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ARPA ORDER NUMBER 5154

Name of Contractor FREQUENCY SYSTEMS, INC.

Effective Date of Contract Dec. 3, 1984

Contract Expiration Date Dec. 2, 1985

Reporting Period Technical Report Dec. 3, 1984 - Dec. 2, 1985

Contract Number MDA903-85-C-0002

Principal Investigator Sidney K. Tally

Tel # (603)883-5000

Title of work New Diazo Process

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FISCAL STATUS

Budgeted amount as per contract December 3, 1984 through December 2, 1985	\$166,963.00
Actual expenditures for same period	<u>119,027.61</u>
Surplus On Contract	<u>\$ 47,935.39</u>

YEAR-END REPORT

CONTRACT #MDA903-85-C-0002 DARPA Order No. 5154

Period: December 3, 1984 through December 2, 1985

SUMMARY

Task Objectives

This project was initiated to explore diazo type compound with spectral response at 520 nm, and stability at ambient storage conditions. Such compounds would permit the direct copying of blue prints and result in major time and dollar savings to blueprint users including federal and municipal government agencies, the military, large and small industries and the construction industry.

Technical Problems

The photochemical sensitivity of the aromatic diazonium salts used in conventional diazo copying systems is limited to a narrow spectral region in the near ultraviolet and the blue, with maximum sensitivity from 375 nm to 400 nm. A new category of diazonium compound, with light sensitivity in the visible spectrum from 500 - 540 nm has been the goal of this project.

There were four compounds (page 4) picked to explore. While information for further development was achieved the breakthrough necessary to reach the goals was not accomplished. A compound related to the original proposal showed future promise.

Cont'd pg. 3

In view of change in personnel in the later part of the project effort will cease on December 2, 1985.

General Methodology

A number of experiments were conducted on the four different compounds as listed on page 3 of the Technical Report. Additional experiments were conducted on a chemical related to the original proposal (page 24) which showed promise.

Bibliography of books, journals, fluorene compounds, naphthalene compounds, pyrene compounds and patents are listed on pages 28, 29 and 30.

Technical Results

Even though significant information was compiled, the achievement of time of exposure was not reached.

Important Findings and Conclusions

As outlined on page 3, the four compounds that were investigated did not produce the required results. A compound outlined on page 24 showed promise.

Special Comments And Implication For Further Research

While naphthalene diazonium compound shows promise (page 24) due to the change in personnel (the death of John Rice, president of Bard Labs and the decision of Wilma Hanson to return to teaching full time) it is recommended that the project be suspended until the right supportive personnel can be arranged.

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Abstract;

Period: December 3, 1984 through December 2, 1985

The exploration of diazo type structures to prepare compounds which are both responsive at 520 nm and stable at ambient storage conditions. Such compounds would permit the manufacture of products for the direct copying of blueprints and would result in major time and dollar savings to blueprint users, including federal and municipal government agencies, the military, large and small industries and the construction industry.

Theoretical Background

The photochemical sensitivity of the aromatic diazonium salts used in conventional diazo copying systems is limited to a narrow spectral region in the near ultraviolet and the blue, with maximum sensitivity from 375 nm to 400 nm. A new category of diazonium compounds, with light sensitivity in the visible spectrum from 500-540 nm has been the goal of this project.

High intensity light absorption in the visible area of the spectrum is characteristic of compounds which have a large number of conjugated double bonds and two or more polar groups of considerable distance apart in the molecule. Compounds with these structural features create a large transition dipole. The transition dipole is a quantum mechanical condition needed in order for lightwaves to transfer their energy to atoms. The energy of a visible or ultraviolet lightwave can be used to transfer an atom's electron from its ground state to the next higher orbital during which process light of the wavelength is absorbed. This phenomenon is known as an electronic transition. In molecules, light of more than one wavelength is absorbed extending over a broad spectral region giving rise to electronic, or ultraviolet and visible, absorption spectra.

The light sensitivity of diazonium salts corresponds closely to their electronic absorption spectral response. This photochemical sensitivity of diazonium salts is not completely understood, however, photolysis

takes place according to the following general reaction:⁴

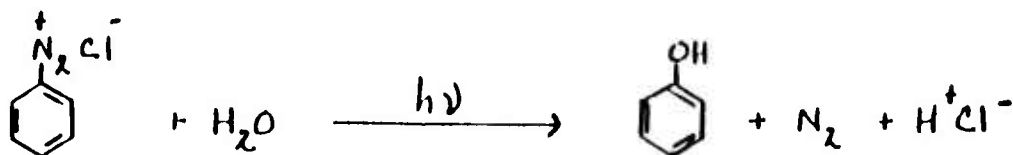


FIGURE 1

This is affected by the environment as well as the chemical species present. The presence of alcohol or additional chloride ions partially diverts the product from a phenol to an aromatic ether or substituted chlorobenzene.³ This becomes an important consideration if these secondary photodecomposition products are colored.

Additional substituents on the aromatic ring of the diazonium salt affect the light sensitivity of diazo compounds. Diazo papers of high light sensitivity and stability are best obtained from diazo compounds which have a positive polar substituent such as dialkylamino, alkoxy, phenylamino or morpholino and piperidino groups. The position of the substituent is most important, with para substitution showing optimum light sensitivity for amine substituents.⁴

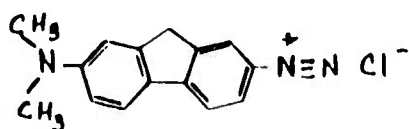
Scope of the Project

In the first year of the research program the work effort concentrated on devising synthesis procedures for, and preparation of, diazo sensitizing materials which would have high intensity light absorption in the visible spectrum. Compounds which are rigidly coplanar, resonantly-coupled aromatic rings were selected as conjugated double bond molecular systems. A diazo group, as the diazonium salt, was to be substituted on one ring. A secondary or tertiary amine group was to be substituted on another ring in a para position symmetrical to the diazonium group. This would give a completely conjugated minimum

path of six atoms between the nitrogens of the two substituents.

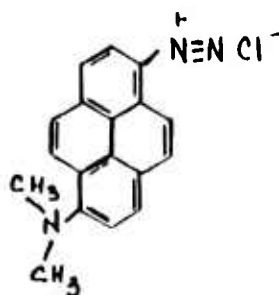
Four classes of diazonium compounds, which meet the above criteria, were selected for initial evaluation. These compounds, of the original proposal are shown in Figure 2. Diazonium salts of fluorene, pyrene, dibenzofuran and naphthalene aromatic ring systems were synthesized and evaluated for spectral response. The results for each class of compound will now be discussed.

Diazonium Compounds for Initial Evaluation
of Light Sensitivity at 520nm



COMPOUND TYPE I

7-N,N-dimethylamino-2-fluorene
diazonium chloride



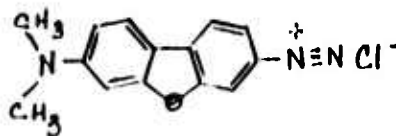
COMPOUND TYPE II

6-N,N-dimethylamino-1-pyrene
diazonium chloride



COMPOUND TYPE III

7-N,N-dimethylamino-2-pyrene
diazonium chloride



COMPOUND TYPE IV

7-N,N-dimethylamino-3-dibenzopyran
diazonium chloride

These four compounds did not produce the required salt.
Naphthalene Diazonium Compounds
FIGURE 2
cont'd pg. 24

