

REACTION OF XANTHYLIUM SALTS
WITH DIMETHYLANILINE

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WITH DIMETHYLANILINE

By

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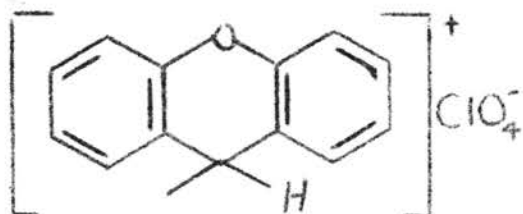
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Introduction

The xanthylium salts are ionic substances, the skeletal structure of which is well established. The positive charge is now believed to be centered on the 9-carbon atom. As such they behave in many respects as carbonium ions.

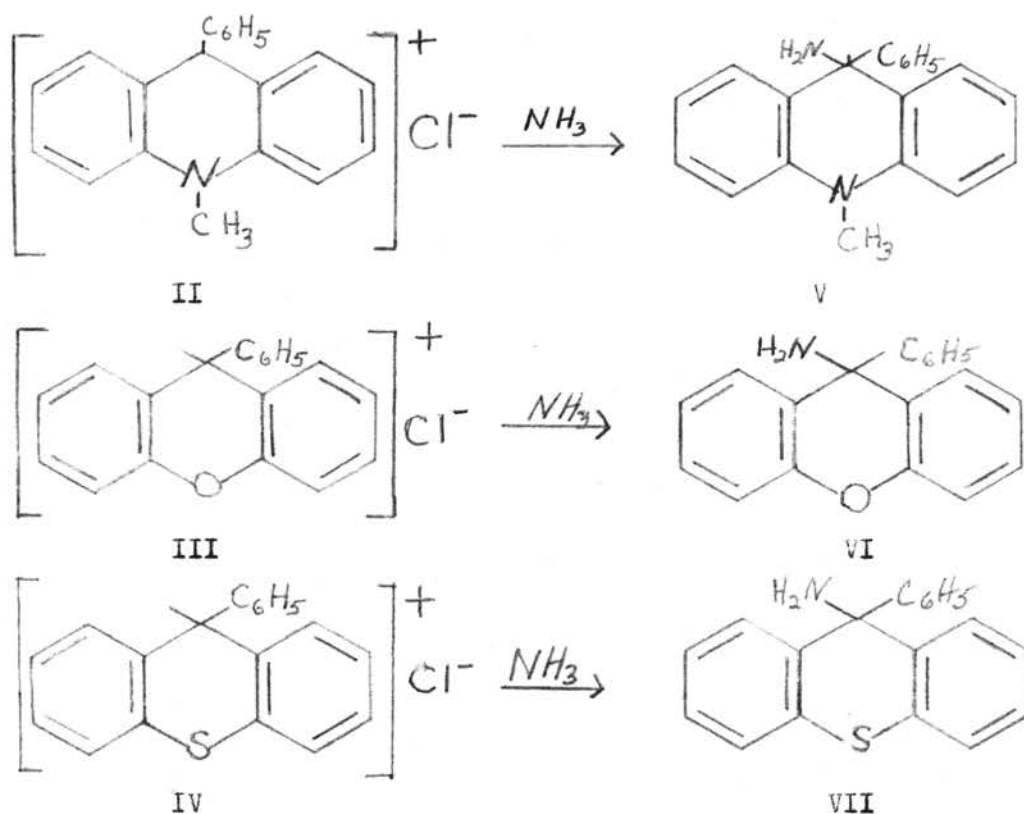
The object of this research was to determine the behavior of the unsubstituted salt, the perchlorate in particular (I), with dimethylaniline and to determine the structure of the resulting compound.



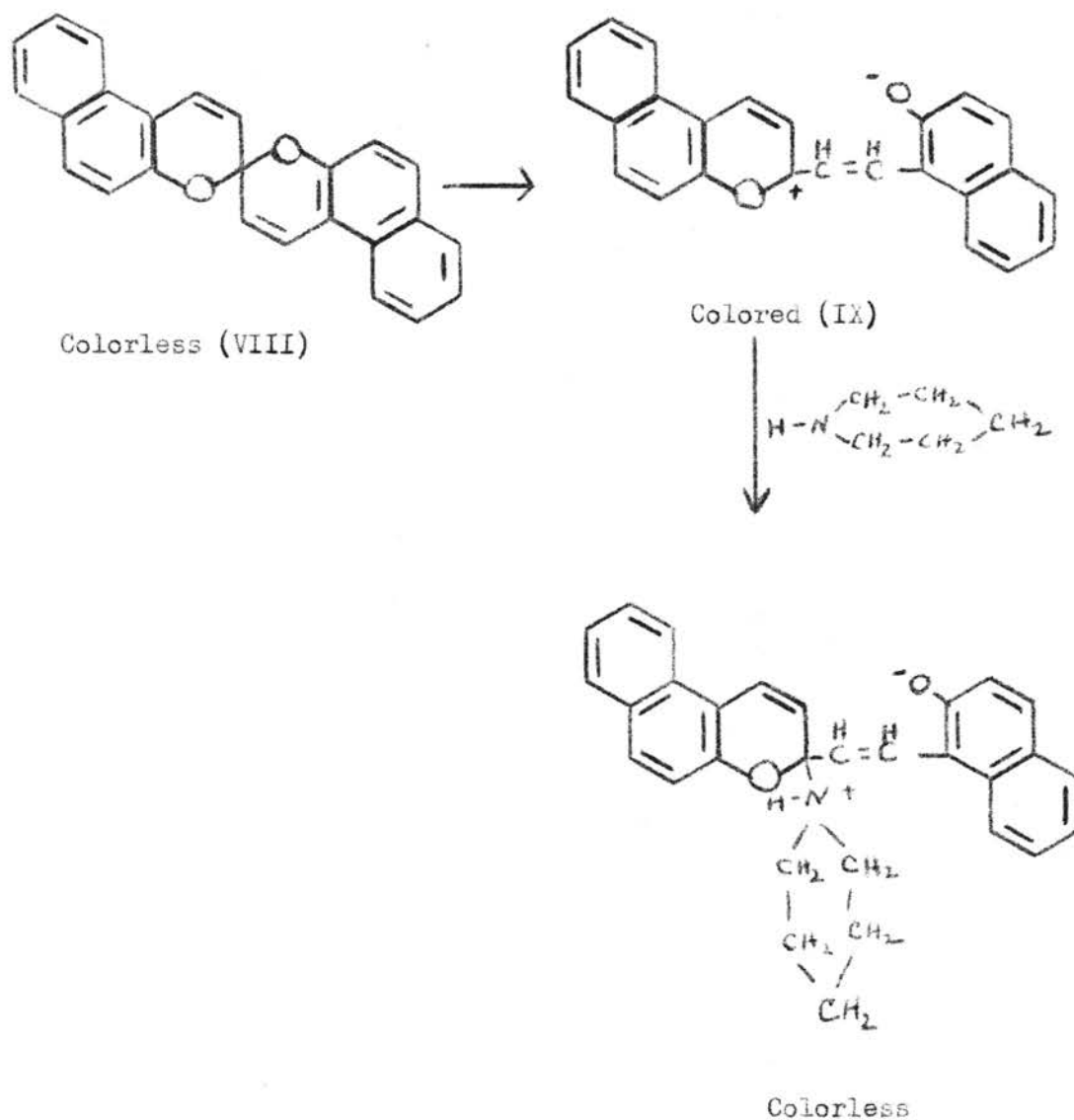
HISTORICAL

Xanthylium salts may be prepared from the xanthydrols by the action of mineral acids with the elimination of water. Hofmann, Roth, Hobold, and Metzler (1) reported the preparation of xanthylium perchlorate from an ethereal solution of xanthydrol and 70% perchloric acid. Other xanthylium salts have been prepared by Gomberg and West (2), Gomberg and Cone (3) and many others.

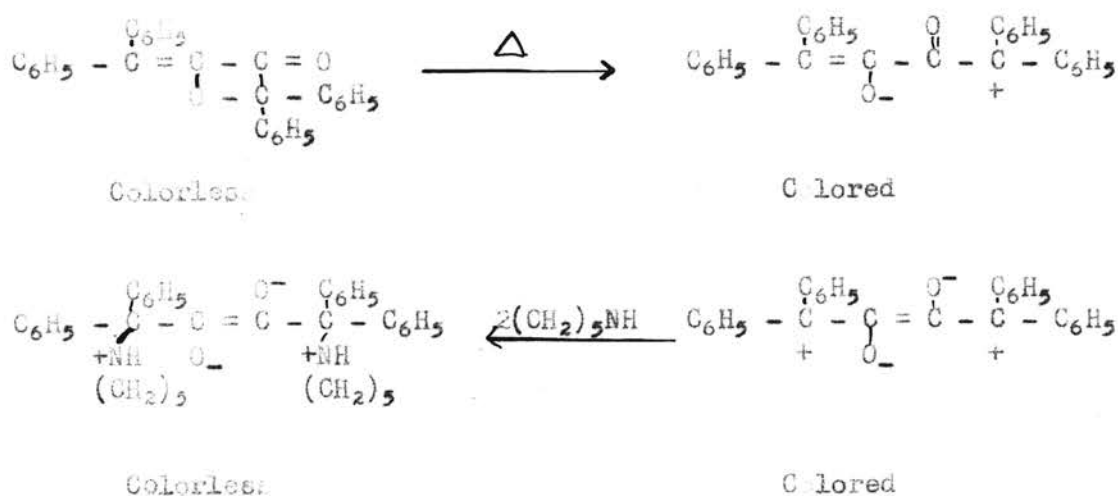
Few investigations have been made concerning the reaction of carbonium ions with ammonia or amines. Decker and Becker (4) reported the reactions of 10-methyl-9-phenyl-acridium chloride (II), 9-phenyl xanthylium chloride (III), and 10-phenyl-thioxanthylium chloride (IV) with ammonia, to give the corresponding amines, (V, VI, and VII).



