

REACTION OF MONONITROFLAVYLIUM PERCHLORATES
WITH DIMETHYLANILINE

By

MARY JUSTINE WARNKE

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Bachelor of Science

Simmons College

Boston, Massachusetts

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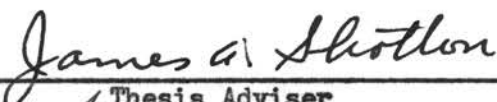
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the Oklahoma Agricultural and Mechanical College
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for the Degree of
MASTER OF SCIENCE

1951

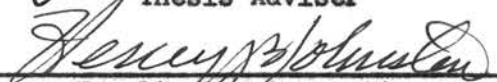
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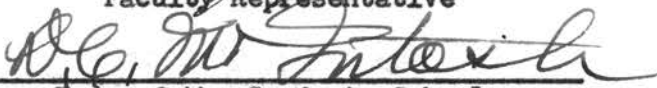
THESIS AND ABSTRACT APPROVED:



Thesis Adviser



Faculty Representative



Dean of the Graduate School

283562

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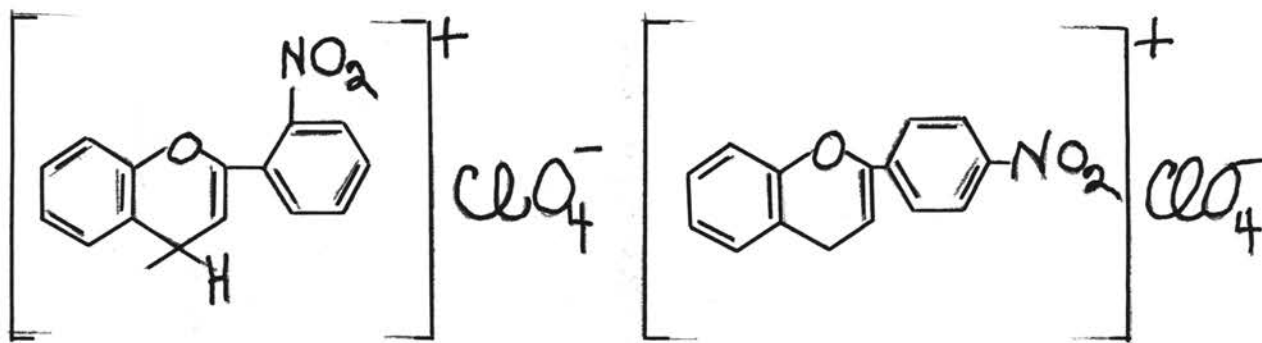
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INTRODUCTION

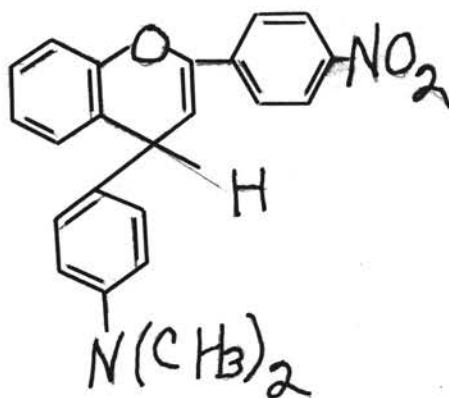
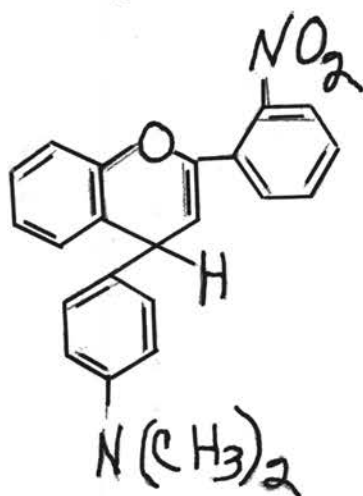
The reaction of flavylum salts with the active hydrogen of ammonia and amines indicates that these salts may behave as carbonium ions.

The object of this research was to prepare the 2-(2'-nitrophenyl)-4-(4"-dimethylaminophenyl)-1,4-benzopyran (II) and 2-(2'-nitrophenyl)-4-(4"-dimethylaminophenyl)-1,4-benzopyranol (III) from the reaction of 2'-nitroflavylum perchlorate (I) with dimethylaniline, and the analogous 4'-nitro derivatives. (IV, V, VI)



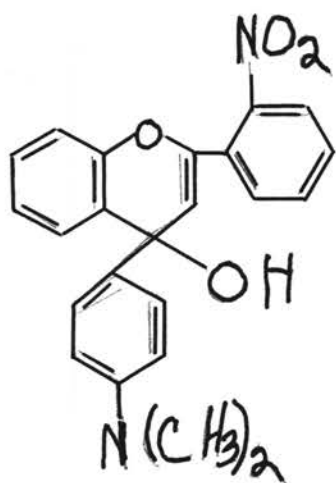
I

IV

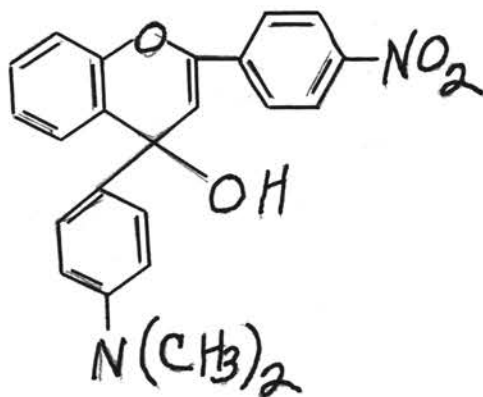


II

V



III

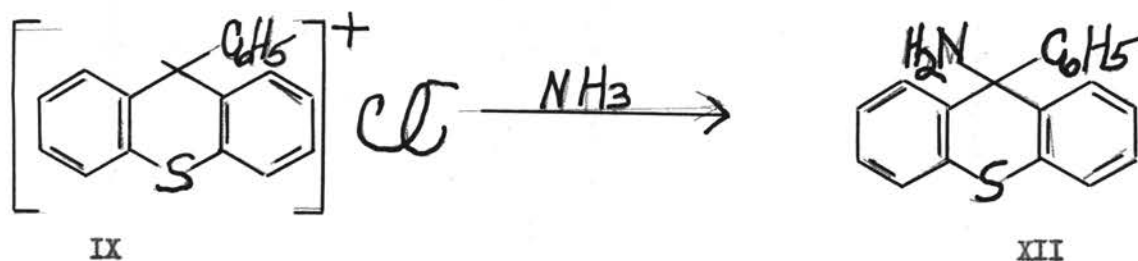
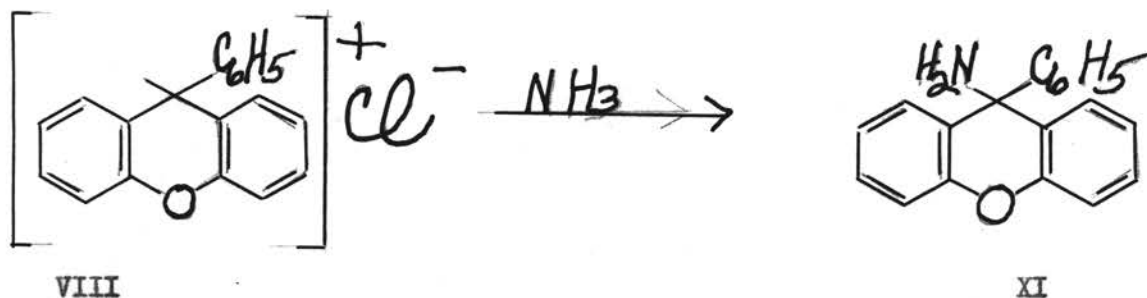
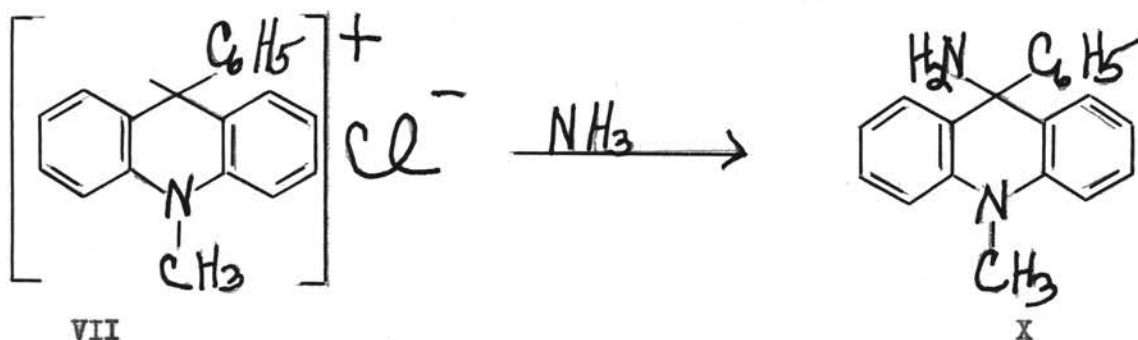