Fluorene Diazonium Compounds Compound Type I

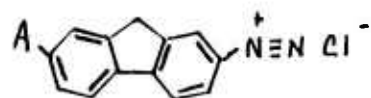
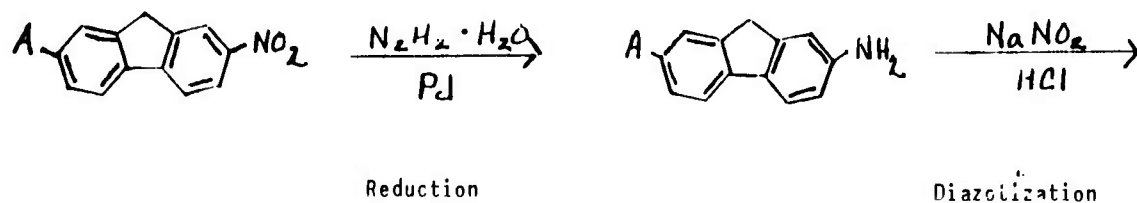
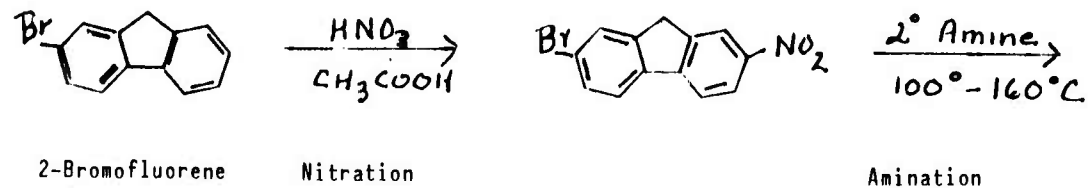
Fluorene compounds and N-alkylamino fluorene compounds have been investigated extensively by T. L. Fletcher and his research associates, under grants from the National Cancer Institute, as several derivatives of fluorene are known carcinogens. Light-sensitive fluorene diazonium salts as diazotype materials were patented by Panasik and Cox in 1968. Light sensitivity with maximum absorption at 515 nm was claimed for the patented fluorene compounds. The syntheses of fluorene compounds performed in this laboratory are diagramed in Figures 3 and 4.

All of the synthetic sequences for the diazonium compounds under investigation require nitration of the aromatic ring system and reduction of the obtained nitro compound to an aromatic primary amine as the site for diazotization. The second substituent on the ring system, preferably a tertiary amine para to the diazotization site, is introduced at intermediate points during the synthesis sequence.

Our investigation of fluorene diazonium compounds initially concentrated on the synthesis of 2-N,N-dimethylamino-7-fluorene diazonium chloride. 2-N,N-dimethylamino-7-nitrofluorene is a key intermediate in the preparation of this diazonium salt. We were unsuccessful in our attempts to introduce the dimethylamine substituent onto the nitro fluorene ring system. The starting material, 2-bromopyrene, was nitrated. Next, 2-bromo-7-nitrofluorene was reacted with N,N-dimethylamine (b.p. 7°C), as a 40% solution in water, using several different procedures. Two alternate approaches, reacting 2-bromo-7-nitrofluorene with N,N-dimethylamine hydrochloride (m.p. 160°C) and refluxing 2-bromo-7-nitrofluorene with N,N-dimethylformamide in the presence of copper II sulfate for 8 hours, were also tried. The melting point of 2-N,N-dimethyl-7-nitrofluorene is $229-230^{\circ}\text{C}$. Although the melting points of the products obtained were within the range of the literature value in many cases, absorption spectra were not. Maximum absorption occurred at 410 nm rather than 492 nm, the reported value. The product from the reaction of 2-bromo-7-nitrofluorene with N,N-dimethylformamide showed a broad absorption band from 520 nm to 330 nm. Reduction of this

SYNTHESIS SEQUENCE FOR FLUORENE DIAZONIUM COMPOUNDS

COMPOUND TYPE 1



7-Tertiaryamino-
2-fluorene diazonium chloride

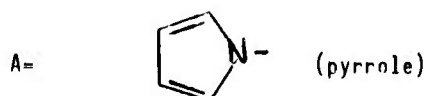
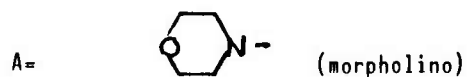
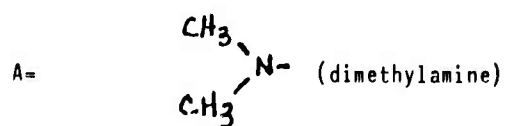
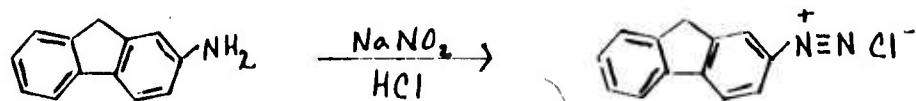


FIGURE 3

SYNTHESIS SEQUENCE FOR FLUORENE DIAZONIUM COMPOUNDS

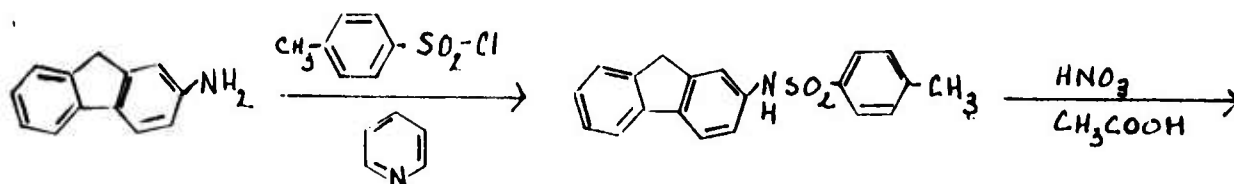
COMPOUND TYPE 1



2-Aminofluorene

Diazotization

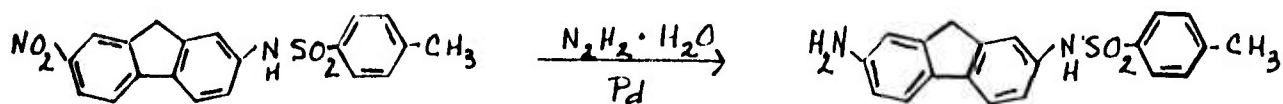
2-Fluorene diazonium chloride



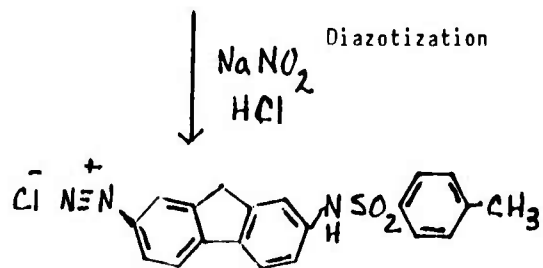
2-Aminofluorene

Tosylation

Nitration



Reduction



Diazotization

7-Tosylamino-2-fluorene

diazonium chloride

FIGURE 4

material yielded a 2-substituted-7-aminofluorene which partially melted at 263-267°C. The literature value for the melting point of 2-N,N-dimethylamino-7-aminofluorene is 147-148°C.

Morpholine and pyrrole were successfully introduced onto the fluorene nucleus in a position para to the nitro group. The nitro group at carbon-7 of the fluorene ring system was reduced to the amine with each product, including the products from the dimethylamine reactions, using hydrazine hydrate in the presence of 10% palladium on charcoal as catalyst. Synthesis of 2-amino-7-tosylamino fluorene was performed by an alternate method as shown in Figure 4.

Diazotization of the fluorene amines was accomplished by the "Direct Method," a standard procedure. Direct diazotization is done by dissolving an aromatic amine dilute in hydrochloric acid, cooling the solution to 0° to 5°C, and adding a sodium nitrite solution while stirring the cold aromatic amine solution. As nitrous acid is formed, diazotization takes place. A deepening color is evidence of successful diazotization. The fluorene compounds under investigation are insoluble in hydrochloric acid. Diazotization was performed on suspensions of the compounds in the acid.