Dilthey, Berres, Holterhoff and Wubken (5) prepared spiro-di-naphthopyran (VIII) and observed that when heated alone this compound-gave a blue colored compound (IX) and when heated with piperidine remained colorless. They explained this by the following transformations;



Schonberg and Sina (6) explained the loss of color when the permanganate colored diphenyl ketene dimer was heated with piperidine by somewhat the same method as that of Diltney for the spiro-di-naphthopyrans. They proposed the following transformations.



Shotton (7) reported the isolation of three products from the reaction of flavylum perchlorate and ammonia, the analysis of which indicated that flavylum perchlorate reacted with ammonia in the ratios of 3 to 1, 2 to 1 and 1 to 1. The reaction of flavylum perchlorate and piperidine gave one substitution product. The products from ozonolysis indicated the compound to be 2-phenyl-4-piperidine-1,4-benzopyran. He reports that flavylum perchlorate and dimethylaniline react to form 2-phenyl-4-(4' dimethylaminophenyl)-1,4-benzopyran. Flavylum perchlorate and aniline yielded three products two of which were tentatively assigned the structures 2-phenyl-4-(4' aminophenyl)-1,4-benzopyranol and N, 4, di-(2-phenylbenzopyranol) aniline.

Ullrich and Engi (8) prepared 4'-amino-9-diphenyl xanthene by condensing 9-phenyl xanthanol with aniline in acetic acid solution. They

also prepared 4'-dimethylamino-9-diphenyl xanthene by condensing 9-phenyl xanthenol and dimethylaniline in acetic acid solution.

Neiderl and Hart (9) condensed a number of phenols with xanthydrol, using glacial acetic acid, sulfuric acid, or anhydrous aluminum chloride as a condensing agent, to produce the corresponding p-hydroxy xanthenes.

Gomberg and Kamm (10) reported that triphenylmethylcarbinol and triphenylmethyl chloride condense with phenol in the presence of very small quantities of acid to give almost quantitatively p-hydroxytetraphenyl methane.

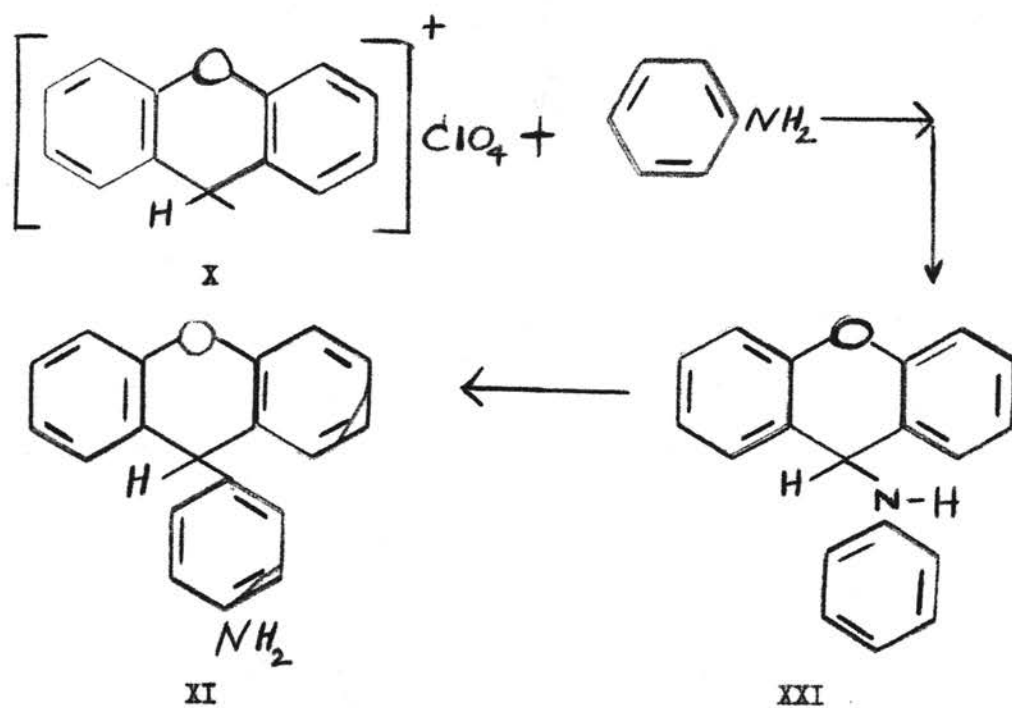
Iddles and Russey (11) reported the condensation of aniline hydrochloride with m-tolyldiphenyl carbinol in glacial acetic acid, to produce m-tolyl-4-amino-phenyldiphenylmethane in 62% yield.

Witten and Reid (12) reported the preparation of p-aminotetraphenyl methane in 70 to 80% yields by refluxing triphenyl carbinol for three hours, in twice its weight of glacial acetic acid, with two equivalents of aniline hydrochloride.

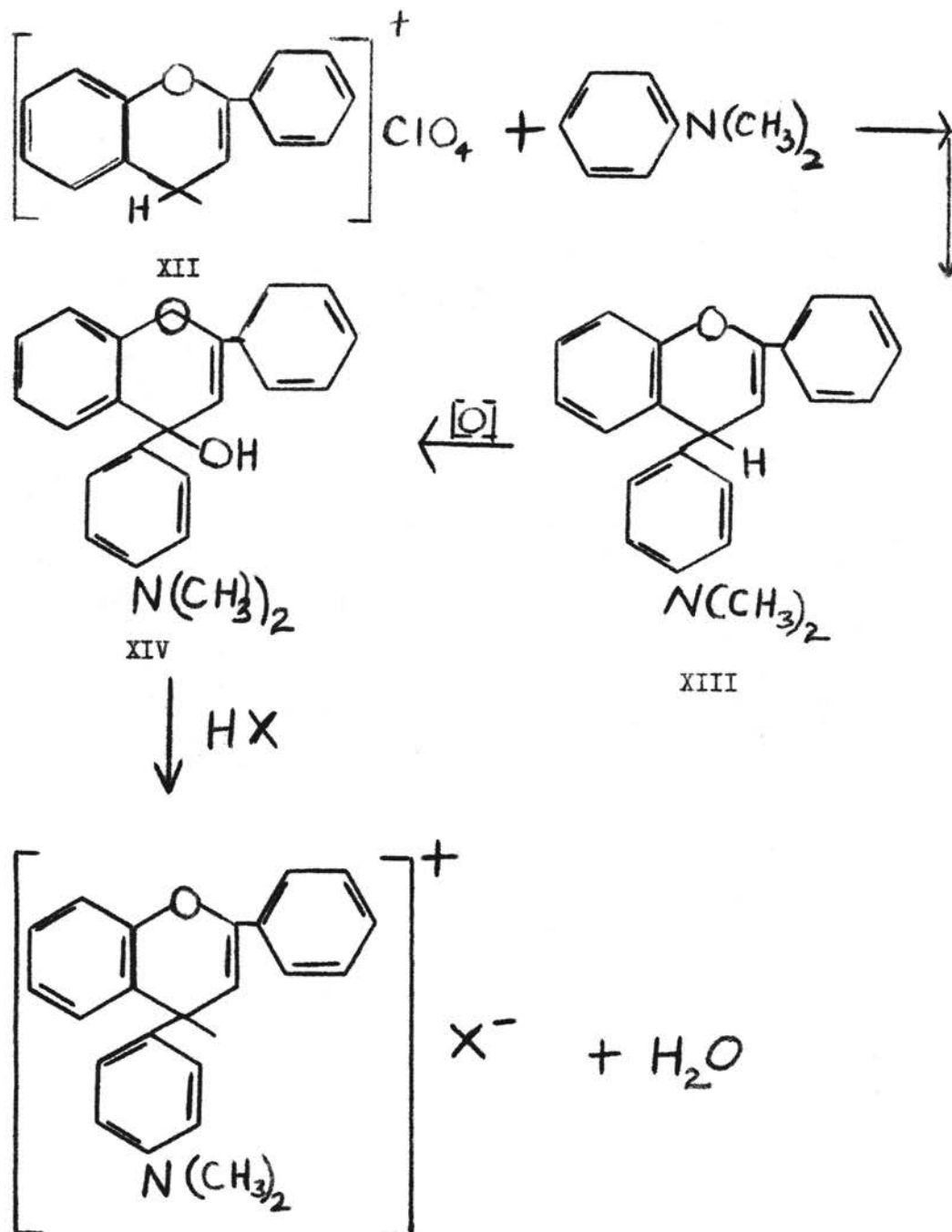
It is possible to consider that the above reactions might proceed via carbonium ions formed from either the triphenylmethylcarbinols or the xanthydrols by the action of the acetic acid or the mineral acids.

