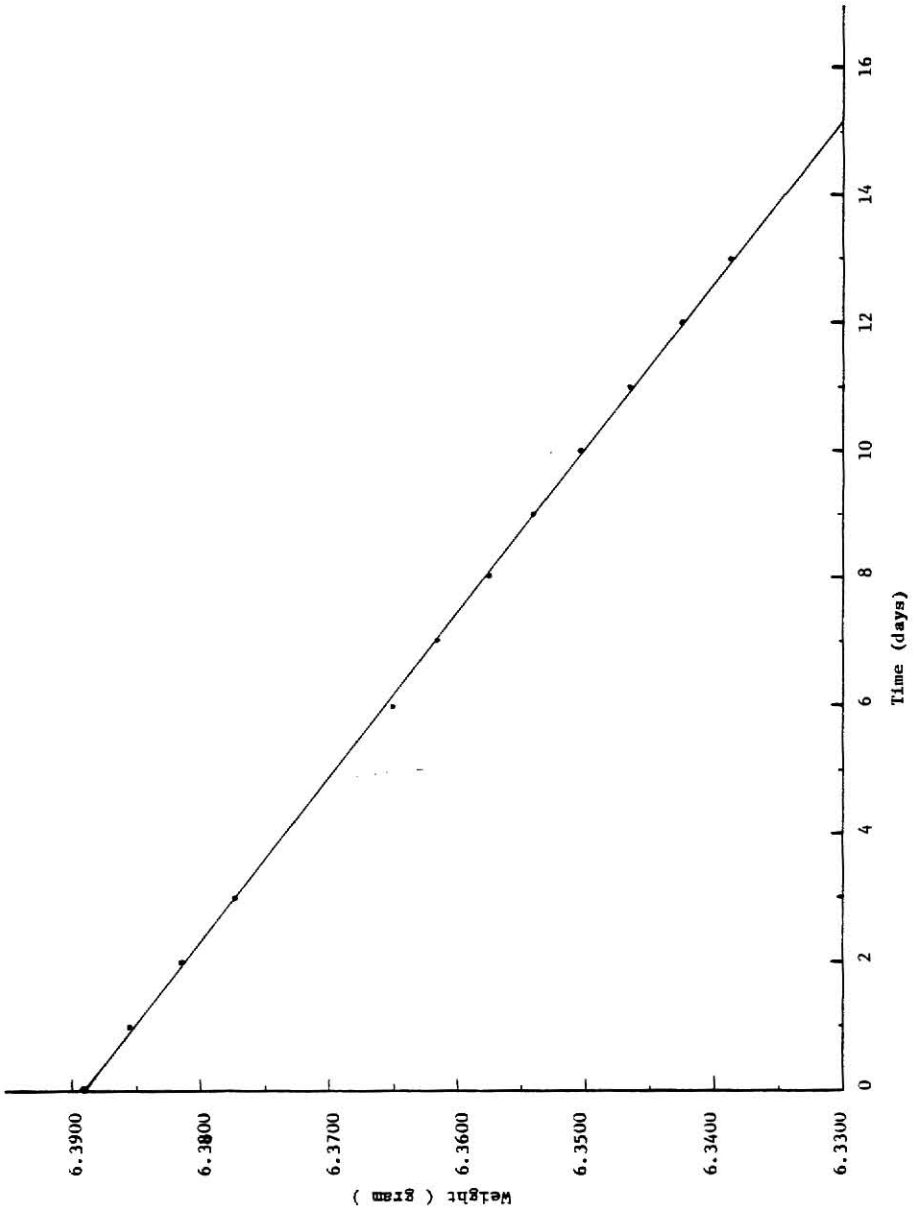

6.3900
6.3800
6.3700
6.3600
6.3500
6.3400
6.3300
Weight (gram)
0
2
4
6
8
10
12
14
16
Time (days)