The fluorene diazonium salts (Figures 3 and 4) which were evaluated are:

1. 2-fluorene diazonium chloride
2. 7-N,N-dimethylamino-2-fluorene diazonium chloride (uncertain)
3. 7-morpholino-2-fluorene diazonium chloride
4. 7-pyrrole-2-fluorene diazonium chloride
5. 7-tosylamino-2-fluorene diazonium chloride

2-Fluorene diazonium chloride, several of the dimethylamino preparations, and 7-pyrrole-2-fluorene diazonium chloride showed no images with the Frequency Systems light source at exposures as long as 4 minutes. These diazonium salts were sensitive to ultraviolet light with

30 second and 1 minute exposures. One of the dimethylamino preparations was sensitive to light from Frequency Systems light source at 4 minutes light exposure. Both 7-morpholino-2-fluorene diazonium chloride and 7-tosylamino-2-fluorene diazonium chloride exhibited spectral response to the Frequency Systems light source at 520 nm with 30 second and 1 minute exposures.

Tinctorial strength and the visual appearance of developed images were sub marginal for all synthesized compounds employing the fluorene nucleus. The developed color of images from the fluorene diazonium compounds was pink with the following couplers:

Coupler III 2,3-Dihydroxy-6-naphthalene sulfonic acid sodium salt

Coupler 122, Betaoxynaphtoic-N-(2-hydroxyethyl) amide

Coupler 144, Betaoxynaphtoic morpholinopropyl amide

Gold images were obtained using phloroglucinol as the coupler. Neither of these colors are satisfactory for use with the Frequency Systems Copying process. Purple images resulted with the use of H Acid, 8-amino-1-naphthol-3,6-disulfonic acid. With adequate tinctorial strength this is an acceptable image color.

The fluorene diazonium salts need further development. The synthesis of 7-tosylamino-2-fluorene diazonium chloride (Figure 4) needs to be perfected. Fluorene compounds with piperidine and diethyl amine substituted at carbon 7 on the ring structure are two additional systems which will have spectral sensitivity at 520 nm. Tinctorial strength of images can be improved with compound purity.

1-Pyrene Diazonium Compounds Compound Type II

Patent rights for pyrene diazonium compounds as diazo type materials, with a photo decomposition range from 360 to 500 nm, were obtained by Tsunoda et.al in 1969. Our synthesis route for preparing 1-pyrene diazonium compounds is shown in Figure 5 and will be discussed in some detail.

Acetylation to protect the amino group of 1-aminopyrene yielded an excellent quantity of pale green crystals as needles which were used in the subsequent nitration. With nitration of 1-acetyl-aminopyrene 4-nitro- and 6-nitro-1-acetylamino pyrene are obtained as an isomeric mixture. These isomers were separated by dissolving the 4-nitro-1-acetyl-aminopyrene in a 50:50 mixture of ethanol and pyridine and removing the 6-nitro-1-acetylamino-pyrene by filtration. The product was obtained as a brown orange powder melting from 275-285°C with red color formation. The filtrate was acidified with 10% hydrochloric acid to precipitate the other isomer which was collected and saved.

The protective acetyl group was removed from the amine by acid hydrolysis of 6-nitro-1-acetylamino pyrene. 1-Amino-6-nitro pyrene was obtained as purplish black granular material. Attempts to purify it by recrystallization were totally unsatisfactory. It was highly insoluble in most solvents. It showed brilliant orange fluorescence in di-isopropyl ether and greenish yellow fluorescence in toluene. It was non-fluorescing in both acetone and methanol and wouldn't crystallize out of these solvents as anything but the same black product. 1-Nitro-6-tosyl-aminopyrene was prepared from this amine. This sythesis is a replacement for the originally proposed 1-N,N-dimethylamino-6-nitro pyrene. It is based on the ease of preparation of the amino tosylate and the toxicity of the reagents, in particular methyl iodide, needed to prepare the dimethylamino compound from 1-amino-6-nitropyrene. The melting range of the 1-nitro-6-tosylamino pyrene, obtained as a dark brown powder, was 170-180°C. It was reduced to 1-amino-6-tosylamino pyrene with hydrazine hydrate in the presence of palladium. The product was

SYNTHESIS SEQUENCE FOR 1-PYRENE DIAZONIUM COMPOUNDS

COMPOUND TYPE II

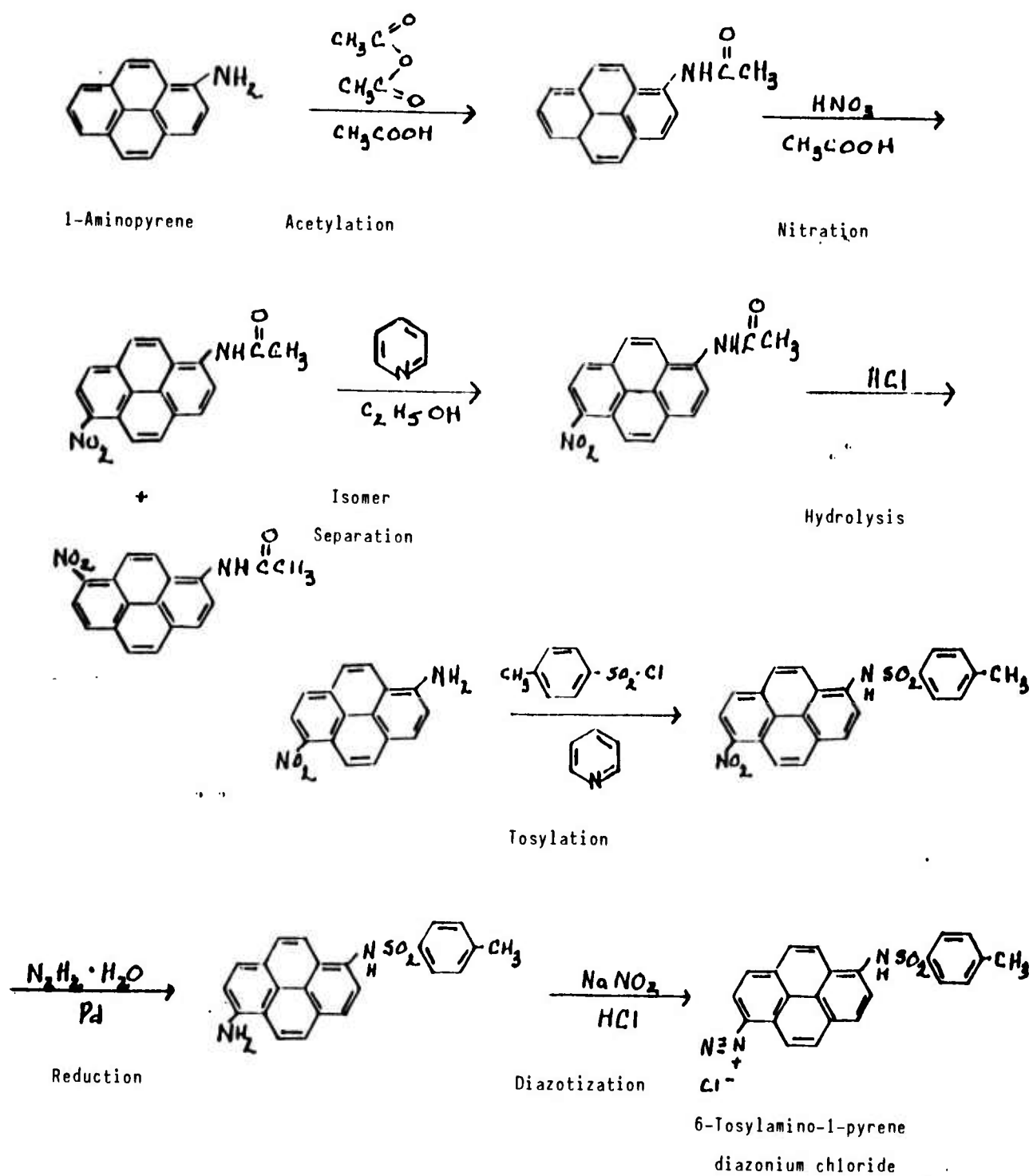


FIGURE 5

muddy olive drab in color.