THEORETICAL AND DISCUSSION

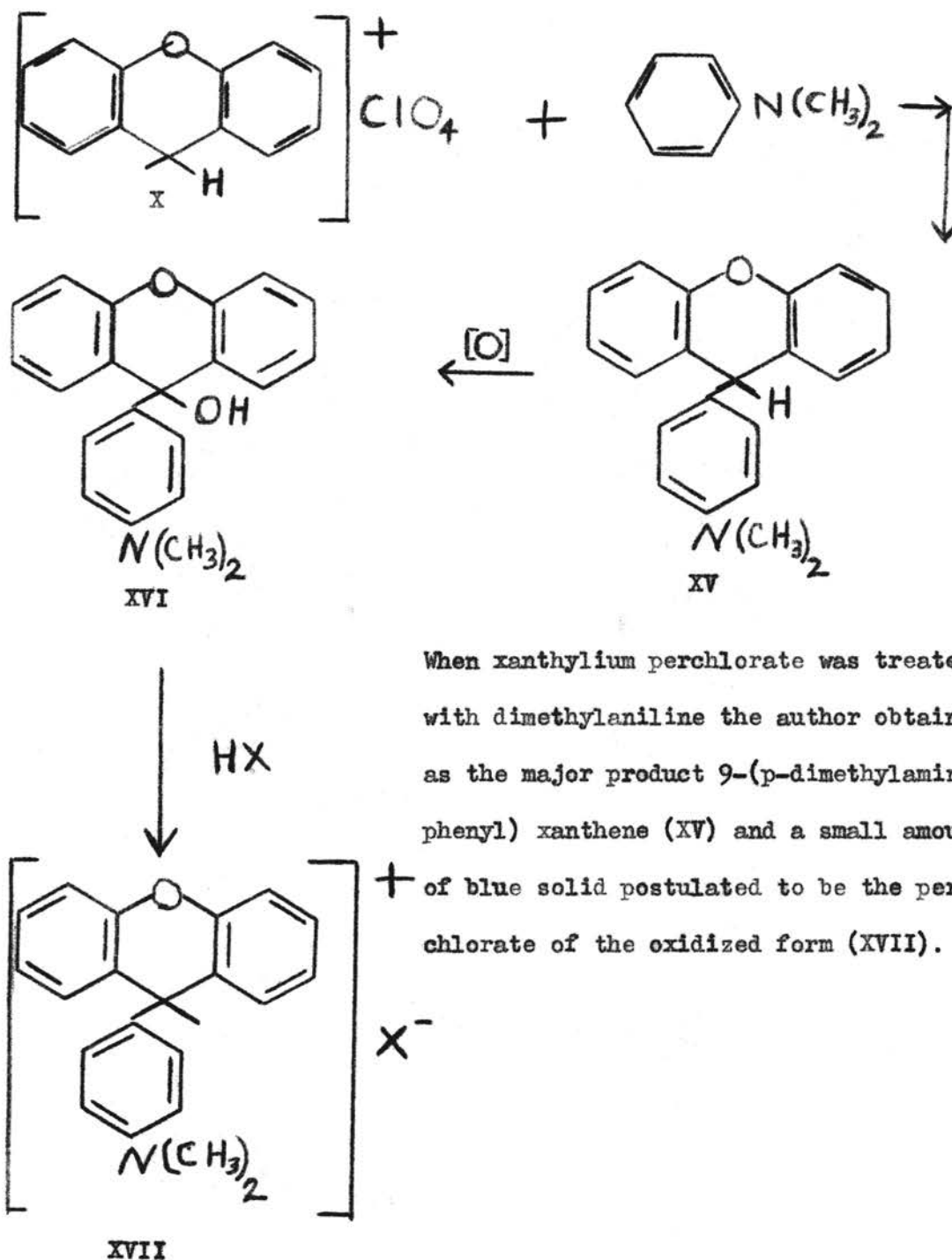
Wolf (13) has shown by the following reaction that the main part of the charge in the xanthylium ion is in the 9 position.



Shotton (7) found that when flavylum perchlorate (XII) reacted with dimethylaniline the following reactions took place;

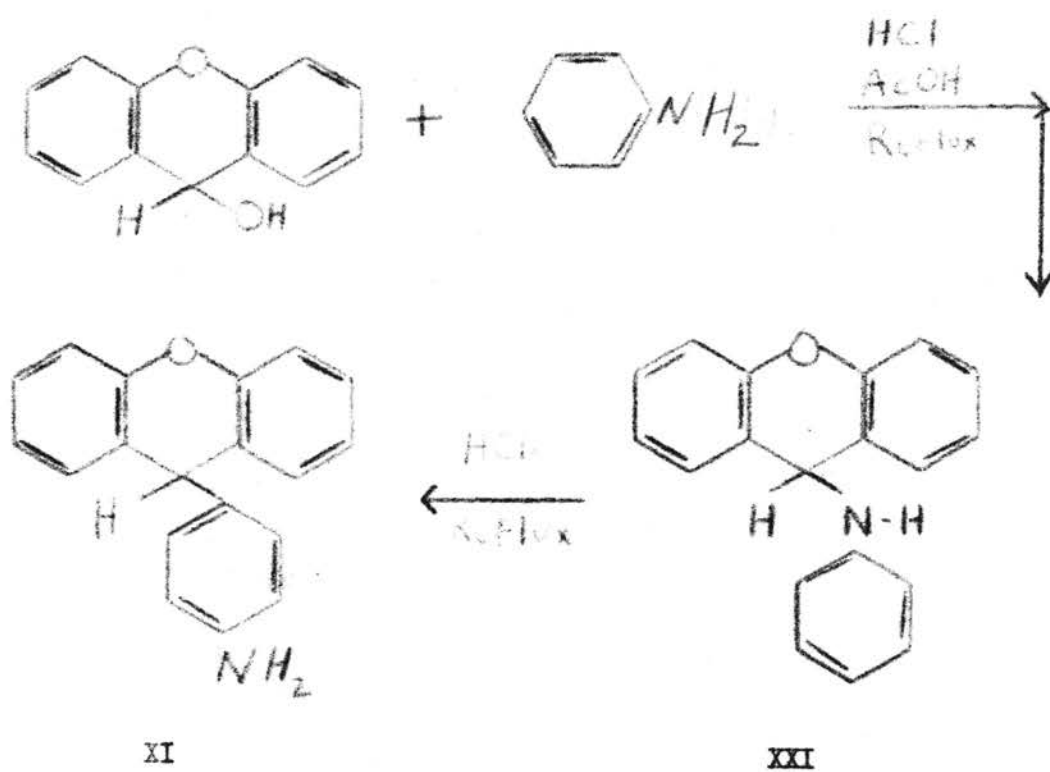


The problem was to study the reaction of xanthylum perchlorate (X) with dimethylaniline. The following reactions were postulated;