Fig. 7. Reflectance Absorption Spectrum of Phloroglucinol-NO_2 Complex

Slit width = 2.0 nm

Wavelength maximum = 420 nm

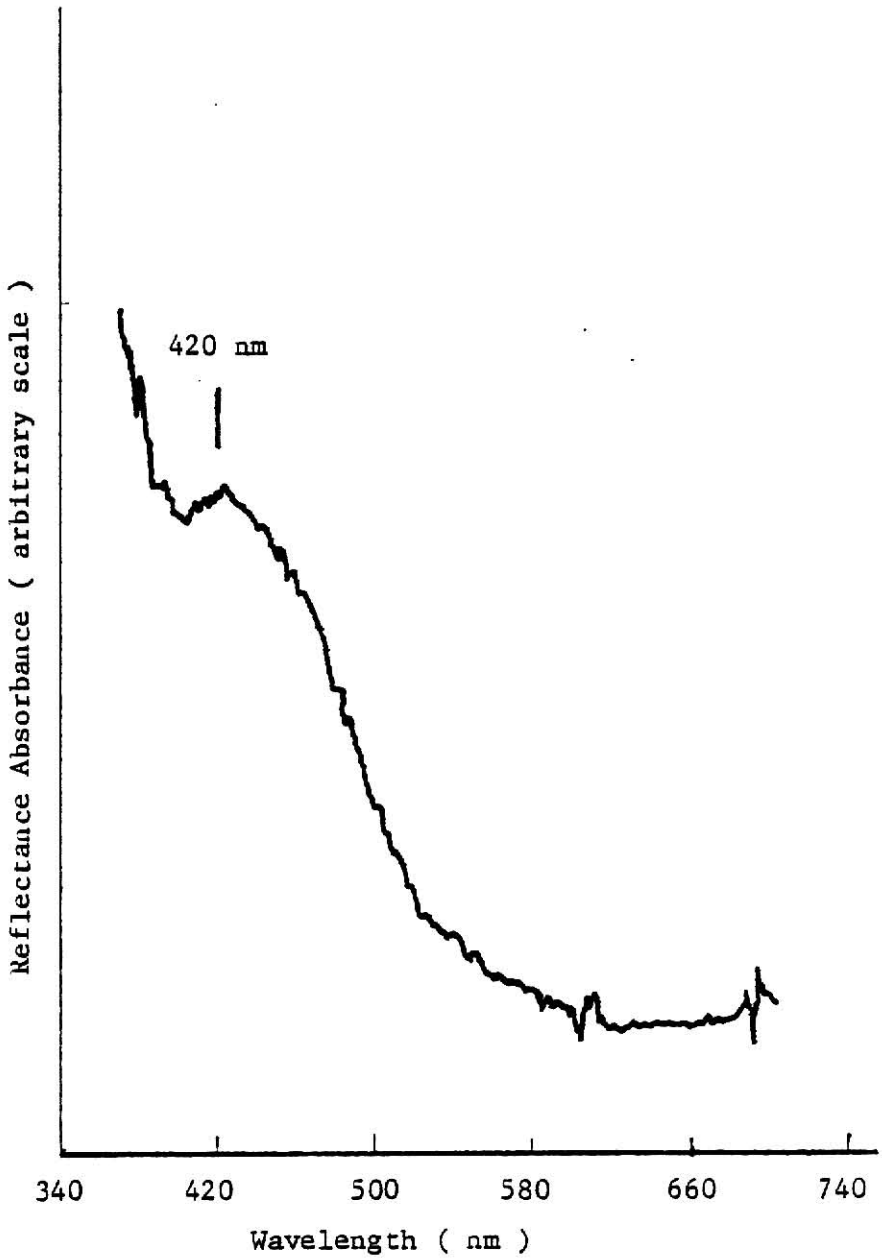

Reflectance Absorbance (arbitrary scale)
420 nm
340
420
500
580
660
740
Wavelength (nm)

Fig. 8. Color Intensity of Phloroglucinol vs. Exposure Time (NO_2 concentration = 10 ppm)

Combination of phloroglucinol/p-aminoacetophenone/ 4-phenylcyclohexanone are:

Curve 1: 1 / 1 / 1 ⊙

Curve 2: 1 / 1 / 2 △

Curve 3: 2 / 1 / 1 ⊡

Curve 4: 1 / 2 / 1 ⬡

Curve 5: 1 / 3 / 1 ×

Each point on the curves is an average of three trials.