VI

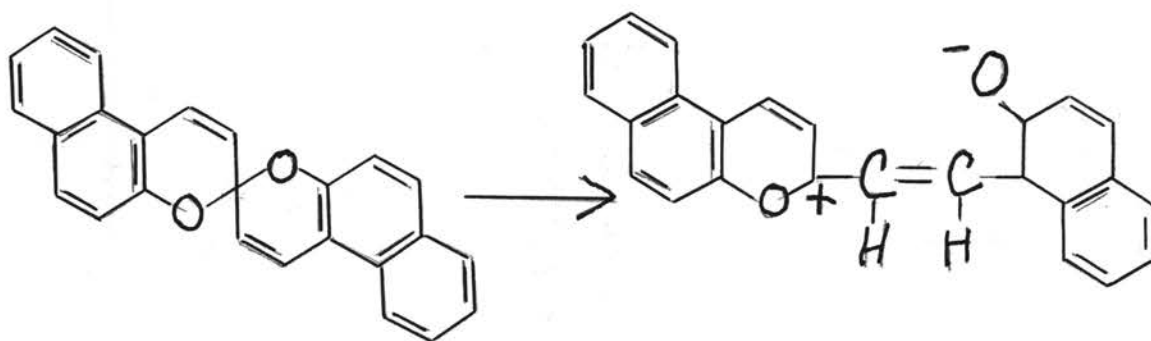
HISTORICAL

The flavylum, or 2 phenylbenzopyrylium, salts may be prepared, in general, by the reaction of the ether solutions of 2-hydroxychalcones with dry hydrogen chloride; or by direct condensation, in ether, of the appropriately substituted acetophenones with salicylaldehyde with dry hydrogen chloride. Hill (5) has written a review on the methods of preparation of benzopyrylium salts.

One of the first of the few investigations of the reaction of carbonium ions with ammonia or amines was done by Decker and Becker (1) in 1913. They reported the reaction of 10-methyl-9-phenyl-acridium chloride (VII), 9-phenyl-xanthylium chloride (VIII), and 10-phenyl-thioxanthylium chloride (IX) with ammonia to give the corresponding amines (X, XI, XII).

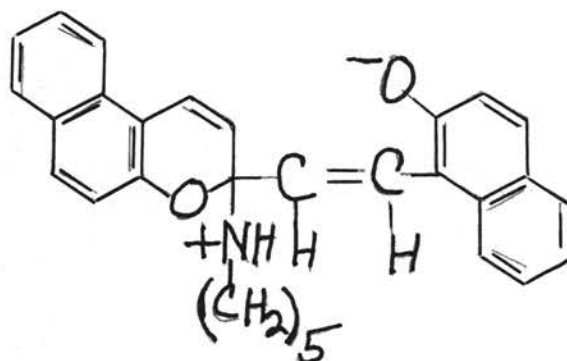
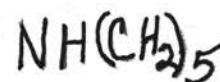


Dilthey, Beires, Holterhoff and Wubken (2) prepared spiro-di-naphthopyran (XIII) and noted that when heated alone, the compound produced a blue colored compound (XIV), whereas when heated with piperidine, it remained colorless. The following explanation was given for the transformation.



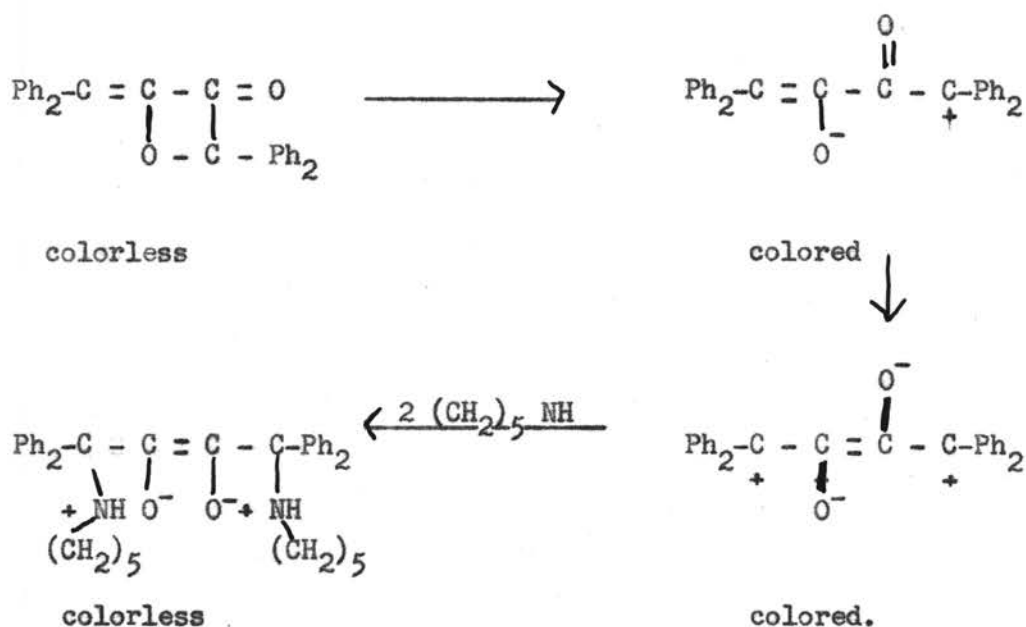
colorless XIII

colored XIV



colorless

Schonberg and Sina (9) explained the loss of color of the permanganate colored diphenylketene dimer on heating with piperidine by a mechanism analogous to that of Dilthey.



Strauss (13) showed that compounds of the general type $(\text{Ar}_2\text{C} = \overset{+}{\text{C}}\text{H}-\overset{+}{\text{C}}\text{H}-\text{Ar})$ Cl^- formed colored complex salts with ferric chloride and perchloric acid, had conductivity in sulfur dioxide, and reacted with alcohols to give alkoxy derivatives. These reactions are all characteristic of the flavylum salts.

Shotton (10) reported that the reaction of flavylum perchlorate with ammonia gave three products which on analysis indicated that the perchlorate had reacted with ammonia in the ratios of 3 to 1, 2 to 1, and 1 to 1. Using piperidine to react with the flavylum salt, only one product was obtained, which from ozonolysis data, indicated that the compound formed was 2-phenyl-4-piperidino-1,4-benzopyran.

Shotton also found that when the flavylum perchlorate was reacted with aniline, three products were obtained, whereas when dimethylaniline was used, only one product, 2-phenyl-4-(4^{''}-dimethylaminophenyl)-1,4-benzopyran (XVI) was found.

Ullman and Engi (14) prepared 4[']-amino-9-diphenylxanthene by the reaction of 9-phenylxanthenol with aniline.

Rice (8) prepared 9-(4[']-dimethylaminophenyl)-xanthene by the reaction of xanthylium perchlorate with dimethylaniline.

The reaction of xanthidrol with phenols using glacial acetic acid, sulfuric acid or anhydrous aluminum chloride as a condensing agent to produce p-hydroxyxanthenes was reported by Nierderl and Hart (7).