Diazotization of 1-amine-6-tosylamino pyrene by the direct method was successful. Exposure to the Frequency Systems light source for 15 and 30 seconds and 1 and 2 minute time intervals gave weak images when developed with Coupler 122. This spectral response was most encouraging but it was apparent that synthesized intermediates as well as the final diazonium salt would need to be obtained in much greater purity to have a satisfactory system for the Frequency Systems copying process.

Two additional pyrene diazonium salts which can be directly synthesized from the intermediates of the pyrene synthesis sequence (Figure 5) are 1-acetylamino-6-pyrene diazonium chloride and 6-nitro-1-pyrene diazonium chloride.

1-Pyrene Diazonium Chloride

The diazonium salt of 1-aminopyrene exhibited as good spectral response to the Frequency Systems light source as any of the molecular structures under investigation. Excellent color development was seen with this compound, and initial stability to ambient temperature and humidity conditions was observed.

1-Aminopyrene is commercially available in research quantities at 97% purity. It was decided in the last quarter of the project to concentrate our efforts on the diazonium salt of 1-aminopyrene. Previous results had shown this material to have a broad spectral response from 550 to 360 nm. Intensely colored images were obtained with 30 second exposures to the Frequency systems light source. The 1-pyrene diazonium system exhibited self coupling exposure to ammonia vapors giving light brown images. Image colors were purple with Coupler 122 as developer and deep blue with H Acid as developer. Some background was present but it was considered minimal. It was the consensus of

Frequency Systems and Bard Laboratories that a commercial system could feasibly be developed with pyrene diazonium chloride. Improvements in the procedure for diazotization of 1-aminopyrene, reduction of the background color of the diazo image and acceptable stability of the diazotype 1-pyrene diazonium paper were the major goals.

Diazotization of 1-aminopyrene can be done by the "Direct Method."

The acidic diazonium salt solution is a deep reddish orange. Coatings on diazo base paper are deep gold in color. The diazonium solutions can be used for paper coatings for a month's period of time if kept in the cold below 5°C. A by-product forms with the diazonium salt, however, as the diazotization reaction proceeds. This by-product is a fine black precipitate and its formation is a slow process whereas the diazotization is a fast reaction. It can be removed from the diazonium solution by filtration, its presence having little or no degradation effect on the diazonium salt in solution.

Other diazotization methods were investigated to optimize diazonium salt formation and eliminate this secondary reaction. Two methods showed improved results. 1-Aminopyrene was dissolved in hot 2N hydrochloric acid and this mixture poured onto ice with efficient stirring. This method is recommended for diazotization of a weakly basic amine.⁶ As the basicity of the amine becomes less, the amount of hydrochloric acid must be increased until just that concentration can be found at which the amine will dissolve in the hot acid. This step is critical because if the amine salts out as the hydrochloride, diazotization will not proceed well. When dissolved, the aminopyrene hydrochloric acid solution is poured over ice; the amine becomes dispersed in the medium as finely divided particles. Rapid addition of an 8% sodium nitrate solution with vigorous stirring causes the solid to pass into solution as the diazonium salt forms. This method is a definite improvement over the "Direct Method" and formation of the interfering black precipitate is minimized.

The other method which showed promising results proceeds as follows. 1-Aminopyrene is dissolved in acetic acid and added to a solution of solid nitrosylsulfuric acid in acetic acid. The diazonium salt can be precipitated as the diazonium sulfate with the addition of a five fold excess of ether. No black precipitate was formed with 1-pyrene diazonium sulfate but the solid product deteriorated. Further investigation is needed to evaluate the merit of this approach.

The background color of diazo images using 1-pyrene diazonium chloride paper coatings was of concern. The significant fact, that some of the photodecomposition products we were obtaining were colored, escaped our attention for some time. When imaging with the Frequency Systems light source undeveloped reversed images appear pale lavender in color. Subsequent development with diazo couplers appear to erase this image in the light exposed areas because there is excellent diazo coupling in the unexposed areas. Photodestruction of the last 10% of the diazo groups, required for background clarity, is difficult however when many of the incident photons of light are absorbed by photodecomposition products.

The first indication of this color reaction was seen with spectral measurements made on the Beckman BD-G Spectrophotometer as reported in the Second Quarter report.

Spectral measurements of aliquot portions of the diazonium reaction mixtures have been made on the Beckman BD-G Spectrophotometer. A diluted portion of the acid diazonium solution is measured from 350 to 700 nm to determine the range of maximum light absorption by the diazonium compound. The measured solution is then directly exposed to ultra-violet light for 1 minute and a second spectral measurement is made. This is followed with a 5 minute exposure to tungsten light and a third

measurement at 350 to 700 nm on the spectrophotometer. Any loss of light absorption properties of the diazonium salt are readily obvious.

The spectral measurements showed maximum absorption bands for

1-pyrene diazonium chloride at 390-500 nm

6-tosylamino-1-pyrene diazonium chloride at 350-500 nm.

With irradiation from ultraviolet light and subsequent irradiation with tungsten light spectral curves changed. Light absorption decreased slightly with 6-tosylamino-1-diazonium chloride. Light absorption increased slightly from 550 to 600 nm with 1-pyrene diazonium chloride.

A second set of measurements made in solution on July 3, 1985 show this phenomenon also. The spectral curve is shown in Figure 6.

Reflectance measurements were made in November on the Beckman DB-G Spectrophotometer of 1-pyrene diazonium chloride coated paper unexposed to light versus exposure to the Frequency System Light source for time intervals of 0, 8, 20, 40, 80, 120, 340 and 720 seconds. Maximum amount of photodecomposition products, absorbing light at 550 nm, formed at 80 seconds light exposure shown in Figure 7.

Attempts to minimize secondary photodecomposition product formation with 1-diazo pyrene included dispersing the diazonium salt in "glassy" polyols, changing to stronger acids for the counterion, use of coordinating acids such as sulfosalicylic or boric acid and fluoroboric adducts, and use of antioxidants. All were of no avail. Repurification of the amine to be diazotized, use of a variety of diazotization procedures, and post-diazotization purification of the diazo compound itself did not help.

Absorption Spectra of

- 1) 1-pyrene diazonium chloride in dilute HCl
- 2) solution 1 after 1 minute uv exposure
- 3) solution 2 after 5 minute tungsten light exposure