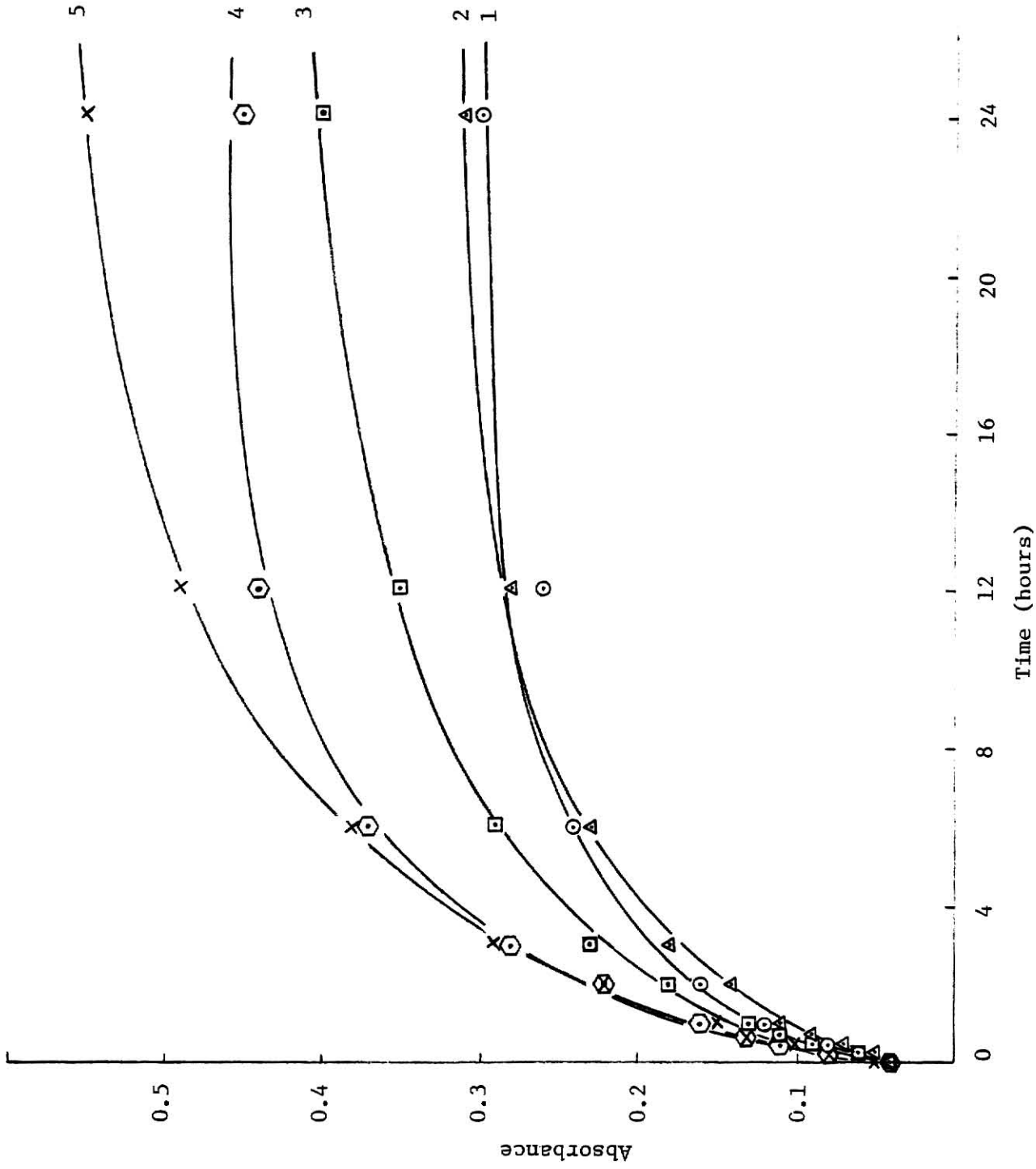

5
4
3
2
1
0.5
0.4
0.3
0.2
0.1
Absorbance
0
4
8
12
16
20
24
Time (hours)

Fig. 9. Color Intensity of Phloroglucinol vs. NO_2 Concentration (Exposure time = 75 min.)