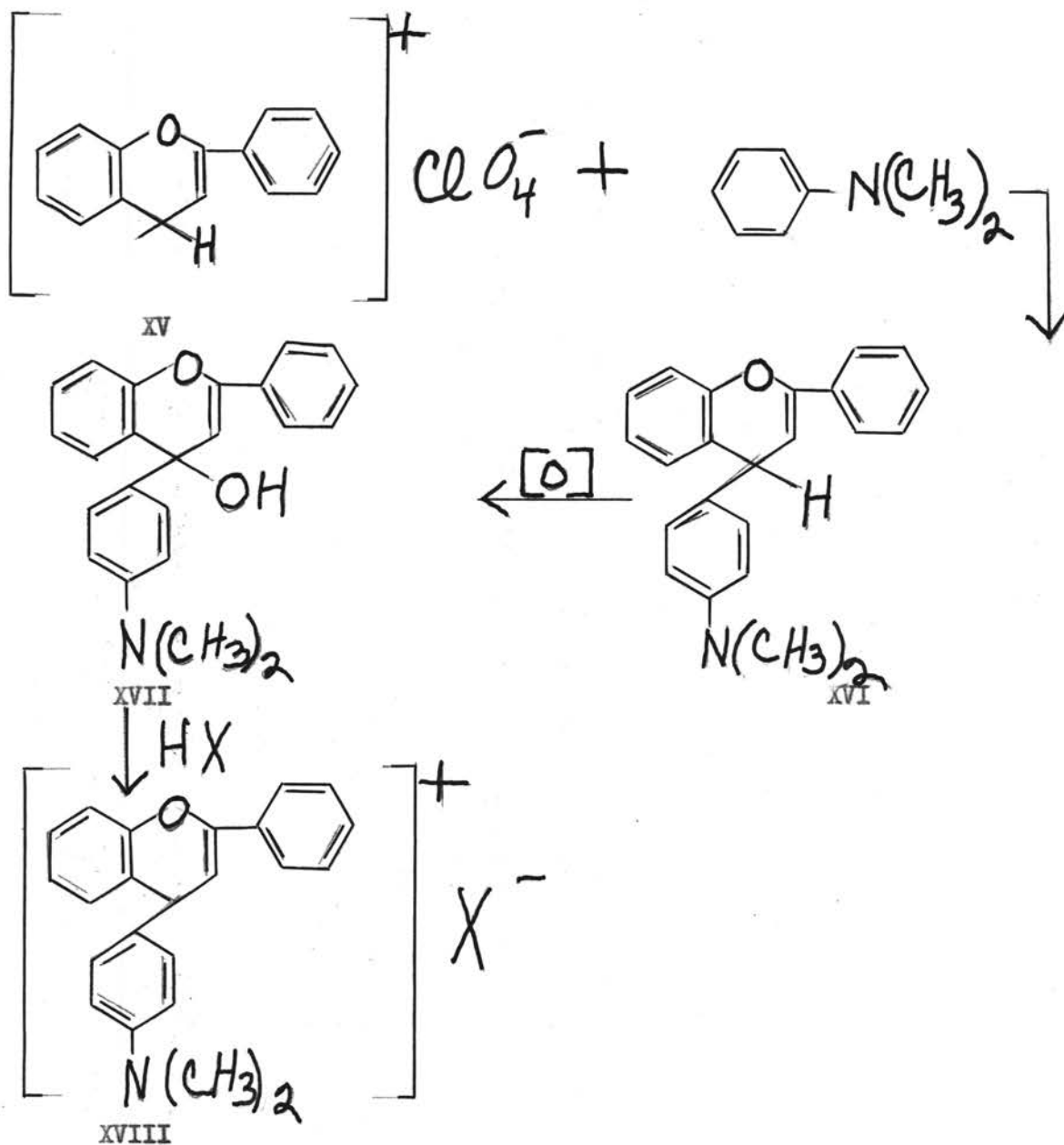
Gomberg and Kamm (4) showed that triphenylmethylcarbinol and triphenylmethyl chloride in the presence of very small amounts of acid, condensed with phenol to give excellent yields of p-hydroxytetraphenylmethane.

Other condensations of tertiaryphenyl alcohols with compounds having an active hydrogen makes it possible to consider that the above reactions might proceed via carbonium ions produced by the action of the acids involved.

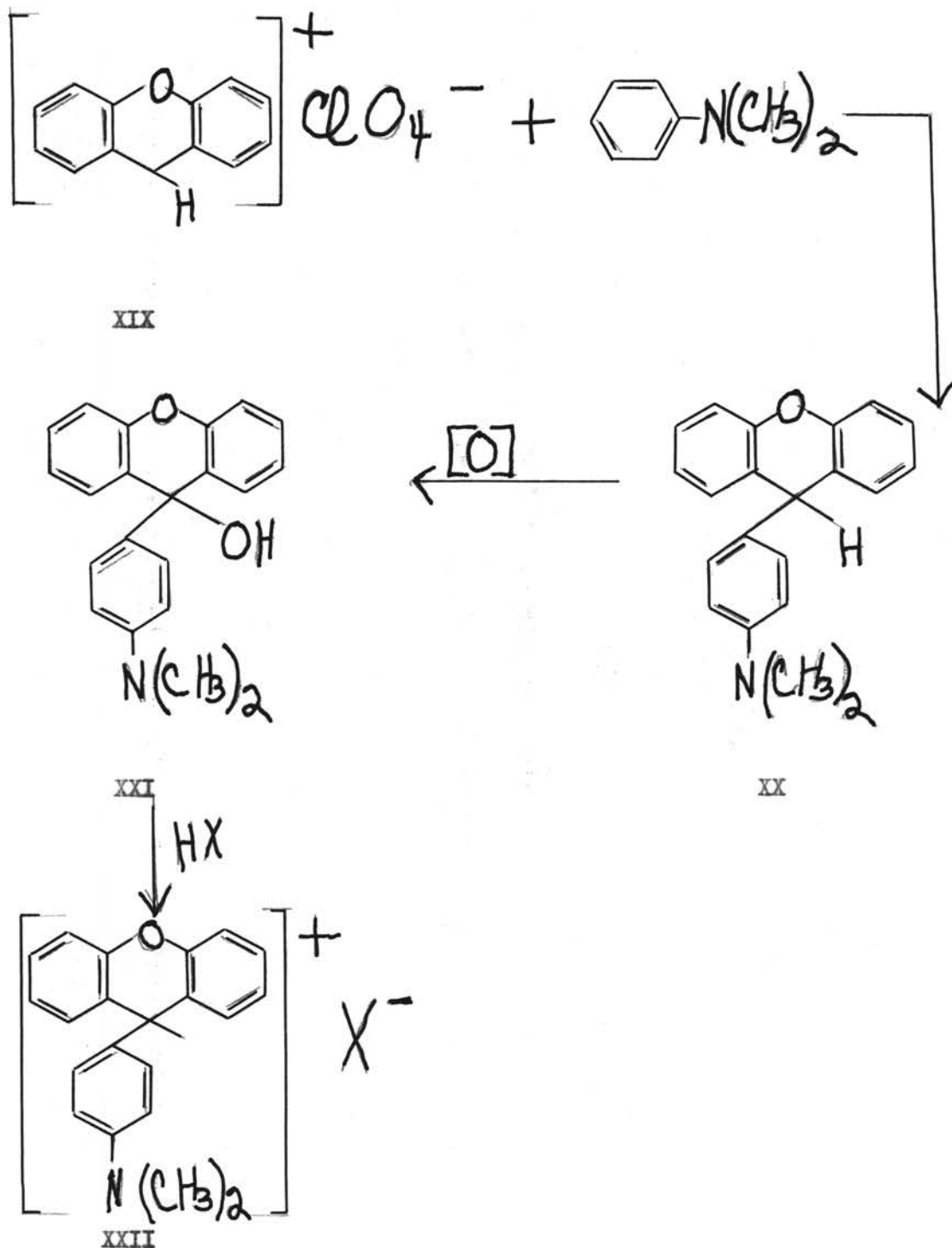
THEORY AND DISCUSSION

Shriner and Moffett (11 and 12) showed that flavylum salts probably exist as carbonium ions with the two main positions for the charge being on the number two and four carbons of the heterocyclic ring.