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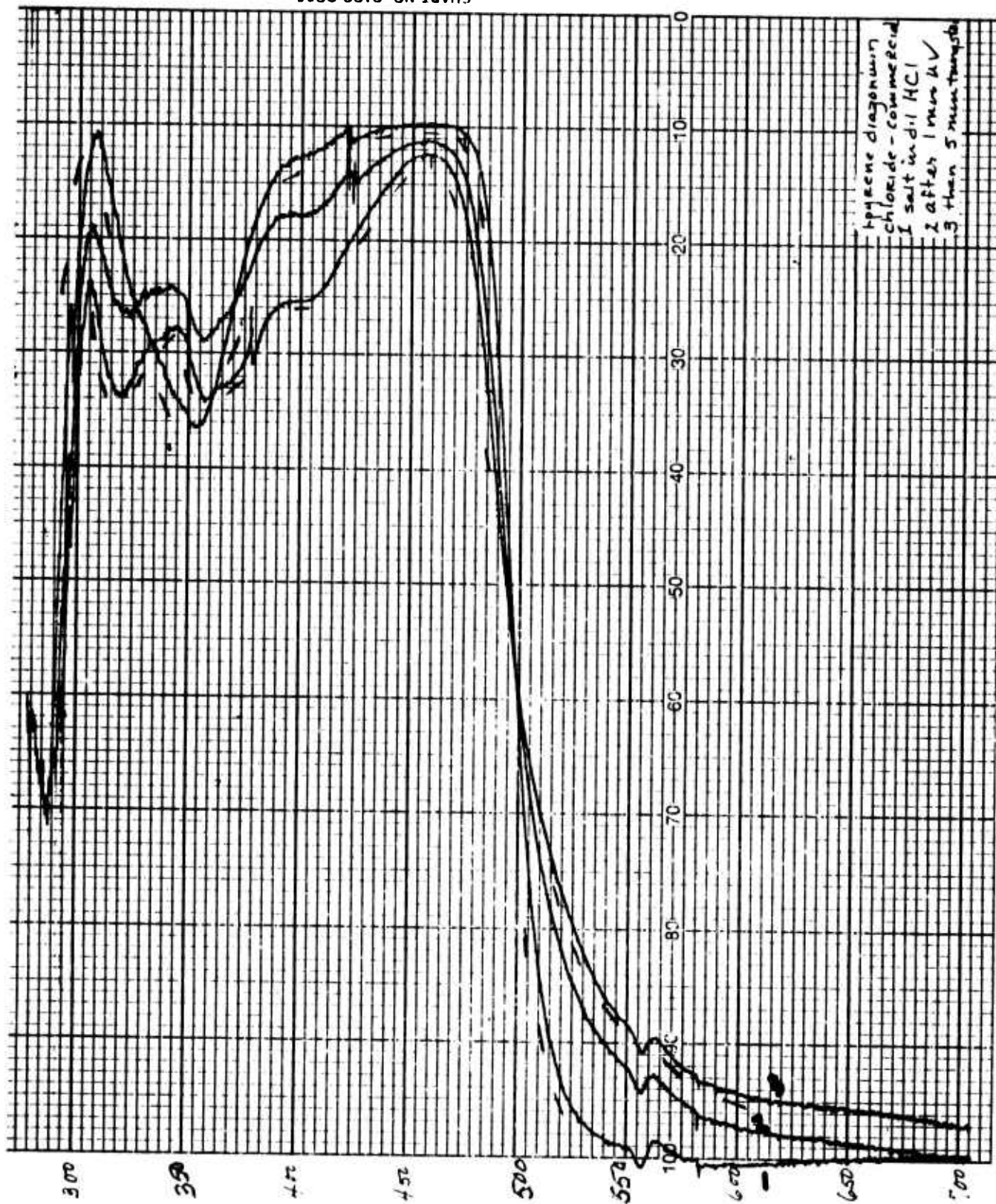
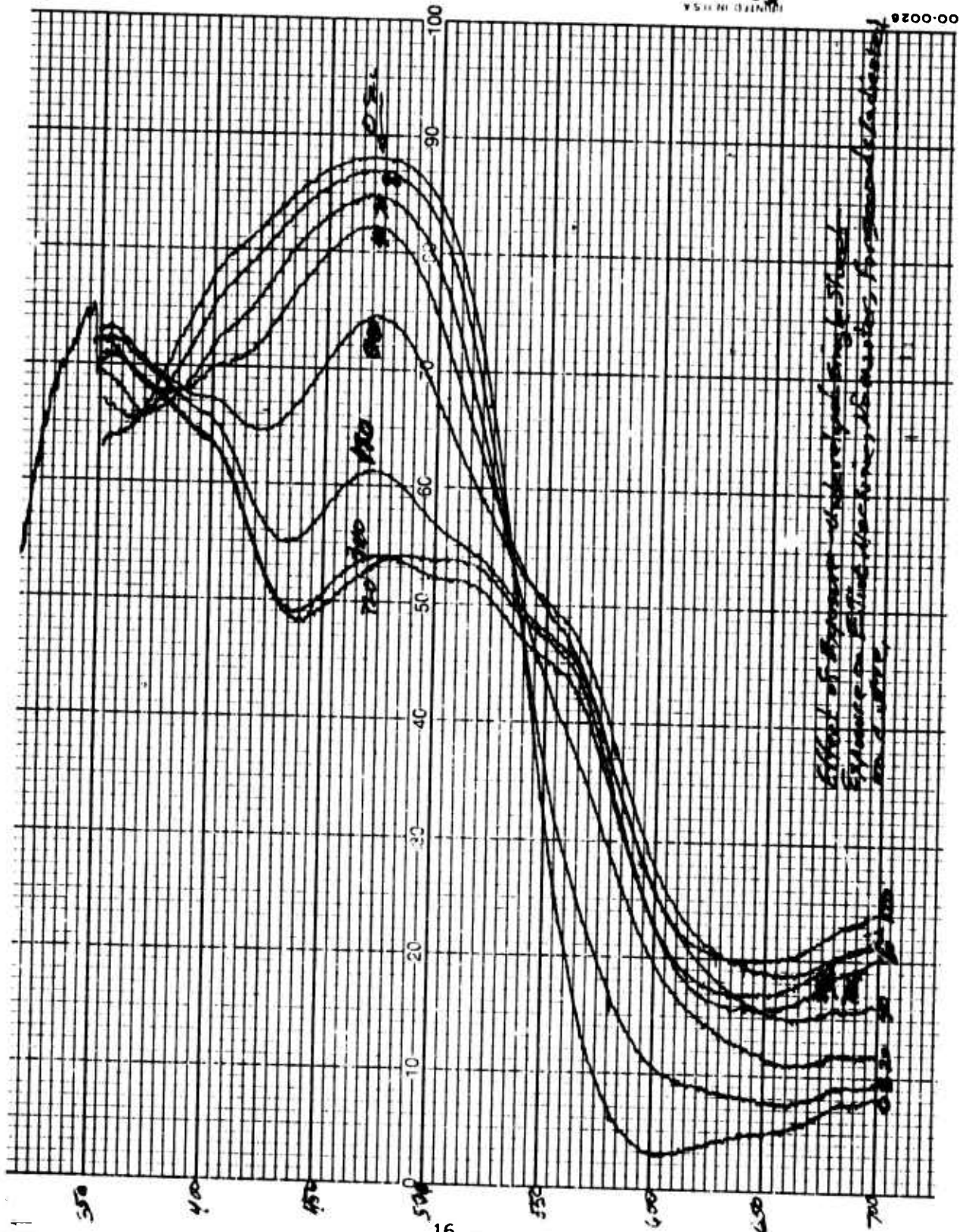


FIGURE 6

Reflectance Spectra of 1-Pyrene Diazonium Chloride Coatings after light exposure to the Frequency Systems light source at 0, 8, 20, 40, 80, 120, 340 and 720 seconds