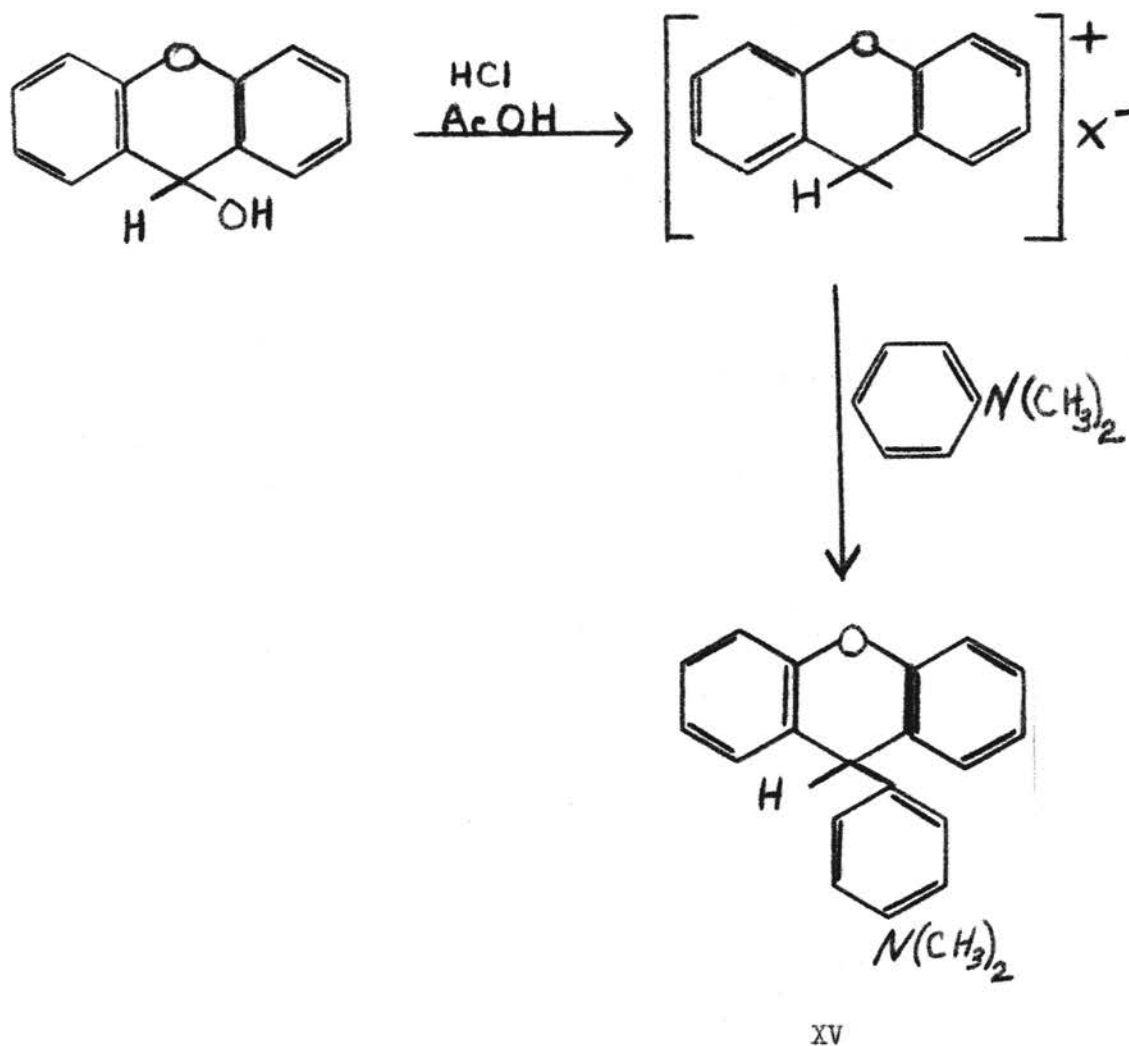


When xanthylum perchlorate was treated with dimethylaniline the author obtained as the major product 9-(p-dimethylamino-phenyl) xanthene (XV) and a small amount of blue solid postulated to be the perchlorate of the oxidized form (XVII).

Wolf (7) also prepared (XXI) by the reaction of xanthydrol with aniline and then rearranged it according to the following reaction to give compound (XI).

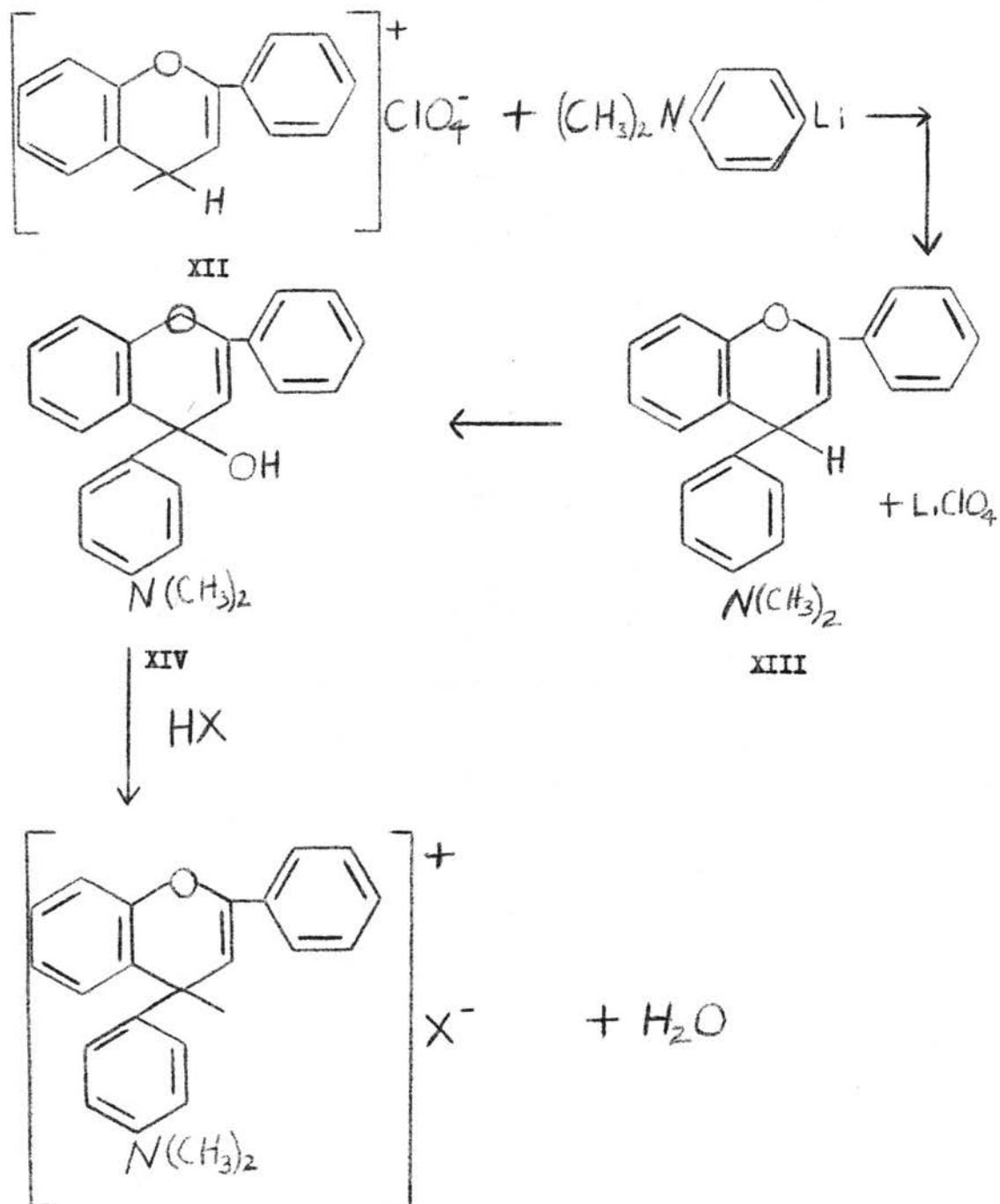


The reaction of xanthidrol with dimethylaniline in glacial acetic acid and in the presence of concentrated hydrochloric acid should give compound (XV). This reaction might well proceed via the formation of a carbonium ion and may be formulated as follows;

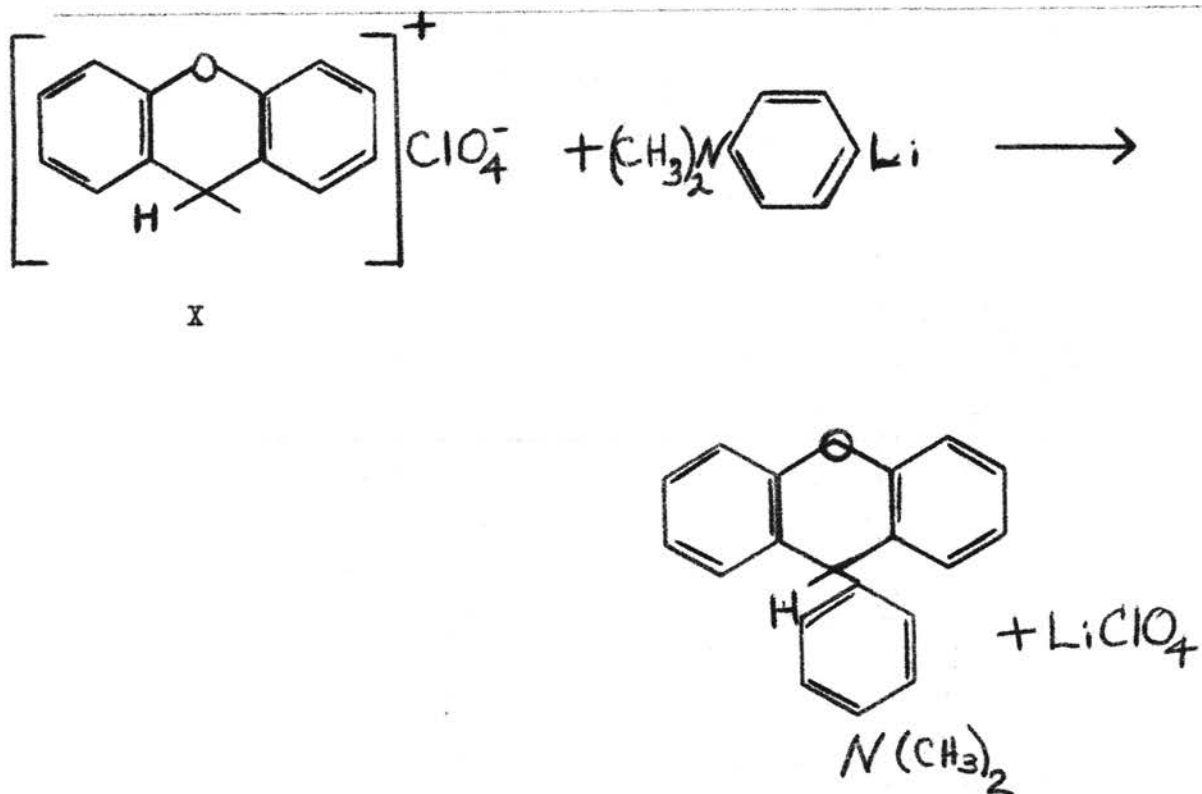


The above reaction proceeded smoothly with the formation of (XV) in good yield.