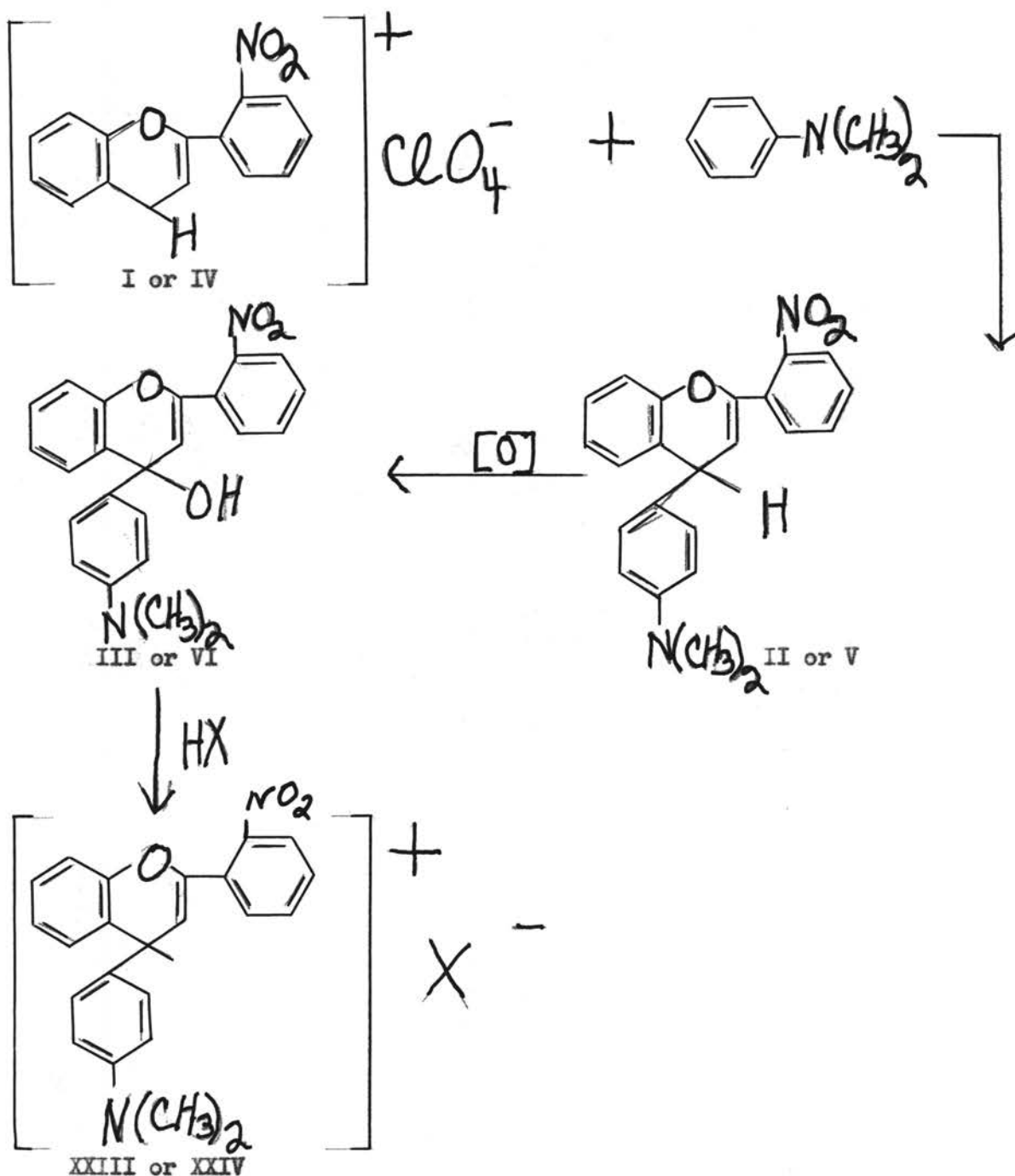
Shotton (10) found that when flavylum perchlorate (XV) reacted with dimethylaniline the following reactions took place.



Rice (8) found that when xanthylium perchlorate (XIX) reacted with dimethylaniline, XX was produced which oxidized to the carbinol XXI which, in turn, formed the salt XXII in the presence of acid.



The problem here was to study the reaction of the 2' and 4' nitroflavylium perchlorates with dimethylaniline. It was expected that steric hindrance would cause the major reaction to occur at the number four position. The following reactions were postulated for the 2' nitro substituted flavylium salt with similar reactions for the 4' nitro substituted flavylium salt.



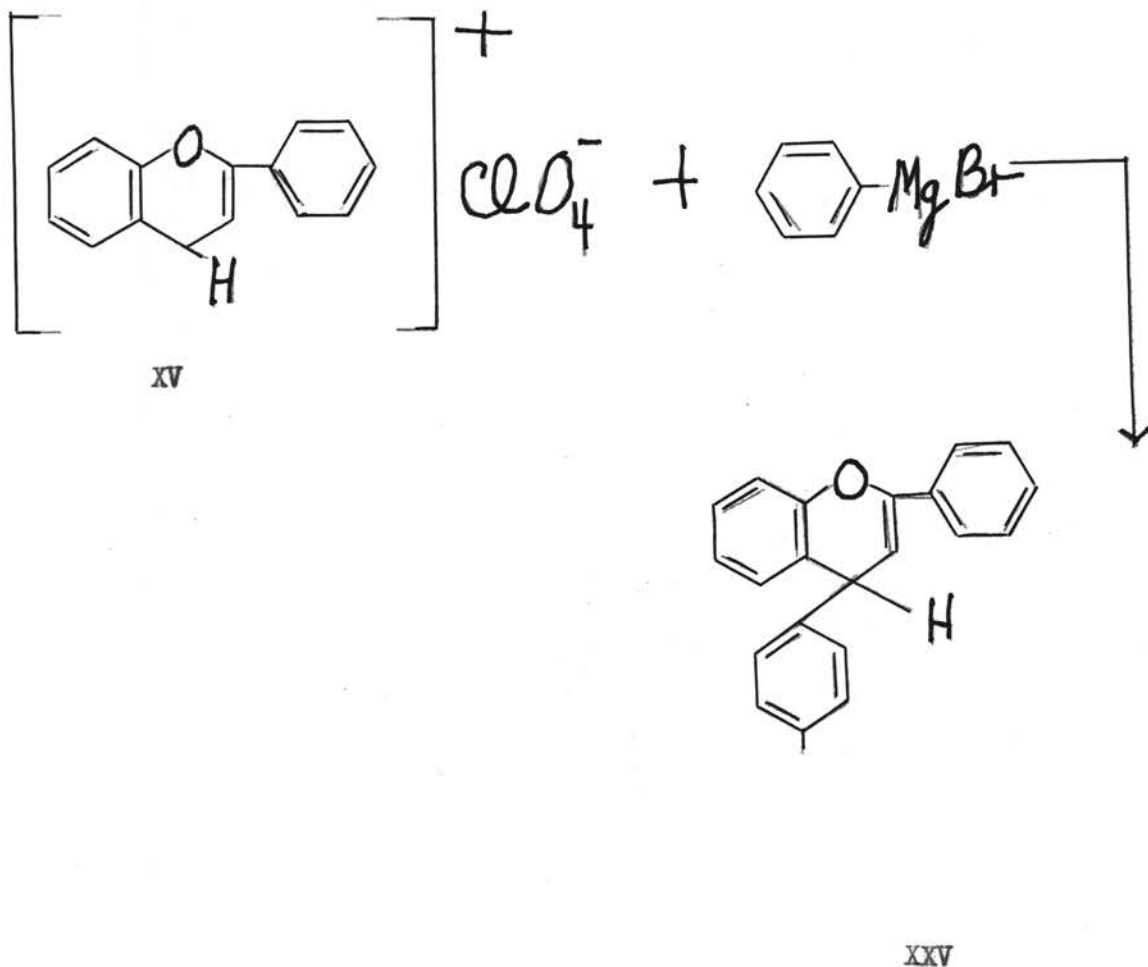
When the 4'-nitroflavylium perchlorate was treated with one equivalent mole of dimethylaniline, the major product was the blue solid perchlorate (XXIV) with some production of the leuco base (V). The salt (XXIV) was made basic and extracted with ether, and the product was the carbinol (VI).