FIGURE 7

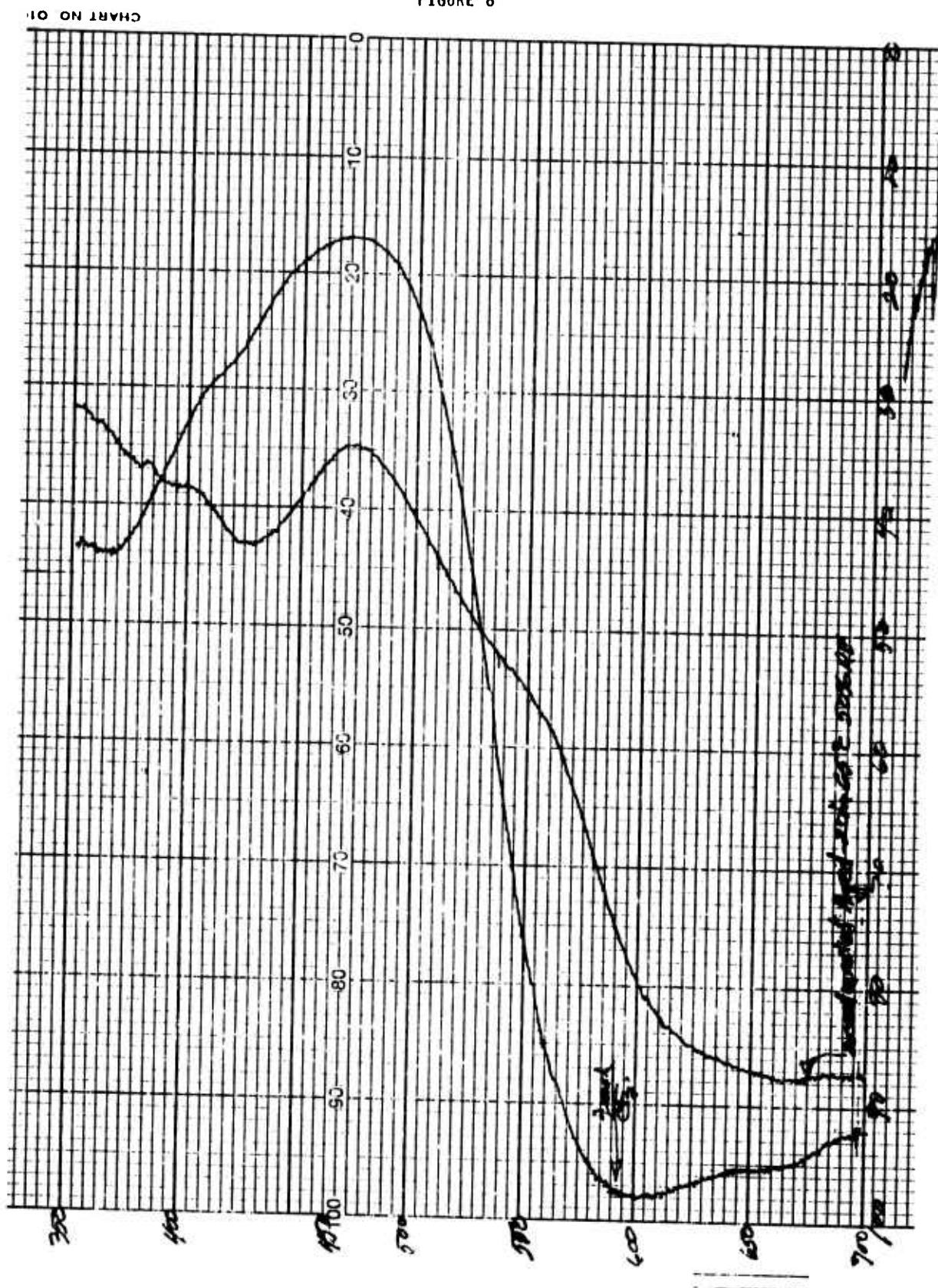


Stability tests on the 1-pyrene diazonium chloride system were done by storing coated paper for 20 hours at 65°C and 50% relative humidity. This is equivalent to one year storage time at normal conditions. The results of these accelerated ageing studies were evaluated by reflectance measurements on the Beckman DB-G Spectrophotometer. An increase in spectral response occurs from 700 to 530 nm due to the formation of colored decomposition products. A partial loss in photo-response occurs between 530 and 390 nm. The absorption curve is shown in Figure 8.

The 1-diazo pyrene ring system is useful for the purposes of this project. It has one major problem: the color of the photodecomposition products in the diazotype process. This problem remains unsolved and needs additional research.

Reflectance Spectra of 1-Pyrene Diazonium Chloride Coating
Spectra Response after Aging

FIGURE 8



2-Pyrene Diazonium Compounds Compound Type III

The 2-pyrene diazonium system represents a modification of the 1-pyrene diazonium compounds under investigation. A literature survey of pyrene compounds substituted at carbon-2 indicates synthesis of this series of compounds, for evaluation with Frequency Systems, would be difficult and of questionable value.²⁷ Carbon-2 on the pyrene nucleus is relatively unreactive. The starting materials to synthesize 2-aminopyrene compounds are (2.2) metacyclophane or 4,5,9,10-tetrahydropyrene, two unconjugated aromatic ring systems.²⁶ Neither of these compounds are commercially available. The structural formulas of these compounds are shown in Figure 9.

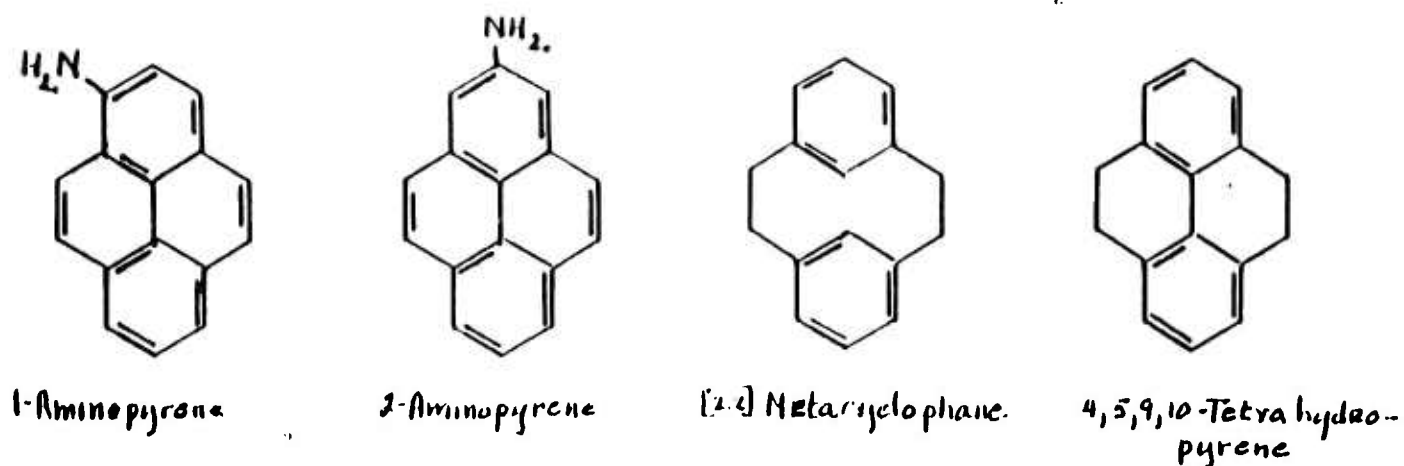


Figure 9

A mixture of 1-amino- and 2-aminopyrene has also been obtained in low yield by reacting 1-bromopyrene with potassium amide in liquid ammonia. The difficulty of separating the aminopyrene isomers and the % yield of 2-aminopyrene make this a poor approach.

A comparison of the ultraviolet absorption spectra of 1-aminopyrene and 2-aminopyrene in alcohol show:

1-aminopyrene		2-aminopyrene	
max (nm)	log ϵ	max (nm)	log ϵ
242	4.63	266	4.80
284.5	4.39	309	3.92
362.5	4.17	338.5	4.52
407.5	3.98	400	3.24

On the basis of this information it is predicted that minimal differences would be observed in the spectral response of 7-tertiary amino-2-pyrene diazonium salts versus 6-tertiary amino-1-pyrene diazonium salts. Synthesis of 2-aminopyrene derivatives was not pursued.

Dibenzofuran Diazonium Compounds Compound Type IV

The dibenzofuran nucleus, with its correct numbering system, and the schematic synthesis procedures for obtaining the desired dibenzofuran diazonium salts are shown in Figures 10 and 11.

Dibenzofuran diazonium salts were investigated as a representative structural modification of the fluorene nucleus. The synthesis route for obtaining these compounds, although involving a multiplicity of steps, proceeded with excellent results.