Shotton (7) proved the structure of compound (XIII) by the reaction of flavylum perchlorate (XII) with p-dimethylaminophenyl lithium and the subsequent oxidation to the carbinol (XIV).

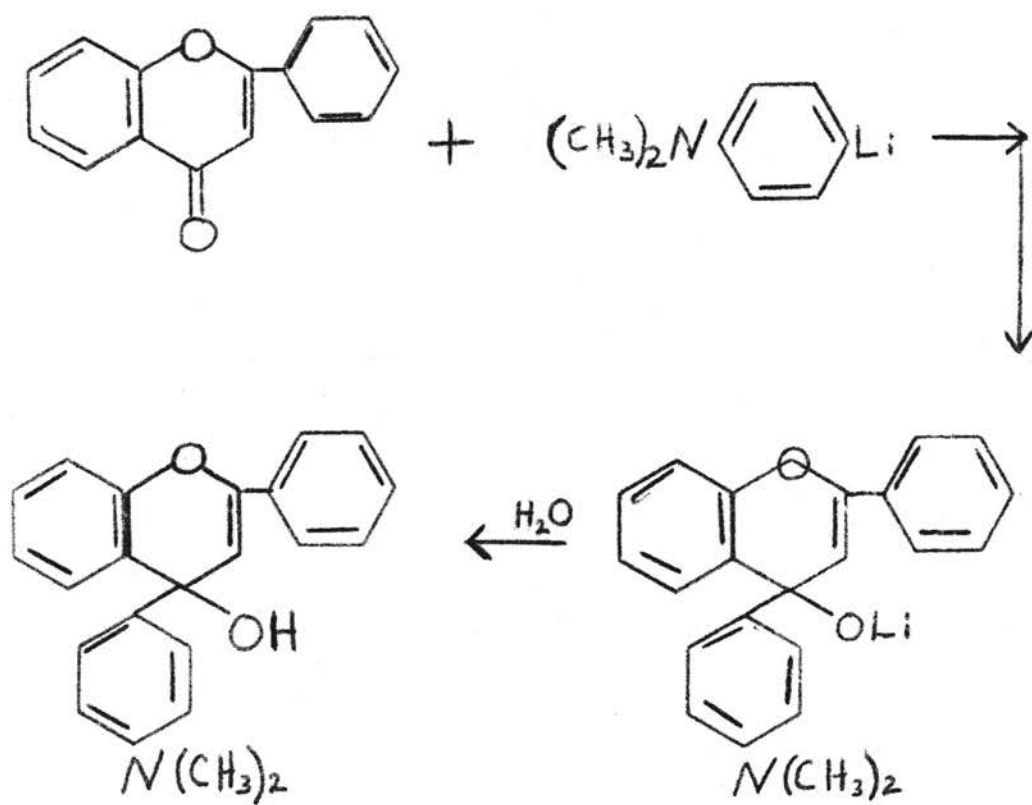


When xanthylium perchlorate (X) was reacted with p-dimethylamino-phenyl lithium the following reaction took place.



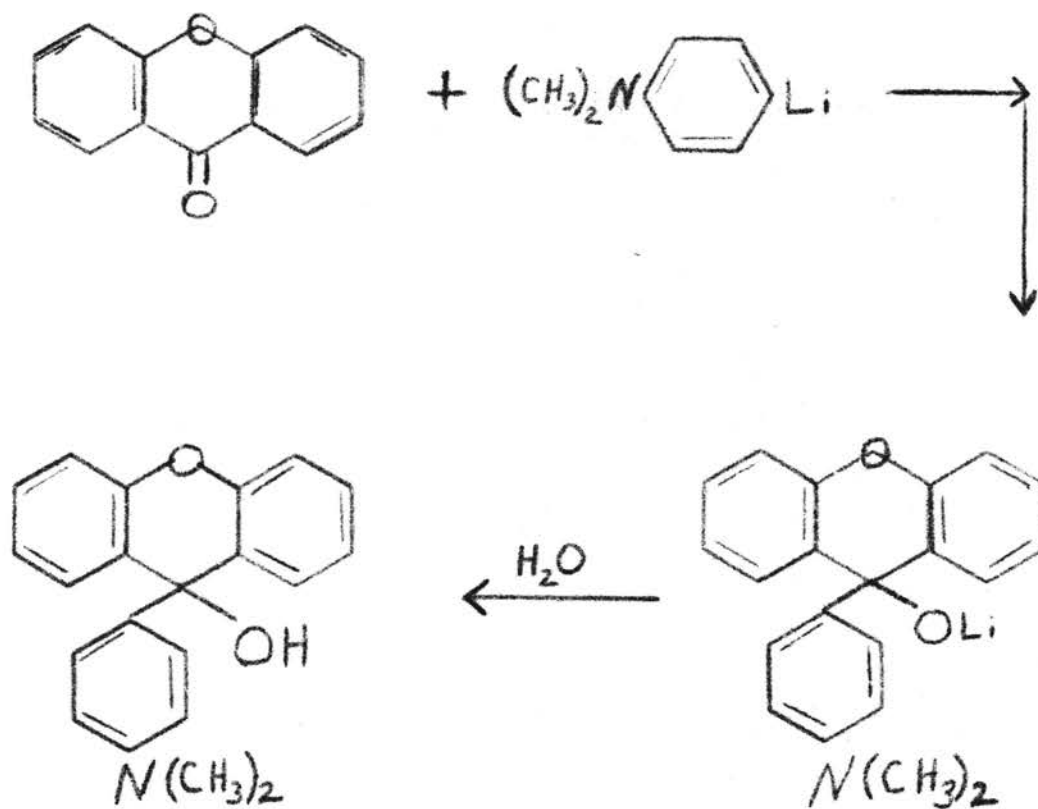
XV

Shotton (7) proved the structure of compound (XIV) by the following synthesis;



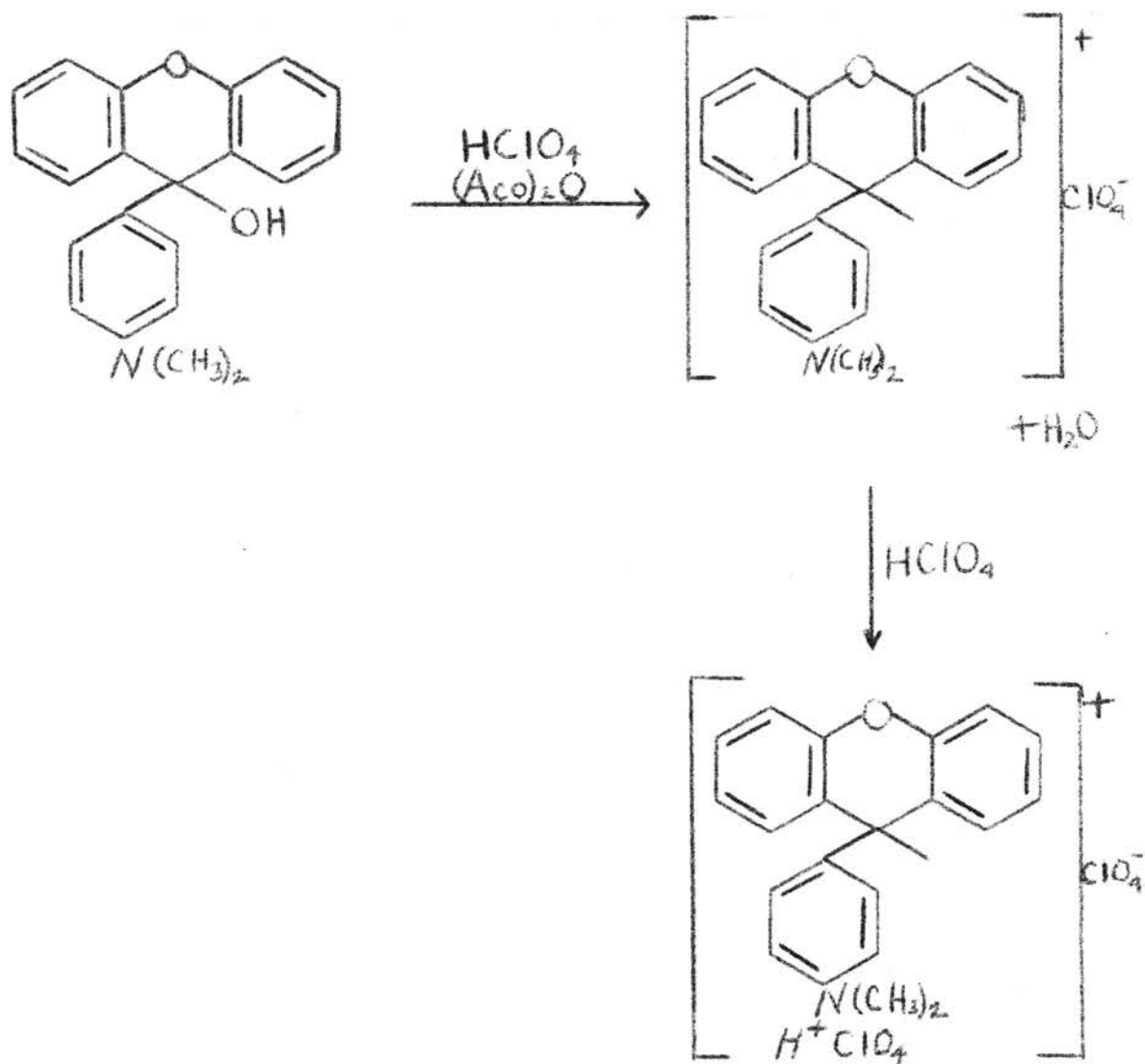
XIV

When xanthone was reacted with p-dimethylaminophenyl lithium the following reactions took place;