When two moles of dimethylaniline were used per mole of 4'-nitroflavylium perchlorate (IV), the amount of the leuco base (V) was slightly increased. It was found that the leuco base could be oxidized to the carbinol, either by air oxidation or by the use of ferric chloride.

When two moles of dimethylaniline were used per mole of the 2'-nitroflavylium perchlorate (I), the major product was the leuco base (II), with a small amount of the salt of the carbinol (XXIII). The leucobase (II) can be oxidized to the carbinol or the salt (XXIII) can be converted to the carbinol, (III).

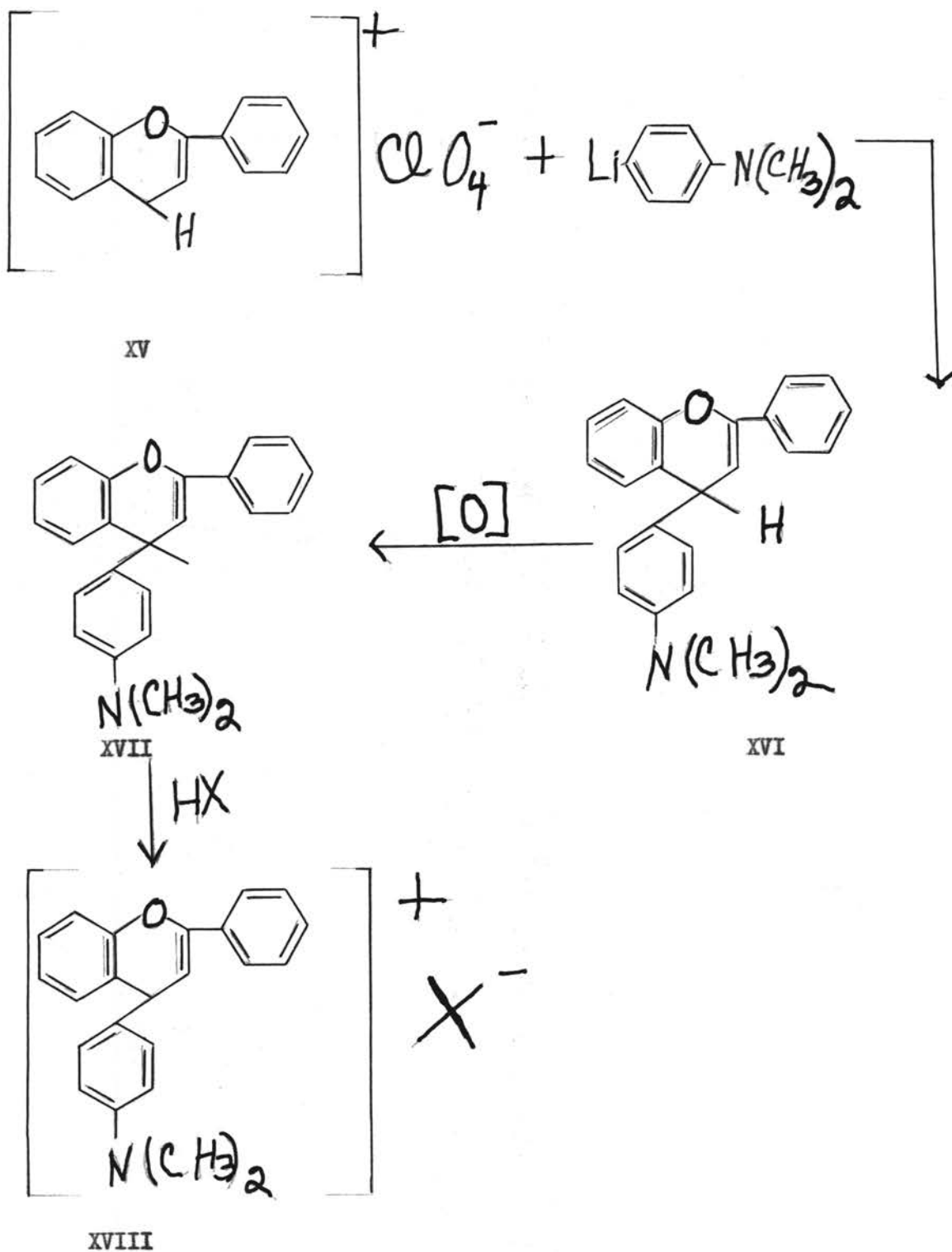
Both the 2' and 4'-nitroleuco bases (II and IV) were bright yellow solids which turned grass green on exposure to air and acid fumes. The carbinols were darker, and had a tendency to gum when wet.

Lowenbein (6) described the preparation of the 2,4-diphenyl-1,4-benzopyran (XXV) by the reaction of phenylmagnesium bromide with flavylum perchlorate (XV).

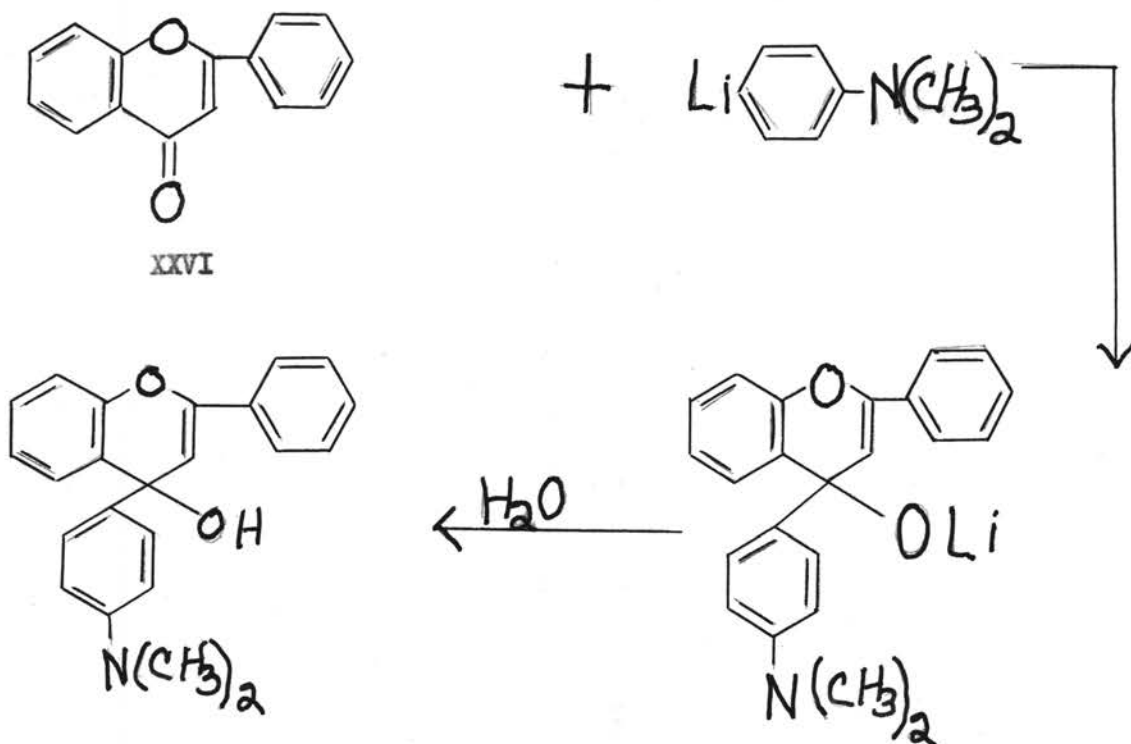


Shotton (10) produced the 2-phenyl-4-(4'' dimethylaminophenyl)-1,4-benzopyran (XVI) by a similar method using dimethylaminophenyl magnesium bromide. However, he found that dimethylaminophenyl lithium could be produced in better

yield and gave the same results. The leuco base (XVI) thus produced was oxidized to the carbinol (XVII) which in acid gave the blue salt (XVIII).



