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The Condensation of the Aminophenols with Maleic Anhydride

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THE CONDENSATION OF THE AMINOPHENOLS WITH MALEIC ANHYDRIDE

By

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THE CONDENSATION OF THE AMINOPHENOLS

WITH MALEIC ANHYDRIDE

This thesis is approved as a creditable, independent investigation by a candidate for the degree, Master of Science, and acceptable as meeting the thesis requirements for this degree; but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Advisor

Head of the Major Department

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Introduction

In the classification of organic reactions, condensation is used in two different ways. In a very narrow sense, condensation means any reaction in which a carbon to carbon linkage is formed. In a broad sense, it refers to an organic double decomposition reaction in which the reactants are both large molecules, and one of the products is a small molecule such as water, ammonia, or hydrogen chloride. An example of a condensation, as defined in the narrow sense, would be the reaction of acetaldehyde to form aldol. However, if the aldol is converted to crotonaldehyde with the elimination of water, then it can be classified as a condensation in the broad sense as well.

Theoretically, a condensation reaction can be considered as a reaction which involves preliminary addition followed by an elimination reaction. Many condensation reactions proceed rapidly when the reactants are mixed together at a suitable temperature, but others require condensing agents such as acids, bases, phosphorus pentoxide or zinc chloride. Sometimes these condensing agents act as true catalysts, but in other cases they are used to aid in the elimination of water (1).

Today many condensation reactions are known and much could be said about them. In this research project, the primary interest is focused on the condensation of a phenolic

compound and maleic anhydride to produce an acid-base indicator.

Historical:

The first condensation reaction between a phenolic compound and an anhydride was reported by Baeyer (2) in 1871, when he prepared phenolphthalein by the condensation of phenol and phthalic anhydride. In this reaction, concentrated sulfuric acid was used as the condensing agent. In 1880, Baeyer (3) reported on the successful use of stannic chloride as a condensing agent in the preparation of phenolphthalein. Recent investigations have shown that phthaloyl chloride could replace the phthalic anhydride in this condensation and condensing agents other than concentrated sulfuric acid and stannic chloride were also discovered (4). A few of these are stannous chloride, zinc chloride, aromatic sulfonic acids, aluminum chloride and boron trifluoride.

Baeyer continued his investigations of the condensation reactions and reported the successful condensation of resorcinol (5), para-chlorophenol (6) and ortho-cresol (7) with phthalic anhydride. The compounds produced had similar structures and some indicator properties.

Little was done on the condensation of phenolic compounds with an anhydride from 1880 to 1919. After 1919, experiments were conducted to determine whether a condensation reaction would occur between a phenolic compound and an anhydride other than phthalic anhydride. Baeyer had shown that

various compounds would react with phthalic anhydride, but would they react with other anhydrides? Successful condensations of phenols with coumarin (8), with diphenic acid anhydride (9) and succinic anhydride (10) were soon reported and it was proven that phenols would form condensation compounds with various anhydrides.

While looking for new dyes, Dass and Tewari (11), in 1941, reported the condensations of pyrocatechol, pyrogallol, ortho-cresol, 2-naphthol, meta-amidophenol and meta-phenylenediamine with maleic anhydride. Since these men were interested only in the compounds as dyes, no mention was made of the indicator properties of these compounds. Sisson (12) prepared several maleins and succineins from the condensation of phenols with maleic and succinic anhydride, respectively. However, difficulty was experienced in purifying them and pure compounds were not obtained. These impure compounds did show some indicator properties.

In 1947, Mehrotra, Tewari and Dube (13) reported the preparation of resorcinol succinein and indicated that it could be used as an adsorption indicator in argentometric titrations. Kamatra and Webster (14), in 1951, prepared and purified phenolmalein, resorcinolmalein and para-bromophenolmalein.

The last reported work on the condensation reactions was presented by Engstrom and Webster (15) in 1953. They

were interested in the preparation of a series of related phenolmaleins to determine the effect on the physical and chemical properties of these compounds produced by changing the position (ortho, para, meta) of the group on the phenolic structure, and the effect produced by changing the group (chloro, bromo, iodo). They prepared and purified para-chlorophenolmalein and ortho-iodophenolmalein, ortho-bromo-phenolmalein and ortho-chlorophenolmalein, and attempted to prepare meta-chlorophenolmalein but analysis showed this compound to be impure. The pure compounds did show some indicator properties, but the impure meta-chlorophenolmalein did not.