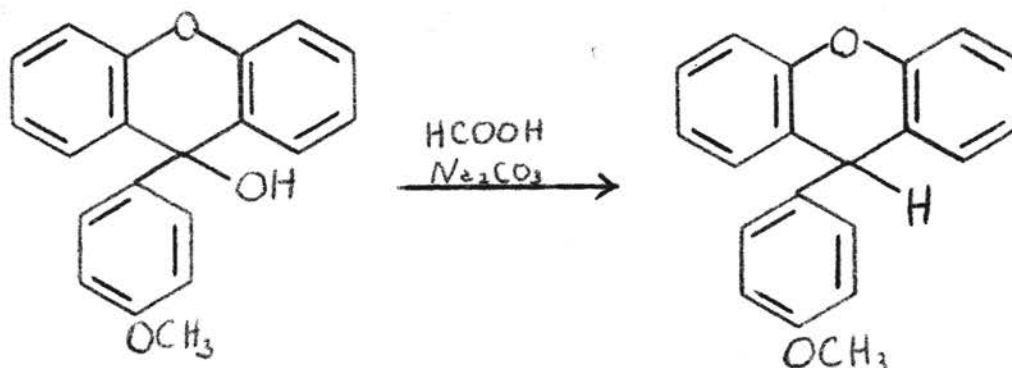


XVI

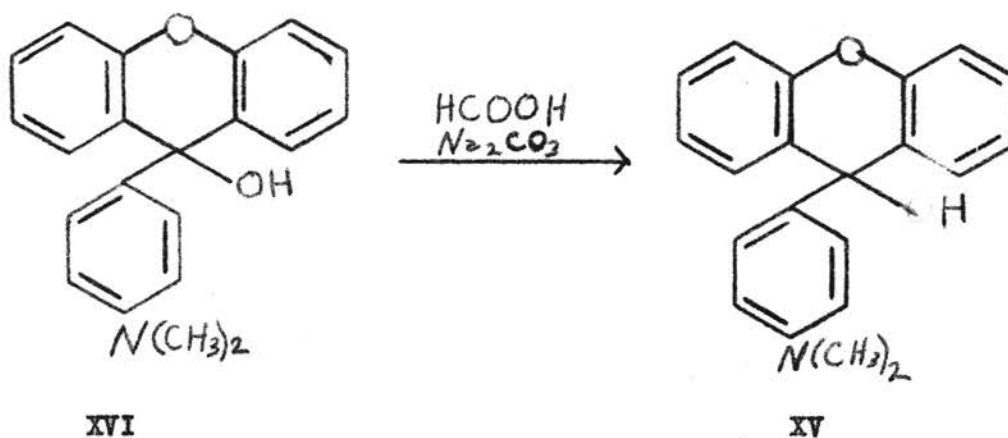
The product (XVI) when treated with excess 70% perchloric acid in acetic anhydride formed a yellow solid. This solid analyzed for two perchlorate ions. The reaction is postulated to be;



Wolf (13) reduced 9-p-methoxyphenyl xanthenol to 9-p-methoxyphenyl xanthene by using a 90% formic acid solution containing sodium carbonate

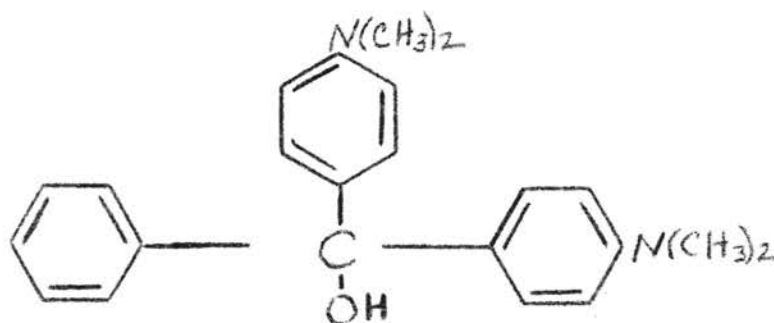


The carbinol (XVI) when refluxed with 90% formic acid containing a little sodium carbonate yielded (XV).



This reduction, coupled with analyses of (XV) and (XVI), served as proofs of structure of these compounds.

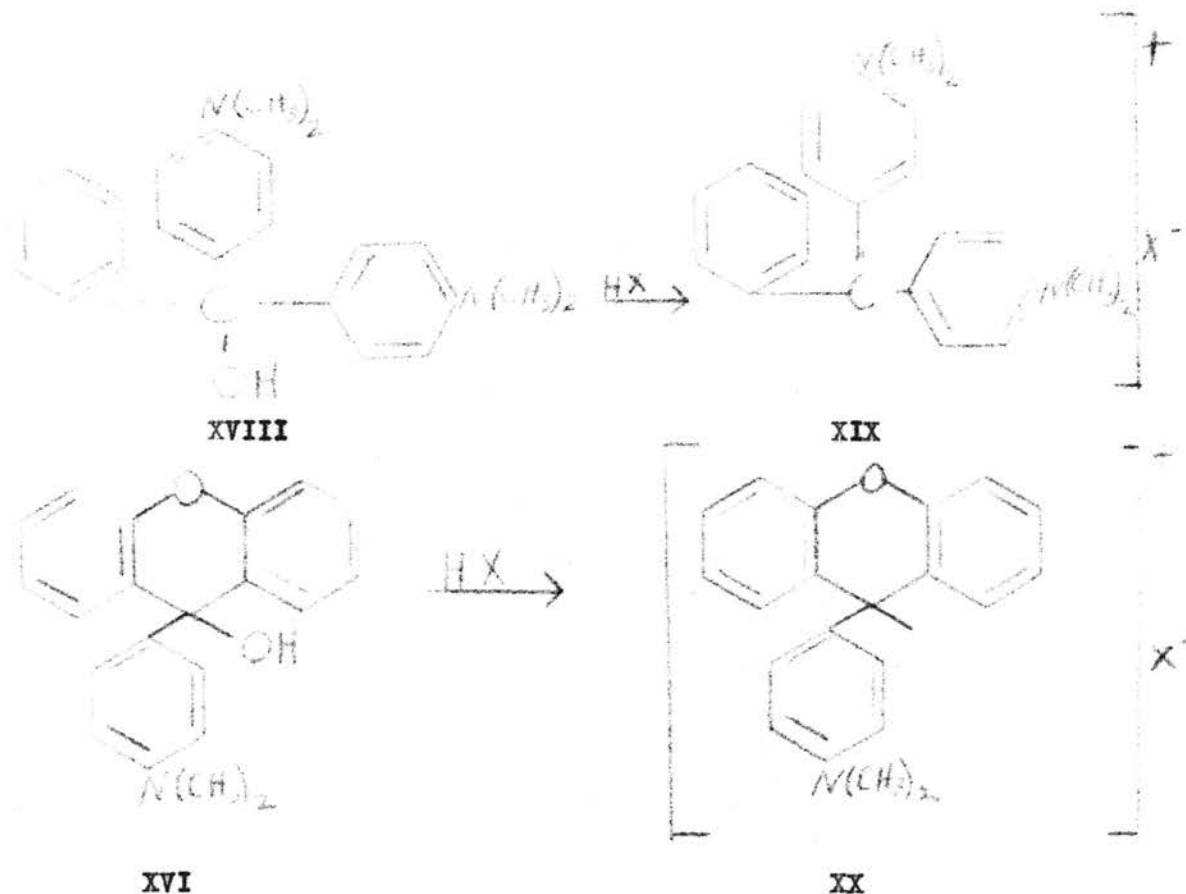
The carbinol (XVI) contains the triphenylmethane grouping and is analogous to malachite green (XVIII).