Combination of phloroglucinol/p-aminoacetophenone/ 4-phenylcyclohexanone are:

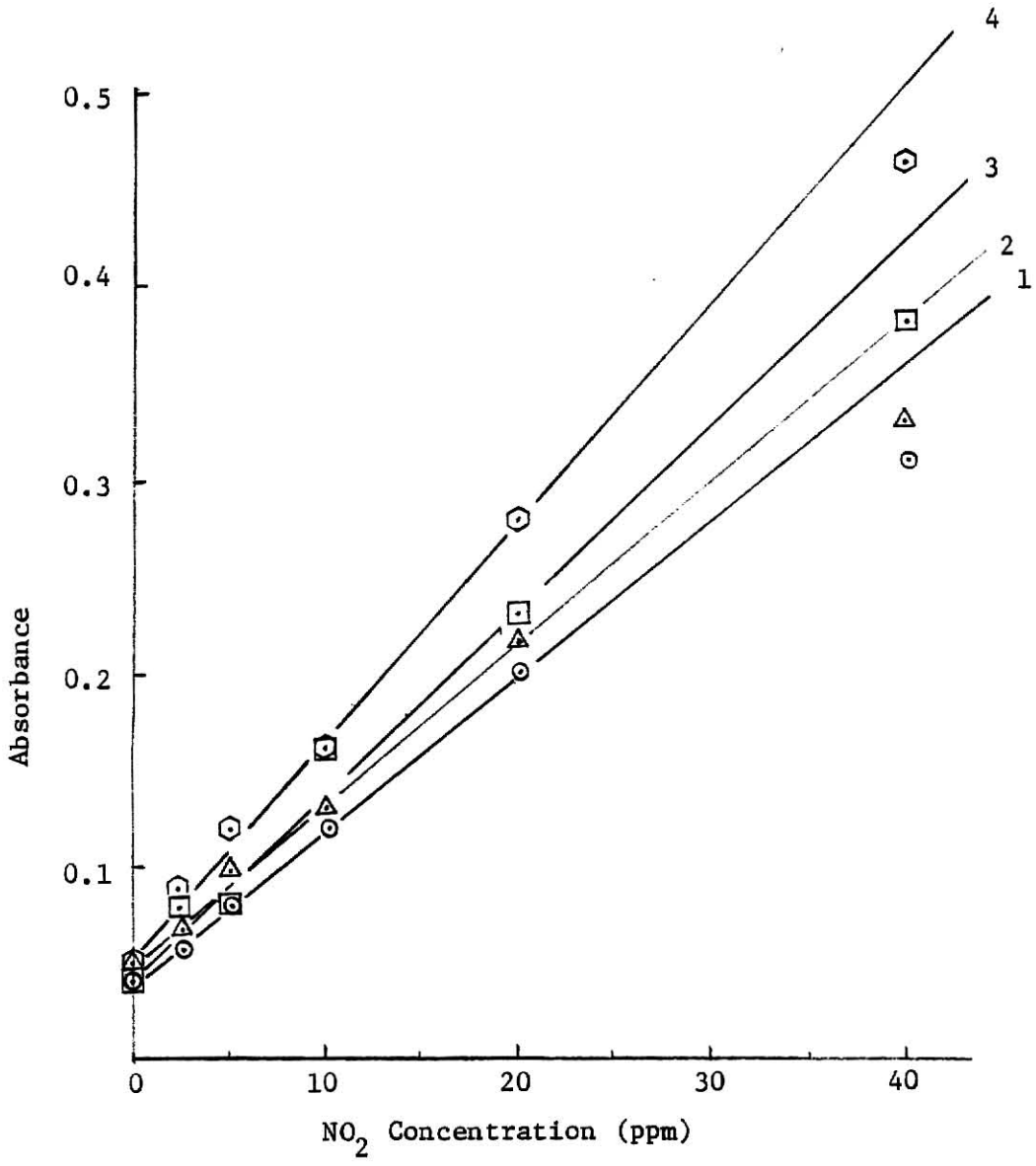
Curve 1: 1 / 1 / 1 ⊙

Curve 2: 1 / 1 / 2 △

Curve 3: 2 / 1 / 1 ⊡

Curve 4: 1 / 2 / 1 ⬡

Each curve at 0 to 20 ppm range shows quite linear but after 20 ppm a negative deviation is observed.