Statement of the Research Problem:

The problem selected for this research project was primarily the preparation of the meta-, ortho- and para-aminophenolmaleins by means of the condensation reaction between the corresponding aminophenols and maleic anhydride. Meta-aminophenolmalein had been prepared previously by Dass and Tewari (11) in 1941, but they failed to report whether or not this compound had indicator properties. The secondary interest was centered upon whether or not the aminophenol-maleins would exhibit indicator properties. It was expected that these compounds could possess indicator properties because they are structurally similar to other indicators.

The research problem was initiated by preparing the meta-aminophenolmalein using the method of Dass and Tewari (11).

By preparing a known compound, familiarity with the process could be attained and difficulties which might arise in preparing the other aminophenolmaleins could be brought to light.

Preparation and Purification of Meta-Aminophenolmalein:

A mixture of twelve grams of maleic anhydride, twenty-four grams of meta-aminophenol and eight drops of concentrated sulfuric acid was heated in an oil bath at a temperature of 160 to 170 Centigrade for six hours. This mixture was stirred frequently to insure complete reaction.

At the end of the reaction period, the melt was removed from the oil bath and allowed to cool to room temperature. To the cooled mixture about one hundred milliliters of boiling distilled water were added and the resultant mixture was placed on a steam bath for about fifteen minutes. The aqueous mixture was then filtered and the filtrate allowed to cool. The precipitate or solid was then dissolved in dilute ammonium hydroxide, filtered and reprecipitated by the addition of dilute hydrochloric acid. The acid was added until the mixture was slightly acidic. The mixture was filtered and the product was further purified by boiling with concentrated alcohol and powdered charcoal.

The aminophenolmalein was obtained by diluting the filtered alcoholic solution with water. A trace of dilute hydrochloric acid was added to aid precipitation. The resultant compound was dried in a dessicator with calcium chloride

as the drying agent.

Meta-aminophenolmalein was a light brown powder which changed color at 212° Centigrade and melted at 225° Centigrade. It dissolved in methyl alcohol, ethyl alcohol, acetone and dilute ammonium hydroxide, but was insoluble in concentrated hydrochloric acid, dilute hydrochloric acid, chloroform, benzene and petroleum ether. A light brown solution was obtained with methyl or ethyl alcohol. The indicator showed a very slight green fluorescence in alcoholic solutions. In the presence of ultra-violet light, the alcoholic solution became dark green and remained green when the solution was made acidic or basic.

The physical properties of this compound correspond to those reported by Dass and Tewari (11) for their amidophenolmalein. Therefore, it may be concluded that these two compounds are the same.

The indicator compound was yellow in acidic and basic solutions. There was some change in the intensity of the color when the pH of the solution was increased. However, for normal titrations this compound would not be an acceptable indicator.

The result of the chemical analysis of this compound may be found in Table IV.

Preparation and Purification of Original Products:

Ortho-Aminophenolmalein:

A mixture of thirty grams of maleic anhydride, sixty grams of ortho-aminophenol and twenty drops of concentrated sulfuric acid was heated in an oil bath for six hours at a temperature of 160 to 170° Centigrade. This mixture was stirred frequently to insure complete reaction.

At the end of the reaction period, the melt was removed from the oil bath and allowed to cool to room temperature. To the cooled mixture about one hundred milliliters of boiling distilled water were added and the resultant mixture was placed on a steam bath for about fifteen minutes. The aqueous mixture was then filtered and the filtrate allowed to cool. The solid product was mixed with dilute ammonium hydroxide and the mixture was filtered. The residue (A) was set aside for further purification. The basic filtrate was made acidic with dilute hydrochloric acid and a dark colored tar was obtained. The tar was dissolved in hot alcohol, to which powdered charcoal was added to aid in the purification of the tar. The resultant mixture was boiled for several minutes and filtered. The filtrate was diluted with distilled water, which contained a trace of dilute hydrochloric acid, until precipitation was complete. A brown solid was obtained which turned to a black tar when left in the dessicator to dry.