XVIII

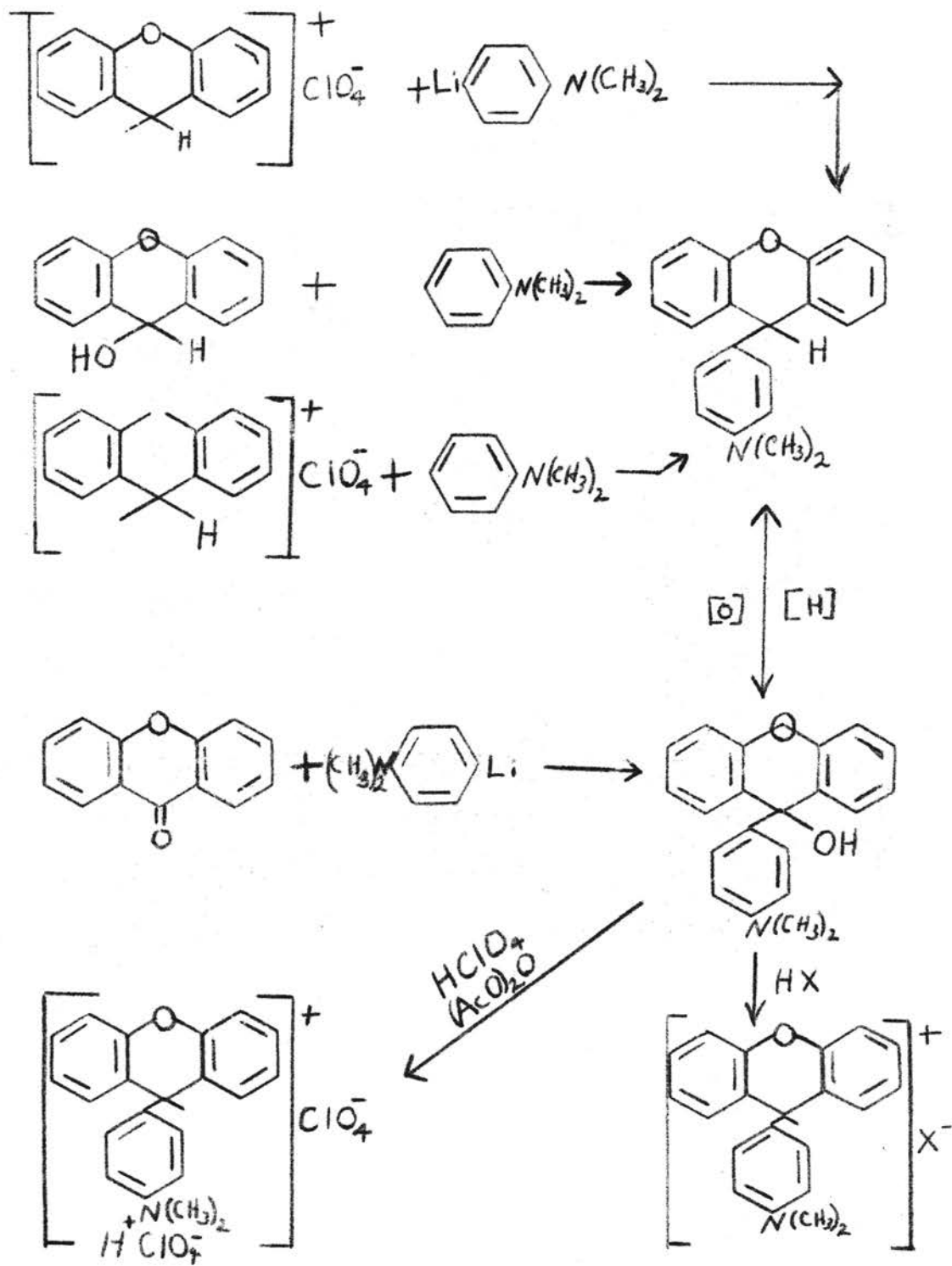
The carbinol (XVI) undergoes many of the characteristic color changes of the triphenylmethane dyes. When dissolved in acetone and treated with a small amount of dilute hydrochloric acid a blue solution is formed. More acid renders the solution a deep green. When strongly acid the solution becomes yellow in color. Treatment with dilute base will reverse these color changes until a colorless solution is obtained. The color changes noted with increasing acidity probably involve elimination of resonance forms due to salt formation.

The transformation of the carbinol form of malachite green (XVIII) to the colored compound (XIX) is similar to the change taking place when (XVI) is treated with acid to give the colored compound (XX).



There are seven possible resonance forms of the carbonium ion in malachite green, seven major forms and one minor form in (XIV) prepared by Shotton (7) and six major forms and two minor forms in (XVI). Since resonance forms are closely tied in with color it was interesting to note that (XVI) was at least qualitatively intermediate in color as predicted by the number of resonance forms.

These reactions may be summarized as follows;



EXPERIMENTAL

Reduction of Xanthone to Xanthidrol (14)

An amalgam of 9.0 g. of metallic sodium (0.39 gram atoms) and 750 g. (55 ml.) of mercury was prepared by placing the sodium in a 500 ml. round bottom flask and covering the sodium with 25-30 ml. of dry toluene. The sodium was melted by careful heating with a free flame, the flame extinguished and 2-3 ml. of mercury added dropwise with shaking. The reaction was very vigorous at first, but soon subsided and the remainder of the mercury added at such a rate that the toluene boiled and finally was completely volatilized.

The amalgam was cooled to fifty degrees and 25 g. (0.13 moles) of recrystallized xanthone suspended in 175 ml. of 95% ethanol were added. The flask was stoppered, held in a towel and shaken vigorously, releasing the pressure from time to time. The temperature rose to sixty or seventy degrees and the xanthone dissolved forming a pale gray solution.

The mixture was vigorously shaken for fifteen minutes and then poured into 2 liters of cold distilled water. The white precipitate was recovered by filtration, washed with water until free of alkali, and dried at 50° to constant weight. The crystalline product melted at 121-122°. The yield was 20.5 g. or 84% of theory.

Preparation of Xanthylum Perchlorate

Forty grams of xanthidrol (0.20 moles) were dissolved in 1000 ml. of anhydrous ether in a 2 liter round bottom flask surrounded by an ice bath. Dry hydrogen chloride was passed in for 30 minutes. A solution of 20 ml. of 70% perchloric acid in 60 ml. of acetic anhydride was then added slowly in small portions. Addition of the perchloric acid-acetic anhydride mixture caused the formation of a bright yellow precipitate. Hydrogen chloride was again passed in until the solution was saturated, about two hours.

The yellow precipitate was collected on a sintered glass funnel, washed twice with absolute ether, and dried by suction. The yield of crude perchlorate was 50 g. or 89% of theory. Recrystallization was attempted using boiling glacial acetic acid but decomposition resulted and no xanthylum perchlorate was recovered. This method also failed on another sample of crude xanthylum perchlorate although other experimenters (15, 16) have used it successfully on similar perchlorates.

Another portion of xanthylum perchlorate was prepared by suspending 25 g. of xanthidrol (0.127 moles) in 750 ml. of anhydrous ether in a flask surrounded by an ice bath. Fifteen ml. of perchloric acid was dissolved in 45 ml. of acetic anhydride using extreme care and cooling with an ice bath. This mixture was added slowly to the ethereal solution, shaking vigorously after each addition. The yellow precipitate which formed was recovered by filtration, washed several times with anhydrous ether and dried in an oven at 105°. Further purification was affected by washing with warm glacial acetic acid followed by washing with anhydrous ether. The yield was 33.8 g. or 93% of theory. Since the melting point given by Hofmann, Roth, Hobold, and Metzler (1) was

only approximate the compound was analyzed for chloride, using Parr bomb procedure, and the melting point of the analyzed xanthylum perchlorate was found to be 234° - 235° .

Analysis: Calculated $C_{13}H_9OClO_4$ Cl, 12.67 Found Cl, 12.77

Reaction of Dimethylaniline and Xanthylum Perchlorate

Twelve and one tenth grams of dimethylaniline (0.10 moles) were dissolved in 200 ml. of anhydrous ether and 14.0 g. of xanthylum perchlorate added in small portions. The flask was stoppered and shaken vigorously after each addition. The xanthylum perchlorate did not dissolve but reacted slowly, the yellow color changing to light green. After a short time snowflake crystals formed in the solution. After all of the xanthylum perchlorate had reacted a blue precipitate was noted in the neck of the flask. The precipitate was recovered by filtration and the ether solution evaporated. A white solid remained. The precipitate remaining after the filtration was extracted several times with ether and all of the white product dissolved leaving a small amount of the blue precipitate. The ether washings were evaporated obtaining more of the white solid. The blue compound was dissolved in methanol and the solution made basic by the addition of dilute hydroxide. Upon the addition of water a white solid formed which was recovered by filtration. The three white solids were combined and recrystallized from ether. The resulting solid melted at 158° and analyzed for 9-(p-dimethylaminophenyl) xanthene. The blue precipitate was probably the above compound contaminated with the perchlorate of its oxidized form, 9-(p-dimethylaminophenyl) xanthenol.

Analysis: $C_{21}H_{19}ON$ Calculated C, 83.7 H, 6.31 N, 4.65

Found: C, 83.6 H, 6.40 N, 4.80

The reaction between dimethylaniline and xanthylium perchlorate was repeated using 10.1 g. of xanthylium perchlorate (0.0364 moles) and 14 g. of dimethylaniline (0.11 moles). This time the reaction was carried out in a 3 necked creased flask, which was fitted with a stirrer. The yield of white product analyzing for 9-(p-dimethylaminophenyl) xanthene was 6.1 g. or 56% of theory and the melting point was 158°.