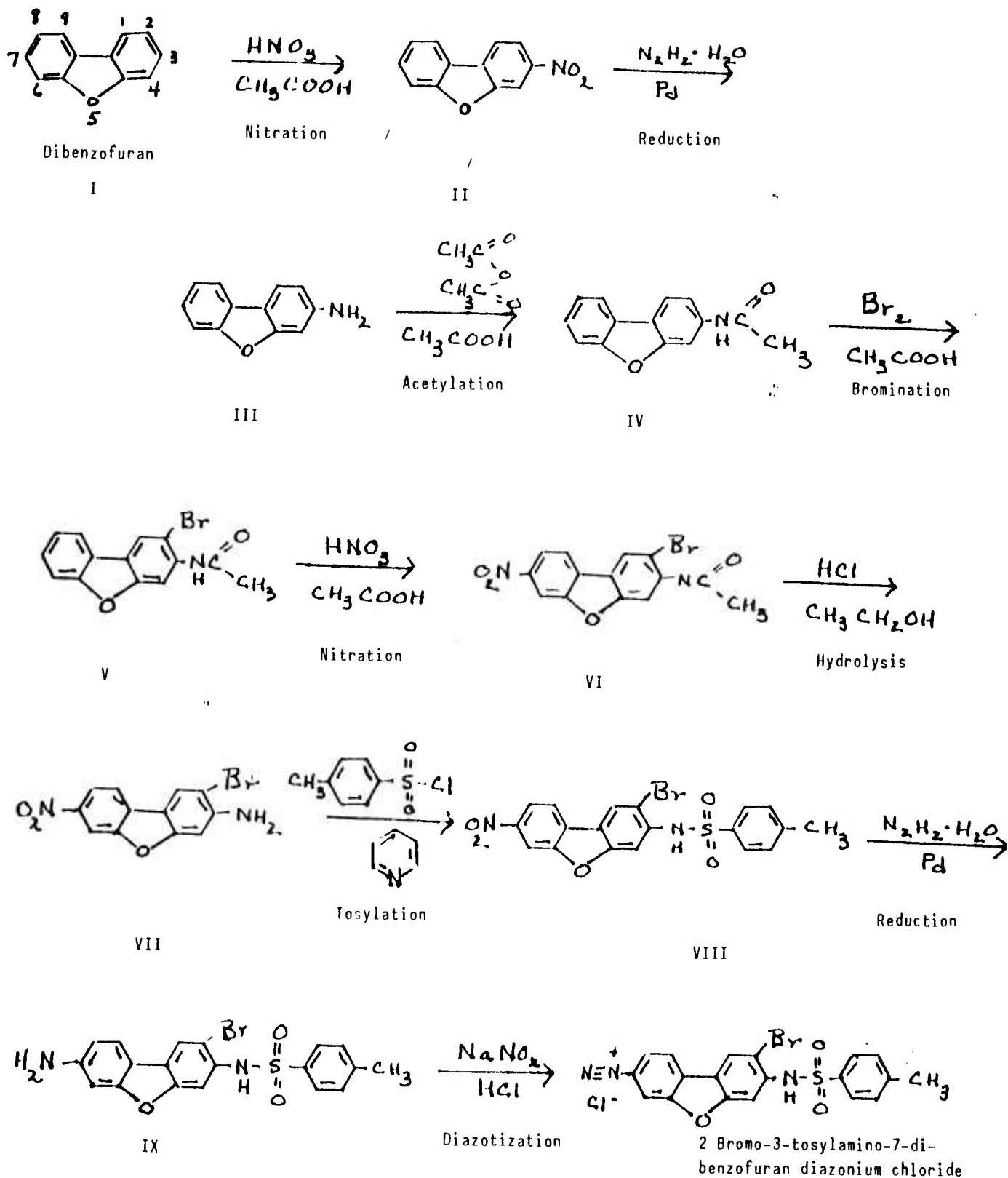
To obtain 3-amino substituted-7-dibenzofuran diazonium salts it is necessary to block carbon-2. This was done by substituting bromine on the dibenzofuran ring system at carbon-2. The presence of bromine here further promotes the positioning of a nitro group on the ring system at carbon-7.

The dibenzofuran diazonium salts which were synthesized are:

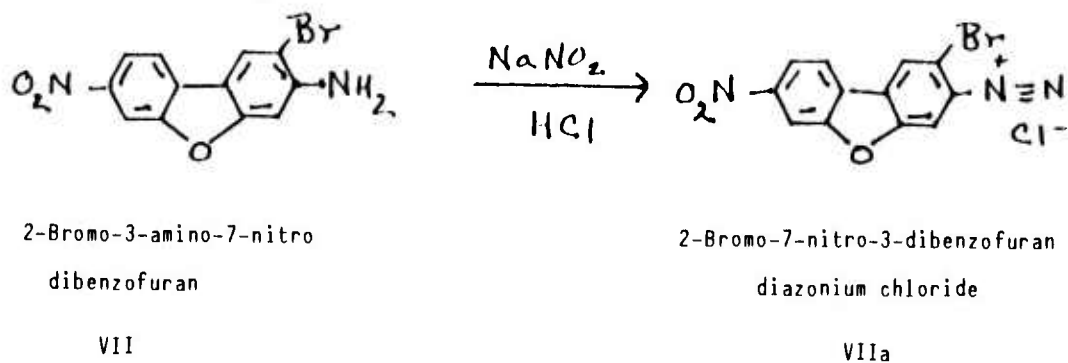
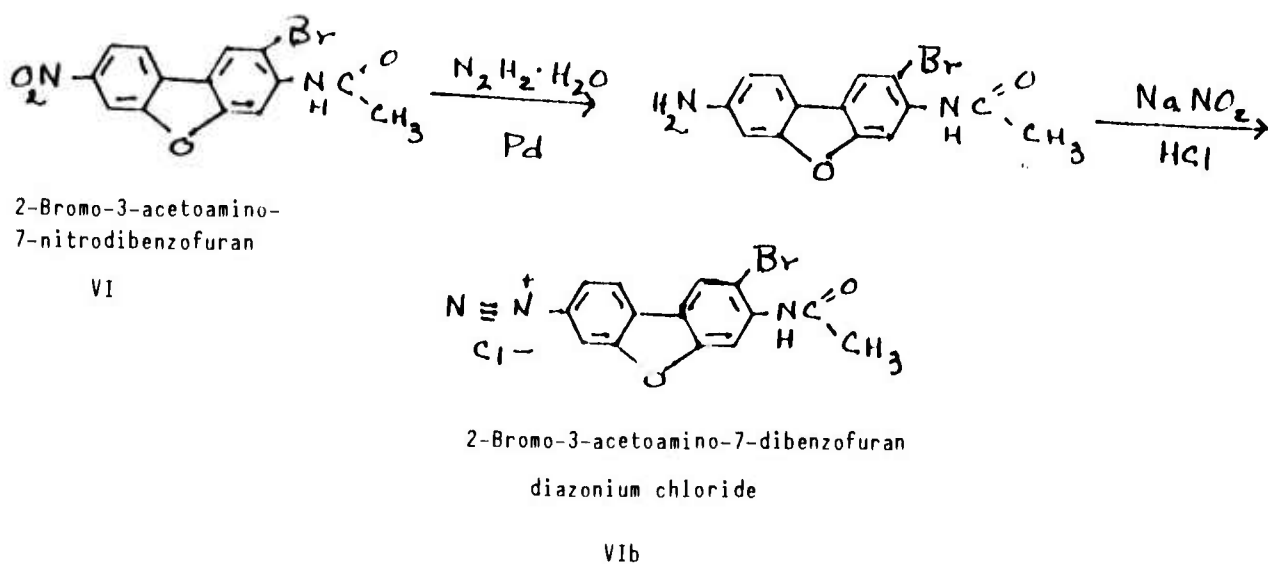
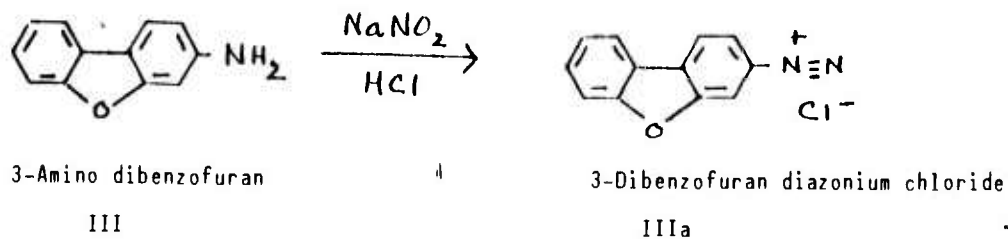
1. 3-dibenzofuran diazonium chloride
2. 2-bromo-3-acetoamino-7-dibenzofuran diazonium chloride
3. 2-bromo-7-nitro-3-dibenzofuran diazonium chloride
4. 2-bromo-3-tosylamino-7-dibenzofuran diazonium chloride