The residue (A) from the basic solution was then pur-

ified by boiling with alcohol and powdered charcoal. It was recrystallized from the filtered alcoholic solution by dilution with water which contained a trace of acid. The sample was dried in a vacuum dessicator which contained calcium chloride as the drying agent.

From preliminary nitrogen determinations, it was found that the precipitate which did not dissolve in the ammonium hydroxide, was the ortho-aminophenolmalein. The analysis also indicated that the sample was very impure and further purification was necessary. The procedure used above to purify the reaction mixture was repeated on this impure sample. A colloidal precipitate was obtained, which was not dry after five days in a vacuum dessicator. When a small amount of the sample was placed in a drying oven at temperatures of 100°, 60° and 30° Centigrade, a black product was obtained. The rest of the sample was then dried in air at room temperature and a light tan sample was obtained. Nitrogen determinations obtained from this sample indicated that the desired purity had been obtained.

Ortho-aminophenolmalein was a dirty white or light tan in color and showed a very faint bluish fluorescence in alcohol. However, in alcohol it formed a yellow colored solution. When this yellow solution was placed under an ultra-violet light, the yellow color was immediately displaced by a glowing blue color. The blue color disappeared when the solution was

removed from the ultra-violet light.

Alcoholic solutions of the ortho-aminophenolmalein do exhibit indicator properties. The yellow alcoholic solution changed to a colorless solution when it was made acidic. When this acid solution was titrated with a base, at a pH of 11 to 11.3, the yellow color was again obtained. When the basic solution was titrated with an acid, this change in color did not occur until a pH of 7 was reached.

The indicator melted at 159° Centigrade. It dissolved in concentrated hydrochloric acid to form a dark green solution, but it was insoluble in dilute hydrochloric acid. When added to concentrated sodium hydroxide a yellow colored solution was obtained.

The results of the chemical analysis of this compound may be found in Tables IV and V.

Para-Aminophenolmalein:

A mixture of thirty grams of maleic anhydride, sixty grams of para-aminophenol and eight drops of concentrated sulfuric acid was heated in an oil bath, at a temperature of 160 to 170° Centigrade, for six hours. This mixture was stirred frequently to insure complete reaction.

At the end of the reaction period, the melt was removed from the oil bath and allowed to cool to room temperature. To the cooled mixture, about one hundred milliliters of boiling distilled water were added and the resultant mixture placed

on a steam bath for about fifteen minutes. The watery mixture was then filtered and the filtrate allowed to cool. The precipitate was then dissolved in dilute ammonium hydroxide, filtered and the residue further purified by boiling with alcohol and powdered charcoal.

The indicator was obtained by diluting the filtered alcoholic solution with water. A trace of dilute hydrochloric acid was added to aid precipitation. The resultant compound was dried in a vacuum dessicator over calcium chloride as the drying agent.

The para-aminophenolmalein was a tan powder which changed color at 150° Centigrade and melted at 159° Centigrade. It dissolved in methyl alcohol, ethyl alcohol and dilute ammonium hydroxide, but was insoluble in concentrated or dilute hydrochloric acid. A dark yellow or brownish solution was obtained, which showed a very slight green fluorescence, when the indicator was dissolved in alcohol. In the presence of an ultra-violet light, the alcoholic solution turned to a dark green color. The color was slightly darker than the meta-aminophenolmalein in alcoholic solution. The green fluorescence was present even though the indicator solution was made acidic or basic.

The para-aminophenolmalein did not exhibit indicator properties. In acid solution a yellow color was produced which did not change when the solution was made acidic.

The results of the chemical analysis of this compound may be found in Tables IV and V.

Determination of the Indicator Range:

Two tenths gram of each indicator was dissolved in one hundred milliliters of ethyl alcohol. Ten milliliters of this solution was made acidic with dilute hydrochloric acid. Dilute sodium hydroxide was then added slowly and the pH of the solution determined by means of a Beckman pH meter. The range was checked by adding dilute hydrochloric acid to the now basic solution.

Theory of Indicator Range:

Acid-base indicators are highly colored organic dyes which exhibit a change in color when the pH of a solution is changed between certain limits. This limit or pH range is not the same for all indicators.