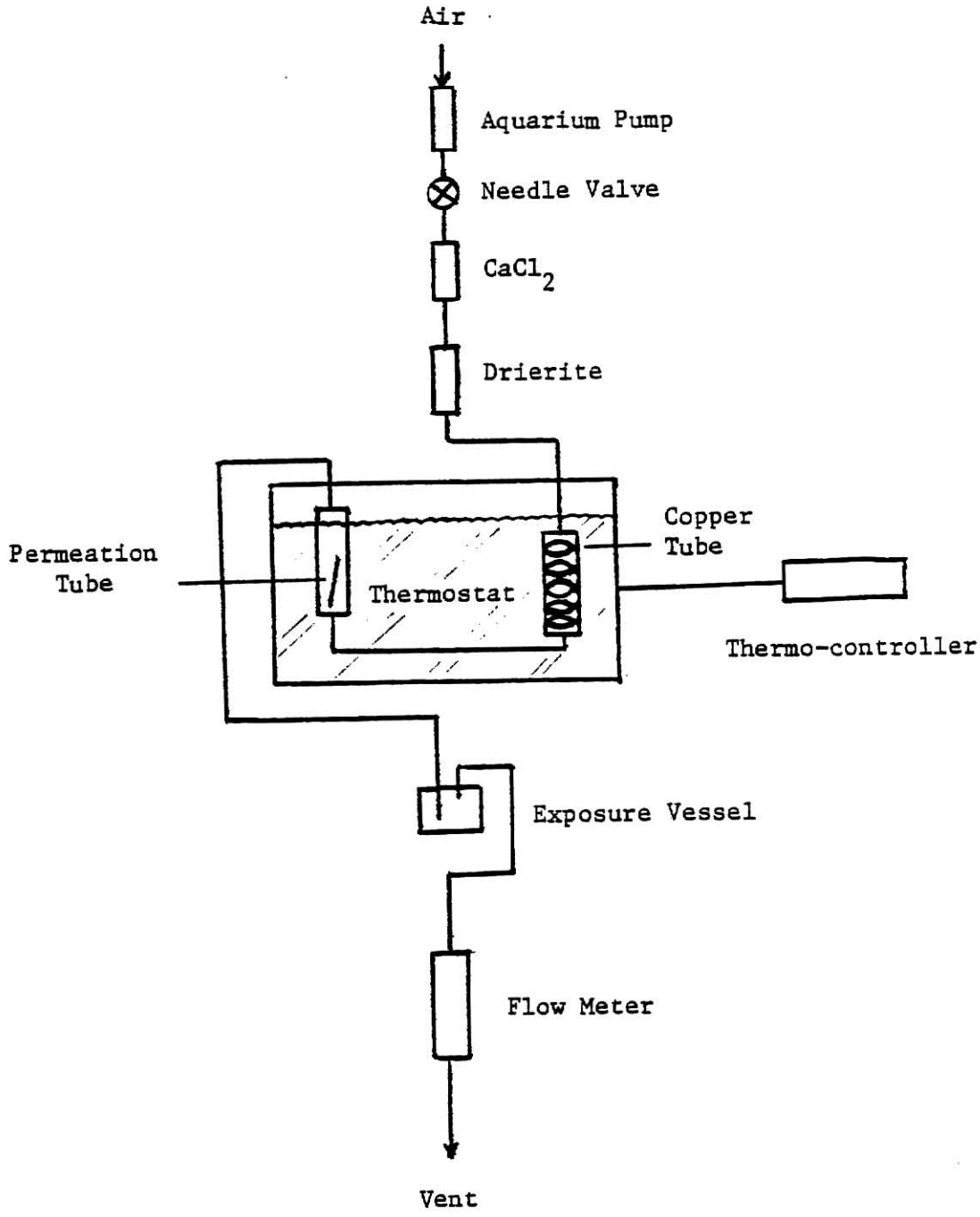

4
3
2
1
0.5
0.4
0.3
0.2
0.1
Absorbance
0
10
20
30
40
NO2 Concentration (ppm)

Literature Cited

1. "Documentation of the Threshold Limit Values for Substances in Workroom Air", Amer. Conf. of Governmental Industrial Hygienists, 3rd Ed. 1971.
2. Griess, P., BER., 12, 426 (1879).
3. Warington, R., J. CHEM. SOC., 39, 229 (1881).
4. Ilosvay, M. L., VULL. SOC. CHIM. Fr., 2, 388 (1889).
5. Weston, R. S., PROC. AMER. CHEM. SOC., 27, 281 (1905).
6. Dr. Lambert, J. L., personal comm., Kansas State University, Manhattan, Kansas 66506.
7. Cheng, T. Y., M. S. thesis, Department of Chemistry, Kansas State University (1981).
8. Lambert, J. L. and Zitomer, F., ANAL. CHEM., 32, 1684 (1960).
9. Sawicki, E., Stanley, T. W., Pfaff, J. and D'Amico, A., TALANTA, 10, 641 (1963).
10. "Reagent for Organic Synthesis", Feiser & Feiser, Vol. I, pp. 1180.
11. Seeboth, ANGEW. CHEM. INT. ED. ENGL. 6, 307 (1967).
12. Drake, ORG. REACT., 1, 106 (1942).
13. McKillop et al., SYN. COMMUN., 4, 35 (1974).
14. Kastens, M. L. and Kaplan, J. F., IND. ENG. CHEM. 42, 402 (1950).
15. Lambert, J. L., Chiang, Y. C. et al. ANAL. CHEM., 54, 1227, (1982).

APPENDIX

A diagram of the NO_2 flow system used in Chapter V is given below:



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VITA

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ANALYTICAL REAGENTS FOR NITROGEN DIOXIDE

by

YUN-LONG LIAW