Shotton further proved that the reaction took place at the number four position by reacting the dimethylaminophenyl lithium with flavone (XXVI) to give a compound which hydrolyzed to produce the carbinol (XVII).



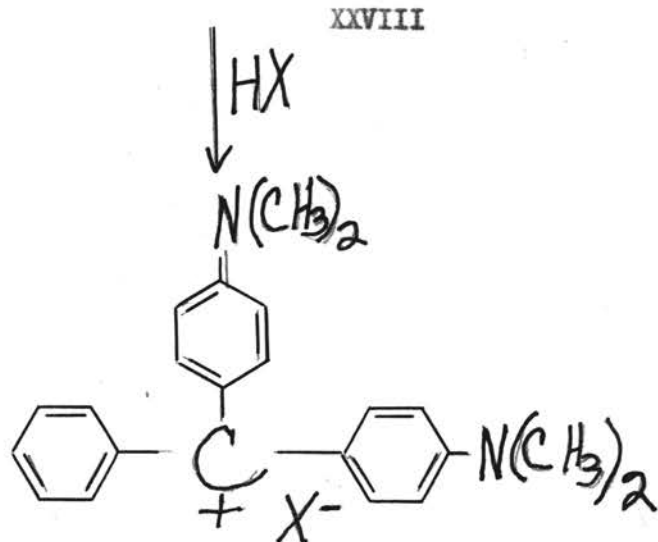
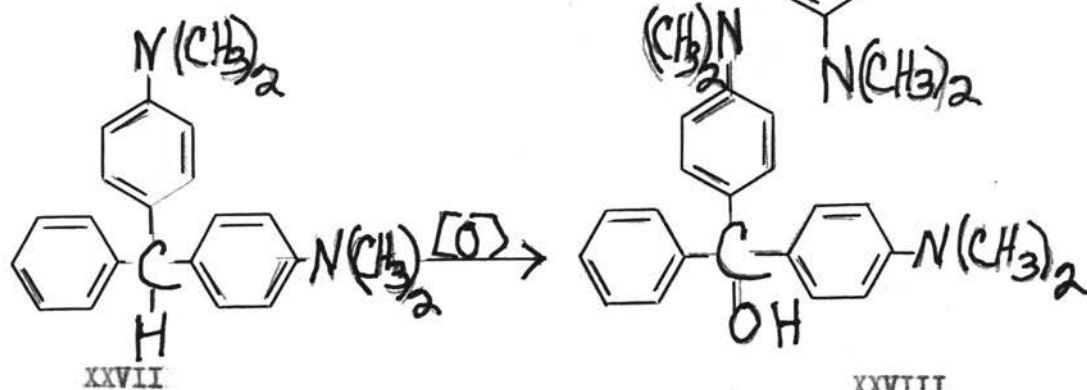
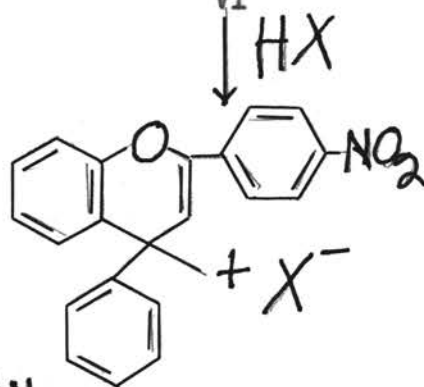
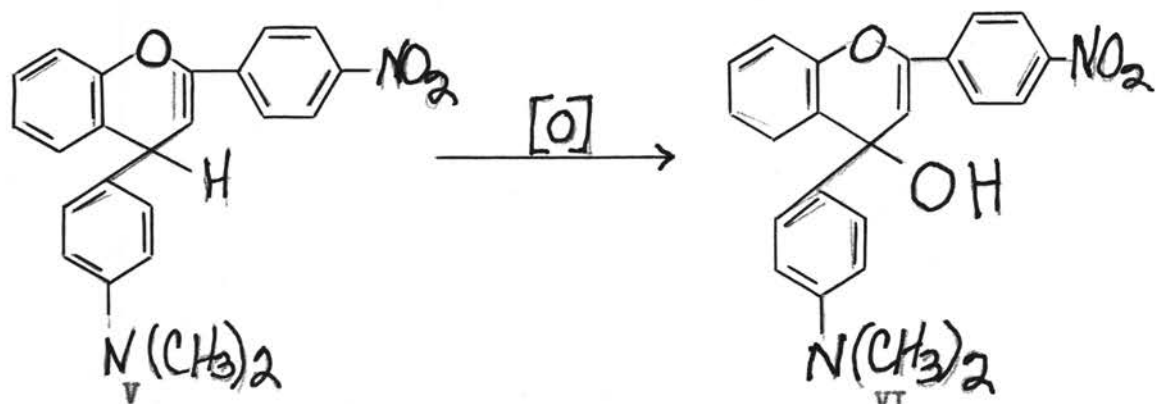
XVII

However, the attempt to prepare the 2-(4'-nitrophenyl)-4-(4''-dimethylaminophenyl)-1,4-benzopyran (V), by reacting the 4'-nitroflavylium salt (IV) with dimethylaminophenyl lithium, failed to give significant results, probably due to the reaction of the lithium compound with the nitro group. The products of the reaction were gummy and gave indefinite melting points.

The 2-(2'-nitrophenyl)-4-(4''-dimethylaminophenyl)-1,4-benzopyran and the analogous 4' nitro derivative formed yellow solutions in acetone which did not change color on acidification. The 2-(2'-nitrophenyl)-4-(4''-dimethylamino-phenyl)-1,4-benzopyranol and the 4' nitro analog also formed a yellow solution in acetone, but on acidification, the solutions turned bright blue. Addition of excess of acid, however, caused a color change of blue to green to yellow again.

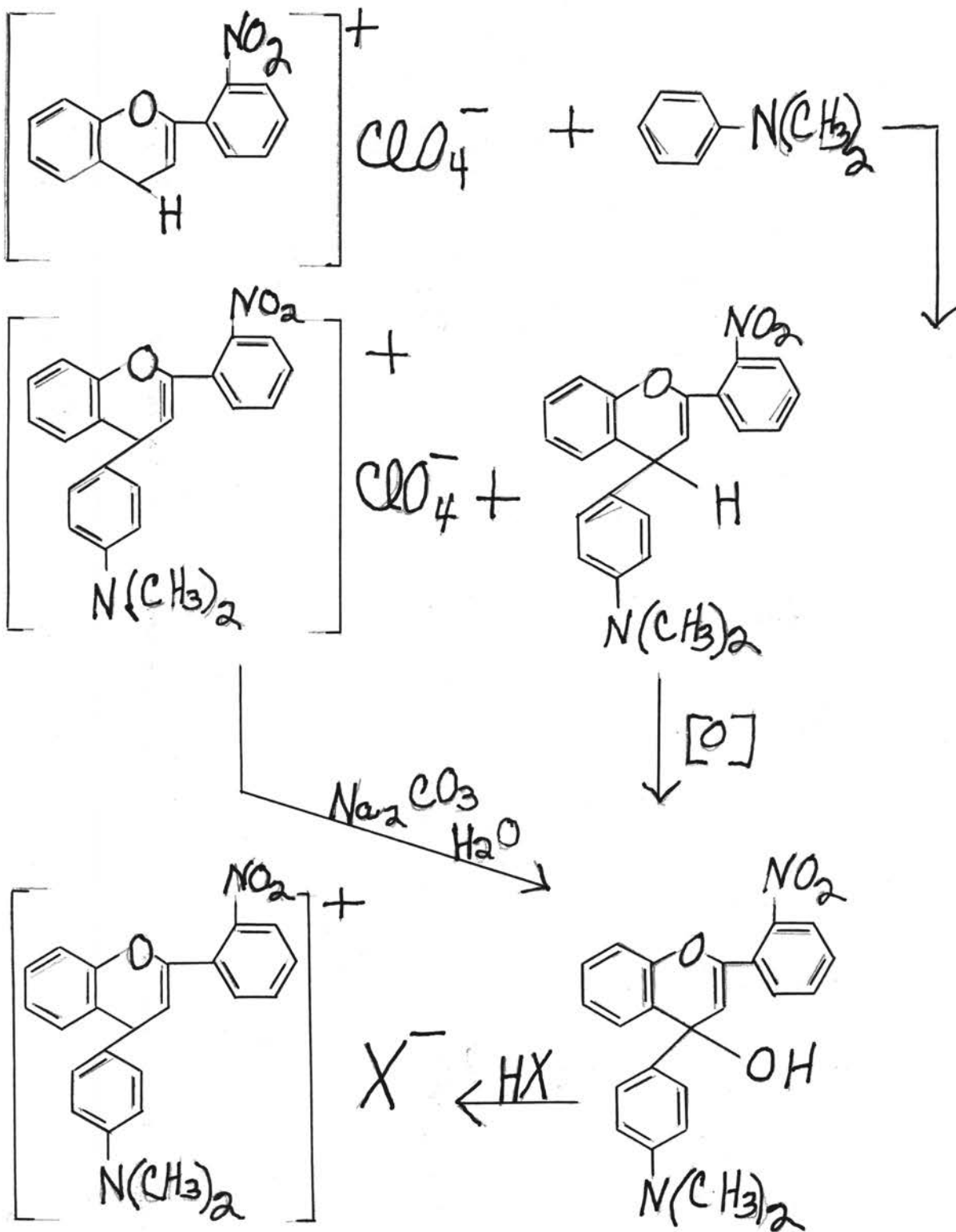
If the substitution had been in the four position of the flavylum salt, then the nitro leuco bases are vinylogs of a leuco base of a triphenylmethane dye.