Kolthoff, Laitinen and others (16) believe that the color change is due to the fact that indicators behave as weak acids or weak bases and their dissociated and undissociated forms have different colors and structures.

When a weak acid indicator dissociates, its dissociation can be represented by:

$$HI \rightleftharpoons H^+ + I^- \qquad (1)$$

where HI is the undissociated acid form containing the acid color and I^- represents the dissociated alkaline form which contains the alkaline color.

Application of the law of chemical equilibrium to the above ionization (1), would give:

$$\frac{(H^+)(I^-)}{(HI)} = K_I \qquad (2)$$

where K_I represents the ionization constant of the indicator.

Rearrangement of the above equation (2) would produce:

$$(H^+) = K_I \frac{(HI)}{(I^-)} \qquad (3)$$

From this equation (3), it is evident that the ratio of the concentrations of the colored forms varies continuously as the hydrogen ion concentration of the solution changes. The color of the indicator depends upon the ratio of the dissociated form (I^-) to the undissociated form (HI).

The change of color of an indicator is determined visually. Since the human eye has a limited sensitivity for the observation of colors, only a certain amount of one form can be detected in the presence of the other. The visible color change is therefore confined within certain limits or pH range. These limits or pH range are designated as the color change interval. The magnitude of this interval is not the same for all indicators because the color of the acid (undissociated form) or alkaline (dissociated form) portion is not always easy to distinguish in the presence of the other.

Assuming that, in a given case, nine percent of the alkaline form can be detected in the presence of the acid form,

we have:

$$\frac{(I^-)}{(HI)} = \frac{1}{10} = \frac{K_I}{(H^+)} \qquad (4)$$

The indicator would begin to change to the alkaline color at

$$(H^+) = 10\ K_I \qquad (5)$$

or at $$pH = p_I - 1 \qquad (6)$$

where p_I represents the negative logarithm of K_I and is called the indicator exponent. Assuming further that the indicator is completely converted into the alkaline form, when about ninety-one percent is present in this form, we would have:

$$\frac{(I^-)}{(HI)} = 10 = \frac{K_I}{(H^+)} \qquad (7)$$

Thus the color change interval of such an indicator may be represented by:

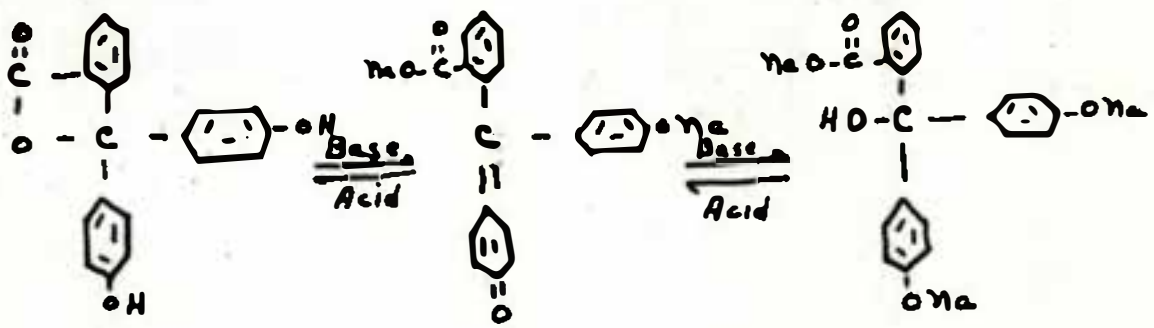
$$pH = p_I \pm 1 \qquad (8)$$

According to the above equation (8), the change in color of the indicator begins at a pH which is one unit smaller than the indicator exponent and is practically complete when the pH is one unit larger than the indicator exponent. The indicator's color change interval should therefore extend over a range of two pH units. Most indicators do possess this two pH unit color change interval.

The titration curves of the three indicators prepared in this investigation may be found on Graphs I, II and III.

Theory of Indicator Color Change:

The Chromophoric Theory (17) originated when Bernthsen (18) and Friedlander (19) almost simultaneously, and independently, showed that phenolphthalein when in acid solution is colorless and has a lactone structure. When in weakly alkaline solutions a red salt is formed which is not derived from a phenol, but has a chromophoric quinone group. In the presence of a large excess of alkali, the quinone is transformed into a colorless trisodium salt. These changes are represented below.