B.S., National Tsing-Hua University, 1971

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY

Manhattan, Kansas

1982

The synthesis of some organic reagents capable of forming an azo dye complex with nitrogen dioxide are described. The characteristic of these organic compounds is a quaternary ammonium ion which serves as an electron-withdrawing group to the diazo precursor while a secondary amino group acts as an electron-donor to the aromatic coupler compound.

The synthesis of a compound that contains both the above diazo precursor and the coupler was attempted. 9-Amino-N-(3-1-naphthylamino)-propyl)-julolidinium chloride and (p-aminophenyl)-dimethyl-(3-(1-naphthyl-amino)-propyl)-ammonium chloride could not be synthesized through the routes proposed.

The syntheses of sodium 1-naphthylaminomethanesulfonate and sodium 2-(1-naphthylamino)-ethylaminomethanesulfonate are described. (p-Amino-phenyl)-trimethylammonium chloride diazotizes in the presence of several parts per million of nitrous acid which in turn couples with these two quaternary ammonium chlorides, respectively, to form a characteristic azo color. The color formed is not stable in hydrochloric acid medium.

Phloroglucinol forms a yellow color (λ_{max} = 420 nm) with nitrogen dioxide gas in the presence of p-aminoacetophenone and 4-phenylcyclo-hexanone. The color intensities formed with mixtures of phloroglucinol and these ketones in different ratios are reported.