Oxidation of the 2-(2' or 4'-nitrophenyl)-4-(4''-dimethylaminophenyl)-1,4-benzopyran (II or V) to the carbinol (III or VI) which formed a colored compound in acid is comparable to the oxidation of the leuco base of malachite green (XXVII) to the carbinol (XXVIII) which also formed a colored compound in acid.



There are seven possible resonance forms of the carbonium ion in malachite green; seven major and one minor in the 2-phenyl-4-(4-dimethylamino-phenyl)-1,4-benzopyranyl carbonium ion and the presence of the nitro group increases the resonance possibilities by two. It was interesting to note that the increase in the number of resonance forms due to the nitro group may be the cause of the yellow color of both the leuco base and the carbinol as compared with the white color of the analogous non-nitrated compounds.

These reactions may be summarized as follows:



EXPERIMENTAL

Preparation of Ortho and Para Nitrophenylmethylcarbinol.

The method used was that of Ford-Moore and Rydon (3) using phenylmethylcarbinol as the starting material.

Phenylmethylcarbinol (224 g.) was added, with cooling, over fifteen minutes, to 400 ml. of acetic anhydride containing 2 ml. of sulfuric acid. After being kept at room temperature for 30 to 40 minutes, the solution was stirred mechanically while 94 ml. of fuming nitric acid (d. 1.50) was added dropwise over 2 to 2 1/2 hours, the temperature being kept below 20°C. by ice cooling. After stirring for a further 1 1/2 hours between 15 and 20°C. the product was poured into a liter of ice and water and let stand overnight. The next day the mixture was filtered and the solid alpha(p-nitrophenyl)ethyl acetate and the oily mixture of the latter and the alpha(o-nitrophenyl)ethyl acetate were treated differently. (Occasionally the solid para derivative does not crystallize and an acetone dry ice bath must be used to induce crystallization.)

The oily mixture of the nitrophenylethyl acetates was separated from the water solution and washed. It was hydrolyzed by refluxing for six hours with a liter of alcohol and 200 ml. of concentrated hydrochloric acid. The low boiling products of this hydrolysis were removed by distilling on a water bath under the reduced pressure of the water pump. The residue was fractionally distilled under a pressure of 2 mm. and the fraction distilling at 125-141°C. was the ortho nitrophenylmethylcarbinol, while the para nitro derivative came off at 143-156°C.

The (p-nitrophenyl)ethyl acetate recrystallized from petroleum ether in colorless prisms and had a melting point of 55-56°C. The acetate was

hydrolyzed using 200 ml. of alcohol and 40 ml. of concentrated hydrochloric acid, and again the low boiling products were distilled off at reduced pressure (water pump). The carbinol was combined with the para nitrophenylmethylcarbinol from the vacuum distillation.

Oxidation of p-Nitrophenylmethylcarbinol.

The p-nitrophenylmethylcarbinol (25 g.) was added to a solution of 76 g. of sodium dichromate in 190 ml. of water and 38 ml. of sulfuric acid previously heated to 60°C. Ten minutes were required for the addition.

The temperature rose from 60 to 95°C. during the addition of the carbinol, and after the temperature had dropped to 60°C. (in about 15 minutes), the mixture was stirred at 60°C. for three more hours and then poured into 250 ml. of ice and water. The product was recrystallized from methyl alcohol as shiny yellow flakes which melted at 79-80°C. The yield from the carbinol was 90%, from the original phenylmethylcarbinol was 18% of theory.

Oxidation of o-Nitrophenylmethylcarbinol.

Continuing the method of Ford-Moore and Rydon (5), 150 g. of o-nitrophenylmethylcarbinol was added to a stirred solution of 266 g. of sodium dichromate in 670 ml. of water and 133 ml. of sulfuric acid, previously heated to 60°C. During the addition the solution turned from the typical orange color of the dichromate to a dark brown and the temperature rose to 95°C. After the temperature had dropped to 60°C. the mixture was stirred for three more hours and then poured into a liter of ice and water.

The product was extracted with 800 ml. of benzene. The benzene solution was washed with about a liter of 10% sodium carbonate and then the benzene extract was dried over solid sodium carbonate. After the benzene was

distilled off at 80°C., the residue was vacuum distilled and at 3 mm. the light yellow viscous *o*-nitroacetophenone distilled at 140°C. The yield was 53% of the theory calculated on the basis of the *o*-nitrophenylmethylcarbinol.

Attempted Preparation of 4'-Nitro-2-Hydroxychalcone.

Salicylaldehyde (12.2 g. ie 0.1 mole) and *p*-nitroacetophenone (16.5 g. ie 0.1 mole) were dissolved in 100 ml. of 10% sodium hydroxide (0.25 mole) and 30 ml. of alcohol. The mixture was let stand with occasional shaking for 24 hours. The solution at the end of this time was a dark reddish brown but on the addition of ice and concentrated hydrochloric acid, the red color disappeared and a dirty yellow precipitate appeared. After letting the acidified solution stand in the ice box overnight, the yellow solid on filtration was found to have a melting point of 95° to 125°C. Evaporation of the solution left a dark red residue which gummed on recrystallization from methyl alcohol. However, on recrystallization from benzene, the benzene soluble portion was found to soften at 165°, gum at 195° and decompose at 219-221°C. This solid was fireman's red when wet and yellow orange when dry. The benzene insoluble portion was a dark maroon solid which decomposed at 125-140°C.

Attempted Preparation of 2'-Nitro-2-Hydroxychalcone

Salicylaldehyde (24.5 g. ie 0.2 mole) and *o*-nitroacetophenone (33 g. ie 0.2 mole) were added to 200 ml. of 10% sodium hydroxide and 60 ml. of alcohol, and on mixing the solution turned a dark red brown. After standing overnight, ice and concentrated acid were added to the mixture. There was some loss of the red color, but after standing in an ice box overnight, a red brown mass

was obtained which on recrystallization from alcohol formed a powdery precipitate having a melting point of 150-2°C. On recrystallization from benzene, a benzene soluble portion, melting point 155-6°C. and a benzene insoluble portion were obtained.

Attempt to Prepare Flavylium Perchlorate by Coupling of 2'-Nitro-2-hydroxy-chalcone with an Acid.