It is believed that the phenolmaleins could show a change in structure similar to the phenolphthaleins. The following equilibrium for para-bromophenolmalein was proposed by George Engstrom (20) in his thesis.

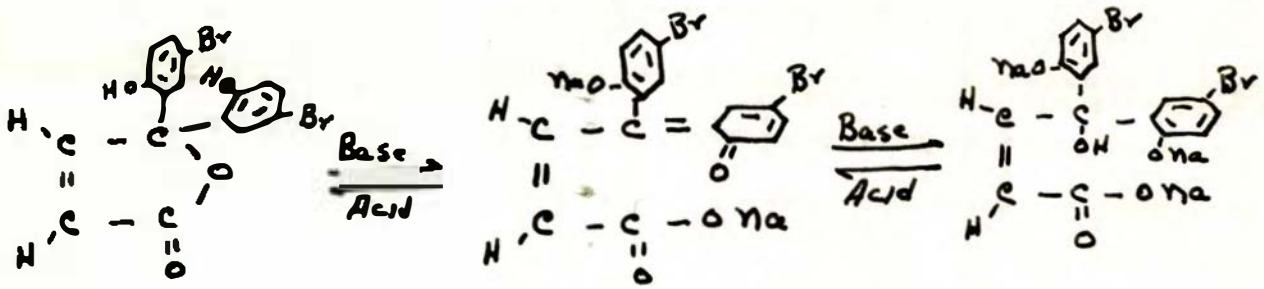


Table I

Titration of m-Aminophenolmalein with 0.104 N. NaOH

NaOH ml.	pH	Color
0000	1.50	Yellow
0.50	1.68	"
1.00	1.70	"
1.50	1.78	"
2.00	1.85	"
2.50	1.92	"
3.00	2.02	"
3.50	2.20	"
4.00	2.45	"
4.50	3.10	"
4.60	3.60	"
4.70	5.00	"
4.75	7.00	"
4.80	9.00	"
4.90	9.90	"
5.00	10.30	"
5.10	10.48	"
5.20	10.55	"
5.30	10.68	"
5.50	10.82	"
5.90	11.00	"
6.00	11.02	"
6.50	11.16	"
7.00	11.28	"
7.50	11.30	"
8.00	11.40	"
8.50	11.43	"
9.00	11.46	"
9.50	11.50	"
10.0	11.52	"
10.5	11.54	"
11.0	11.56	"
11.5	11.58	"
12.0	11.60	"
14.0	11.62	"
16.0	11.68	"

Table II

Titration of o-Aminophenolmalein with 0.104 N. NaOH

NaOH ml.	pH	Color
0000	1.75	Colorless
1.00	1.82	"
2.00	1.90	"
3.00	1.98	"
4.00	2.10	"
5.00	2.22	"
6.00	2.42	"
7.00	2.72	"
7.30	2.90	"
7.50	3.10	"
7.75	3.44	"
7.90	3.90	"
8.00	5.65	"
8.10	6.40	"
8.20	7.40	"
8.30	8.95	"
8.44	9.58	"
8.50	9.64	"
8.60	9.92	"
8.70	10.08	"
8.82	10.36	"
9.00	10.54	"
9.20	10.70	"
9.40	10.80	"
9.60	10.90	"
9.80	10.98	"
9.90	11.00	Very faintly yellow
10.1	11.06	" " "
10.3	11.12	" " "
10.5	11.18	" " "
10.7	11.26	" " "
10.9	11.30	" " "
11.0	11.32	Definitely yellow
11.2	11.36	" "
11.4	11.38	" "
11.6	11.42	" "
11.8	11.48	" "
12.0	11.52	" "