Evaluation of these dibenzofuran diazonium compounds showed them to be very stable in solution. Their spectral response was slow requiring a minimum of 4 minutes light exposure to the Frequency Systems light source. 3-Dibenzofuran diazonium chloride showed spectral response in only the ultraviolet. The color of developed images using Coupler 122 was pink. A suitable coupler, giving sepia or purple images, was found to be H acid. On the basis of the slow spectral response of the dibenzofuran diazonium compounds, and the long involved synthetic route to obtain these compounds no further work was done with the dibenzofuran series.

FIGURE 10
SYNTHESIS SEQUENCE FOR DIBENZOFURAN DIAZONIUM COMPOUNDS



from Dibenzofuran Synthesis Sequence Figure 3



Naphthalene Diazonium Compounds

Certain dialkylamino diazonaphthalene compounds ^{cont'd} meet the criteria specified for compounds to be investigated. Naphthalene is a rigid planar carbon ring system. Both 5-dimethylamino-1-naphthalene diazonium chloride (Example 1) and 6-dimethylamino-2-naphthalene diazonium chloride (Example 2) possess the relatively long electrically conductive paths between appended polar nitrogens. 4-Dimethylamino-1-naphthalene diazonium fluoborate was patented in 1960 by Bruni and Morgan as a diazo compound with sharp absorption at 420 nm, the blue end of the visible spectrum. This has a shorter electrically conductive path than the diazo naphthalene compounds we are proposing.

On the basis of these facts, the ready availability of starting materials and the marginal results from the fluorene and dibenzofuran diazonium systems, synthesis was initiated on the above named naphthalene diazonium salts. The naphthalene ring system is shown below to illustrate the numbering system for this compound and the α and β carbons of the naphthalene ring.

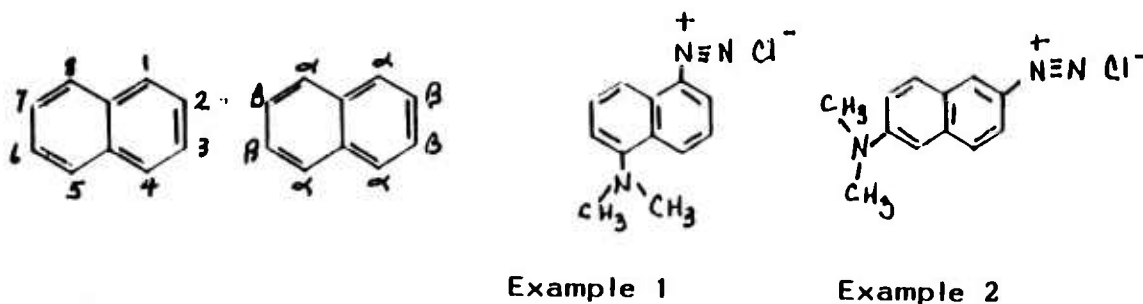


Figure 12

Synthesis of disubstituted naphthalene compounds, particularly with a substituent located on each of the two rings, is difficult because there is a strong tendency for contamination by unwanted isomers. Two promising, unidentified products, sensitive in the desired

Wavelength range, have been obtained. One was roughly comparable in color and speed to diazopyrene. The other, though slower, was deep red in color.

The synthesis route chosen for initial attempts to prepare materials of the Example 1 class is as follows: 1-nitro naphthalene is available commercially as starting material. A nitro group deactivates any aromatic ring to which it is attached. The other ring behaves in part as a 4-carbon conjugated aliphatic connected at each end to the aromatic ring. As a conjugated aliphatic, it can add bromine as bromine's 1,4 addition to butadiene. Thus, the product is a partially hydrogenated 5,8-dibromo-1-nitro naphthalene. However, on heating, HBr splits off and the naphthalene ring structure is recreated. The bromine remaining will, for the most part, be attached to ring carbon 5, but with some 8-bromo isomer. By isolating and purifying the 5-bromo-1-nitro naphthalene and high temperature cooking in a "bomb" with diethylamine, 1-nitro-5-diethylamino naphthalene results. When purified and reduced to 1-amino-5-diethylamino naphthalene, it can be diazotized with nitrous acid to form the targeted Example 1 analog, 1-diazo-5-diethylamino naphthalene for isolation and photospectral response evaluation.

Synthetic routes to produce specific naphthalene derivatives are dominated by a recognition that initial attack by modifying reagents occurs 30 to 100 times more readily on α carbons, than on β carbons. This increased reactivity also extends to radical exchange, i.e., replacement of substituents previously attached. The usual method employed to introduce substituents on the β carbons relies on high temperature sulfonation. Because sulfonation is reversible, α substituted products initially formed are repeatedly made and unmade during prolonged high temperature reaction with sulfuric acid. However, any β substituted product formed is much more stable and its presence on the ring in the β position renders the adjacent α carbon much less reactive. Consequently, by prolonged heating with sulfuric acid at about 150°C,

followed by water dilution and reaction at 80-100°C to remove any α attached sulfonic acid groups yields of β sulfonic acid in excess of 95% are readily attained. Reacting the substituted naphthalene sulfonic acid with sodium hydroxide leads to replacement on the β carbon of (the sulfonic acid group) by a hydroxyl group. Amine groups can, in turn, replace this hydroxyl group by cooking under pressure with aqueous amine bisulfite solutions. Other groups can then replace the primary amine.

An alternative route to β nitro derivatives, is to first catalytically hydrogenate one of the two rings, forming tetrahydro naphthalene (tetralin). If this is nitrated in the regular way for alkyl benzenes and catalytically dehydrogenated back to the naphthalene ring system, the nitro group will be in the β position. The latter reaction conditions can optionally be extended to reduce the nitro group to a primary amine as well. Another useful technique is to preexhaust the competitive more reactive sites on the ring by displacing the α hydrogens with a substitute group such as halogen atoms. This leaves the less reactive sites free to undergo the desired substitution reactions.

A variety of proposed routes to the desired target compounds have been conceived. However, they have not been sufficiently perfected to assure reasonable yields, nor have suitable purification techniques been developed for each of the several sequential steps involved in preparing the naphthalene derivatives proposed.

For future work, it is proposed initially to prepare, purify, and evaluate at least one naphthalene derivative of each of the compounds illustrated by Examples 1 and 2 of Figure 12. Dimethylamine is highly volatile so, to facilitate laboratory procedures without detriment to photospectral response, an alternative dialkylamino group would be employed. Both diethylamine, and morpholine are much easier to use in syntheses.

Predicted advantages for these compounds over those based on pyrene include colorless photodegradation products and good availability of raw materials without sacrifice of spectral characteristics. Ring substitutions for products typified in Example 1 are on naphthalene's more reactive carbons. Electrical forces between the two active radicals attached to the rings in Example 1 are slightly unbalanced but, it is believed, not sufficiently so to appreciably degrade storage stability. Electrical balance for products typified in Example 2 is much better, and their storage stability is predicted to be excellent.

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