Nineteen and nine tenths grams of 2'-nitro-2-hydroxychalcone (m.p. 155-6°C.) (0.074 mole) was dissolved in 500 ml. of ether. Dry hydrogen chloride was passed into the solution. Seven and four tenths grams of perchloric acid dissolved in 18 ml. of acetic anhydride was added to the solution. The hydrogen chloride was fed into the ice cooled solution for about 2½ hours, at the end of which time, the solution was apparently saturated. The precipitate was filtered on a sintered glass filter and washed with ether and glacial acetic acid. The precipitate was found to be the original chalcone, (m.p. 155-6°C.). The solid was put back in solution and more cold dry hydrogen chloride was passed into the solution. After standing overnight, the solid was again filtered and washed and it was found that this substance exploded on ignition and melted with decomposition at 170-172°C. The yield however, was only 3.6 g., or 14% of theoretical.

Preparation of o-Nitroflavylium Perchlorate by Direct Condensation.

Twenty one and six tenths grams (0.18 mole) of o-nitroacetophenone and 22 grams (0.18 mole) of salicylaldehyde were mixed in 180 ml. of ether, and dry hydrogen chloride was passed into the solution until saturated. The solution turned from a light yellow to a deep red color when saturated. Fifty grams of 72% perchloric acid (0.36 mole), dried by adding slowly, with cooling, to 108 ml. of acetic anhydride, were added, with shaking, and the

solution was let stand for 24 hours. The dark red brown precipitate was filtered on a sintered glass filter and washed with dry ether and glacial acetic acid. The dry, dark maroon amorphous powder exploded on ignition, shrank at 211°C. and melted with decomposition at 219-220°C. The yield was 4 g. or 6.3 % of theory.

Preparation of 4'-Nitroflavylium Perchlorate by Direct Condensation

Sixteen and five tenths (0.1 mole) of p-nitroacetophenone and 12.2 g. of salicylaldehyde (0.1 mole) were placed in a 600 ml. portion of absolute ether. Dry hydrogen chloride was passed into the solution until it was saturated. Then a solution of 28 g. of 72% perchloric acid (0.2 mole) was added to the dark red saturated solution and the mixture was placed in the ice box for two days. The precipitate was filtered on a sintered glass filter and washed with acetic acid and ether. The rust or copper colored amorphous compound exploded on ignition, softened at 203° and melted with decomposition at 219-220°C. The yield was 18.9 or 54 % of theory.

Reaction of 2'-Nitroflavylium Perchlorate with Dimethylaniline.

Four grams (0.012 mole) of o-nitroflavylium perchlorate and 2.90 g. (0.024 mole) of dimethylaniline were mixed in dry ether and let stand about forty minutes with periodic shaking. The yellow ether solution was filtered from the greenish solid and the ether washings of the solid were combined with the original ether solution. The ether solutions were then evaporated under pressure. The 2-(2'-nitrophenyl)-4-(4"-dimethylaminophenyl)-1,4-benzopyran was yellowish green in color and had a melting point of 141-143°C. The yield was 0.5 g. or 11 % of theory.

Analysis for $C_{23}H_{20}O_3N_2$	Calculated % C	<u>74.2</u>	H	<u>5.42</u>
	Found	% C <u>74.4</u>	H	<u>6.30</u>

The leuco base can be oxidized to the carbinol by air oxidation or by ferric chloride. The carbinol was yellowish green in acetone, but became bright blue on acidification. This carbinol was hard to purify, probably due to the inclusion of salts and unoxidized leuco base. The melting point of the impure carbinol was 83 to 95°C. Recrystallization from both ether and methyl alcohol failed to give a pure compound. An attempt to obtain the pure carbinol by recrystallizing the perchlorate from glacial acetic acid produced the perchlorate which on making basic with sodium carbonate yielded the carbinol.

Reaction of 4'-Nitroflavylium Perchlorate with Dimethylaniline.

Fourteen grams of 4'-nitroflavylium perchlorate (0.039 mole) and 4.84 g. (0.04 mole) of dimethylaniline were mixed in ether and the mixture was let stand, with shaking for about an hour. The ether solution was separated from the blue insoluble solid by filtration. On evaporation at reduced pressure (water pump), the leuco base was obtained in bright yellow needles which turned green on standing. The solid on recrystallization from methyl alcohol had a melting point of 153-4°C. The yield of 2-(4'-nitrophenyl)-4-(4"-dimethylaminophenyl)-1,4-benzopyran was 2 g. or 14% of theory.

Analysis of $C_{23}H_{20}O_3N_2$

Calculated % C 74.2 H 5.42

Found % C 74.3 H 5.65

The ether insoluble portion was a blue solid which exploded on ignition. The yield was 12.5 g. or 71 % of theory. After the solution had been made basic and extracted with ether, a light orange brown gum was obtained which had a melting point of 85-96°C. The acetone solution of this

substance was yellow which turned a royal blue on acidification. The substance was purified by recrystallizing the perchlorate from hot glacial acetic acid and converting to the carbinol by sodium carbonate. The recrystallized perchlorate was found to have a melting point of _____ and the carbinol now melted at _____.

Analysis of $C_{23}H_{20}O_4N_2$	Calculated %	C	<u>71.1</u>	H	<u>5.20</u>
For impure carbinol	Found %	C	<u>69.4</u>	H	<u>4.94</u>
For repurified carbinol	Found %	C		H	

Preparation of Dimethylaminophenyl Lithium.

One tenth of a gram (0.28 mole) of lithium was cut into small pieces and covered with anhydrous ether. After the mixture was placed in a three necked flask equipped with a dropping funnel, ice cooled condenser and stirrer, 1.5 g. of p-bromodimethylaniline was dissolved in 25 ml. of ether and one third of the solution was added to the lithium-ether mixture. The mixture was refluxed to start the reaction and the remainder of p-bromodimethylaniline was added at a rate to keep the ether refluxing. After all the p-bromodimethylaniline was added, refluxing was continued for half an hour on the steam bath. At the end of this time all the excess lithium was removed.

Reaction of Dimethylaminophenyl Lithium with 4'-Nitroflavylium Perchlorate.

To the solution of p-dimethylaminophenyl lithium prepared as above, 4.9 g. (0.014 mole) of p-nitroflavylium perchlorate was added with shaking in small portions. Only a trace of white precipitate was formed which was separated from the greenish yellow ether solution by filtration. After evaporation of the ether solution under pressure, the green gummy solid was washed with ether. On taking a melting point, it was found to soften

at 117° and decompose at 129-130°. A mixed melting point with the leuco base of the 2-(4'-nitrophenyl)-4-(4''-dimethylaminophenyl)-1,4-benzopyran gummed at 116-117° and possibly decomposed at 155°C.

SUMMARY

Four new compounds were prepared and characterized and another, whose melting point was not given in the literature, was prepared and its melting point determined.

2-(2'-Nitrophenyl)benzopyrylium perchlorate was prepared by the direct condensation of salicylaldehyde and 2-nitroacetophenone with dry hydrogen chloride and perchloric acid. Its melting point, which was not given in the literature, was found to be 219-220°C. with decomposition.

2-(2'-Nitrophenyl)-4-(4"-dimethylaminophenyl)-1,4-benzopyran and the analogous 4'-nitro derivative were prepared by the reaction of the appropriate 2-(2'- or 4'-nitrophenyl)benzopyrylium perchlorate with dimethylaniline.

2-(2'-Nitrophenyl)-4-(4"-dimethylaminophenyl)-1,4-benzopyranol and the 4'-nitro analog were prepared either by oxidation of the appropriate benzopyran or by neutralization of the perchlorates which were also formed by the reaction of the nitro flavylium perchlorate with dimethylaniline.

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BIOGRAPHY

Mary Justine Warnke was born in Webster, Massachusetts on November 19, 1927. She received her grade school training with the Sisters of St. Joseph and graduated from the Norwood, Senior High School.

In June of 1949, she received her degree of Bachelor of Science from Simmons College. In the following fall, she began her graduate work at Oklahoma A. and M. College where she had the aid of a Graduate Fellowship in the Chemistry Department.

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NAME OF AUTHOR: Mary Justine Warnke

THESIS ADVISER: Dr. James A. Shotton

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