Reaction of Dimethylaniline and Xanthidrol

Five grams of xanthidrol (0.025 moles) were dissolved in 30 ml. of glacial acetic acid and 1.5 ml. of concentrated hydrochloric acid added to form an orange red solution. Four and four tenths grams of dimethylaniline were added to this solution and the mixture refluxed for four hours. The addition of the dimethylaniline caused the solution to become green in color, but this faded to a pale yellow-green at reflux temperature. The solution was poured into 500 ml. of water containing 5 g. of sodium carbonate. The light green solid which formed was recovered by filtration and washed with water. The light green solid was recrystallized from ether and melted at 158°, the melting point of the 9-(p-dimethylaminophenyl) xanthene. The yield was 5.9 g. or 79% of theory.

Preparation of p-Bromodimethylaniline

One hundred grams of dimethylaniline were dissolved in 200 ml. of glacial acetic acid and cooled in an ice bath. Seventy grams of bromine were added slowly from a dropping funnel. After the addition was completed, the flask was nearly filled with ice water and shaken vigorously. This resulted in the formation of a white precipitate. The precipitate

was collected and washed several times with water. Recrystallization from 95% ethanol gave a white compound melting at 55°. The yield was 105 g. or 63% of theory.

Preparation of p-Dimethylaminophenyl Lithium

The method described by Austin (17) and Gilman, Zoelner, and Selby (18) was used. Eighteen hundredths of a gram of lithium (0.028 gram atoms) was cut into small pieces, covered with ether and placed in a three necked flask which was equipped with a dropping funnel, double surface condenser, and a stirring motor. One and five tenths grams of p-bromodimethylaniline were dissolved in 25 ml. of ether and one third of this solution was added to the mixture. The mixture was refluxed to start the reaction and the remainder of the p-bromodimethylaniline solution added at such a rate as to keep the ether refluxing. After the addition of the p-bromodimethylaniline the refluxing was continued for one half hour by heating on a steam bath. By this time nearly all of the lithium had reacted.

Reaction of p-Dimethylaminophenyl Lithium with Xanthylum Perchlorate

To a solution of p-dimethylaminophenyl lithium, prepared as described above, 2.8 g. of xanthylum perchlorate (0.01 moles) were added in small portions. A dark precipitate immediately separated out which was recovered by filtration. The precipitate on the filter was washed with ether and the combined ether solutions evaporated to dryness. Recrystallization of the residue from the ether solution yielded 2.0 g. or 66% of the theoretical yield of 9-(p-dimethylaminophenyl) xanthene. The melting point was 158°.

Reaction of p-Dimethylaminophenyl Lithium with Xanthone

A solution of p-dimethylaminophenyl lithium was prepared as described above using 0.95 g. of lithium (0.137 gram atoms) and 13.1 g. of p-bromodimethylaniline (0.066 moles). To this solution was added 14.6 g. of xanthone suspended in 150 ml. of dry ether. The solution was refluxed for one hour, with stirring. The lithium compound was decomposed by pouring the contents of the flask into 200 ml. of ice water. The excess lithium decomposed gently. The insoluble white precipitate which formed was removed by filtration. The ether layer was separated, dried with anhydrous sodium carbonate and then evaporated to dryness.

The light yellow solid remaining after the evaporation of the ether was recrystallized. It melted (decomposed) from 145-150°. When dissolved in acetone and treated with dilute hydrochloric acid a blue solution was formed indicating the presence of 9-(p-dimethylaminophenyl) xanthenol. However, the analysis for nitrogen was significantly low and this solid was probably a mixture of the unreacted xanthone and the above compound, such a mixture would be colored in acid solution.

The white insoluble solid was recrystallized from ethanol-acetone and water. It melted (decomposed) at 191-192°. This compound also produced a blue solution when dissolved in acetone and acidified with dilute hydrochloric acid. The addition of dilute base to this solution rendered the solution colorless again. This solid analyzed to be 9-(p-dimethylaminophenyl) xanthenol. The yield was 10.8 g. or 51% of theory.

Analysis: Calculated for $C_{21}H_{20}O_2N$ C, 79.2 H, 6.34 N, 4.40

Found: C, 79.7 H, 6.35 N, 4.59

Reduction of 9-(p-Dimethylaminophenyl) Xanthenol to 9-(p-Dimethylamino-phenyl) Xanthene

One gram of 9-(p-dimethylaminophenyl) xanthenol (0.0031 moles) was dissolved in 25 ml. of 90% formic acid, which contained 0.5 g. of sodium carbonate. This solution was refluxed for one hour. The original solution was a very dark green which turned to blue on heating. The blue color faded on refluxing and after standing for twelve hours a very light green solution was obtained. The solution was poured into water and a white precipitate formed. The white solid was recovered by filtration, washed with water, and recrystallized from ether. White snow-like crystals were obtained melting at 158°. The yield of 9-(p-dimethylamino-phenyl) xanthene was 0.77 g. or 63% of theory.

Preparation of the di-Perchlorate of 9-(p-Dimethylaminophenyl) Xanthenol

Three and two tenths grams of 9-(p-dimethylaminophenyl) xanthenol were dissolved in the minimum amount of dry ether and 2 ml. of 70% perchloric acid dissolved in 8 ml. of acetic anhydride added slowly and with vigorous shaking. The solution turned blue with the first addition of the perchloric acid-acetic anhydride mixture. Further addition caused the formation of a blue or green precipitate and finally a light yellow precipitate was formed. This was filtered, washed with glacial acetic acid, and finally washed with dry ether. The yellow solid which was somewhat hygroscopic was dried to constant weight at 105° in an oven. The melting point (decomposition) was 247°. Analysis indicated that the perchlorate of the carbinol and the perchlorate of the dimethylamino group had both formed.

Analysis: Calculated for $C_{21}H_{19}O_9Cl_2N$ Cl, 14.18 Found Cl, 14.46

SUMMARY

Three new compounds were prepared and a fourth, whose melting point as given in the literature was only approximate, was prepared, analyzed and its melting point redetermined.

9-(p-Dimethylaminophenyl) xanthene was prepared by three different methods. It was prepared from xanthylium perchlorate and dimethylaniline, from xanthylium perchlorate and p-dimethylaminophenyl lithium and by the reduction of 9-(p-dimethylaminophenyl) xanthenol.

9-(p-Dimethylaminophenyl) xanthenol was prepared by reacting xanthone with p-dimethylaminophenyl lithium. When dissolved in acetone and then treated with dilute acid this compound yielded a blue solution which turned a deep green and finally yellow as more acid was added.

Xanthylium perchlorate was prepared from xanthydroxol and 70% perchloric acid. Since Hofmann, Roth, Hobold, and Metzler (1) listed the melting point (decomposition) as about 235° this compound was analyzed and the melting point redetermined. The melting point (decomposition) obtained by this author was 234-235° which substantiated the value given above.

BIBLIOGRAPHY

1. Hofmann, Roth, Hobold, and Metzler, Ber., 43, 2624 (1910)
2. Gomberg and West, J. Am. Chem. Soc., 34, 1529 (1912)
3. Gomberg and Cone, Ann., 370, 142-208 (1910); via C. A., 4, 1172 (1910)
4. Decker and Becker, Ber., 46, 976 (1913)
5. Dilthey, Beires, Holterhoff and Wubken, J. Prakt. Chem., 114, 179 (1926) via Shotton, Ph. D. Thesis, Iowa State University, 1949.
6. Schonberg and Sina, J. Chem. Soc., 1947, 175
7. Shotton, Ph. D. Thesis, State University of Iowa, 1949
8. Ullman and Engi, Ber., 42, 2625 (1904)
9. Neiderl and Hart, J. Am. Chem. Soc., 59, 719 (1937)
10. Gomberg and Kamm, J. Am. Chem. Soc., 39, 2013 (1917)
11. Iddles and Hussey, J. Am. Chem. Soc., 63, 2769 (1941)
12. Witten and Reid, J. Am. Chem. Soc., 69, 973 (1947)
13. Wolf, Ph. D. Thesis, State University of Iowa, 1949
14. Holleman, "Organic Syntheses", Collective Volume I, John Wiley and Sons, Inc., New York, 1943, p. 554
15. Conant, Small and Sloan, J. Am. Chem. Soc., 48, 1743 (1926)
16. Conant and Small, J. Am. Chem. Soc., 47, 3068 (1925)
17. Austin, J. Am. Chem. Soc., 54, 3727 (1932)
18. Gilman, Zoelner, and Selby, J. Am. Chem. Soc., 55, 1253 (1933)

BIOGRAPHY

Thomas Brown Rice was born at Medora, Illinois, June 27, 1925. He received his grade and high school training in the Medora Public Schools.

He entered the naval service in the summer of 1943 and received a commission as an Ensign in the Naval Reserve in July of 1945. In July of 1945 he was married to Alpha Jean Tober.

In June of 1948 he was graduated from the University of the South with the degree of Bachelor of Science. He attended Michigan State College Graduate School for the fall quarter of 1948, serving as a Graduate Assistant in the Chemistry Department. In January, 1949, a son, Thomas Brown, was born. In the summer of 1949 he entered Oklahoma A. and M. College and in the fall of 1949 he was appointed a Graduate Fellow in the Chemistry Department.

TYPIST: Jo Fowler

Stillwater, Oklahoma