Table III

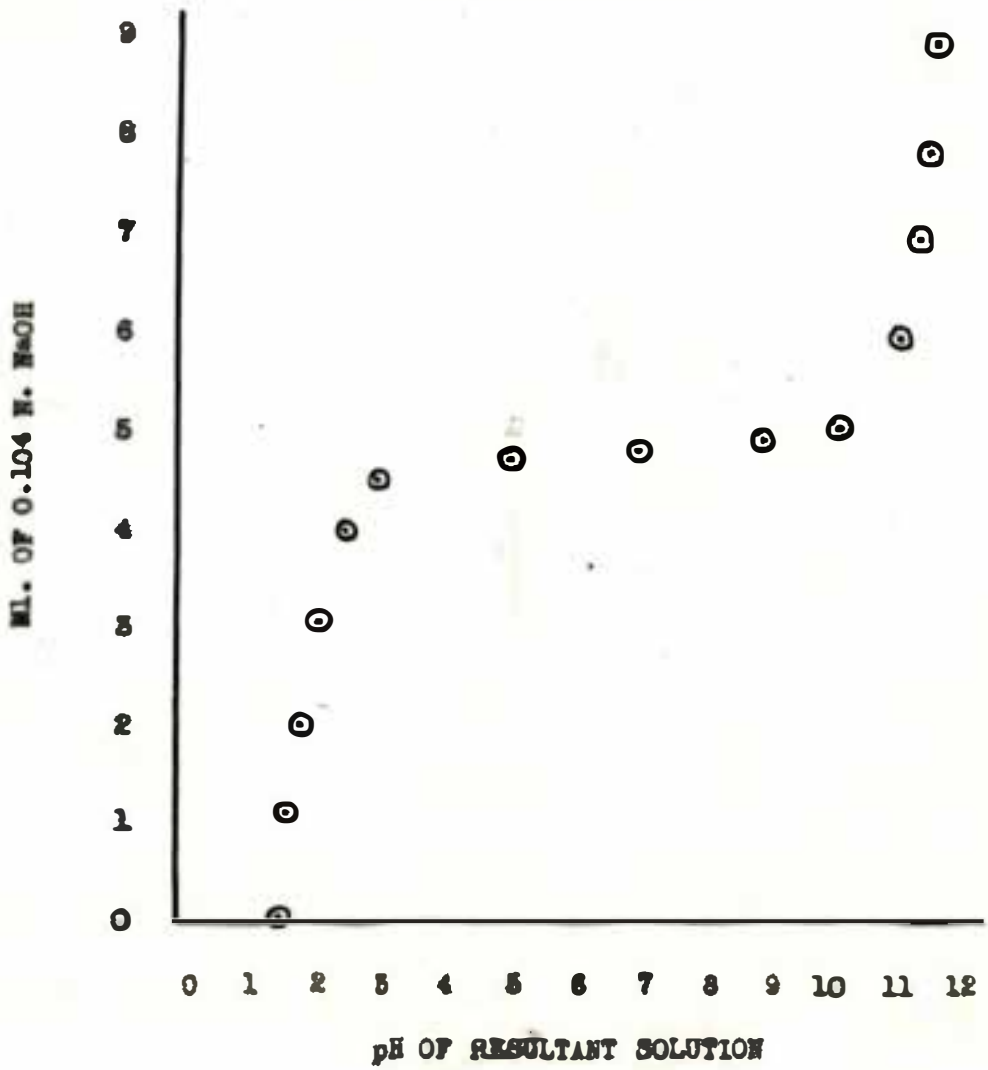
Titration of p-Aminophenolmalein with 0.104 N. NaOH

NaOH ml.	pH	Color
0000	2.00	Yellow
0.50	2.08	"
0.90	2.16	"
1.40	2.22	"
1.60	2.30	"
1.80	2.32	"
2.00	2.40	"
2.30	2.54	"
2.50	2.68	"
2.70	2.78	"
2.90	3.02	"
3.20	3.80	"
3.25	6.00	"
3.30	8.30	"
3.40	9.30	"
3.50	9.96	"
3.60	10.30	"
3.70	10.52	"
3.80	10.64	"
4.00	10.92	"
4.20	11.02	"
4.40	11.14	"
4.60	11.20	"
4.80	11.30	"
5.20	11.40	"
5.60	11.46	"
6.00	11.58	"
7.00	11.60	"
8.00	11.70	"
9.00	11.74	"
10.0	11.78	"
14.0	11.88	"
18.0	11.94	"

GRAPH I

TITRATION OF AN ACIDIC SOLUTION

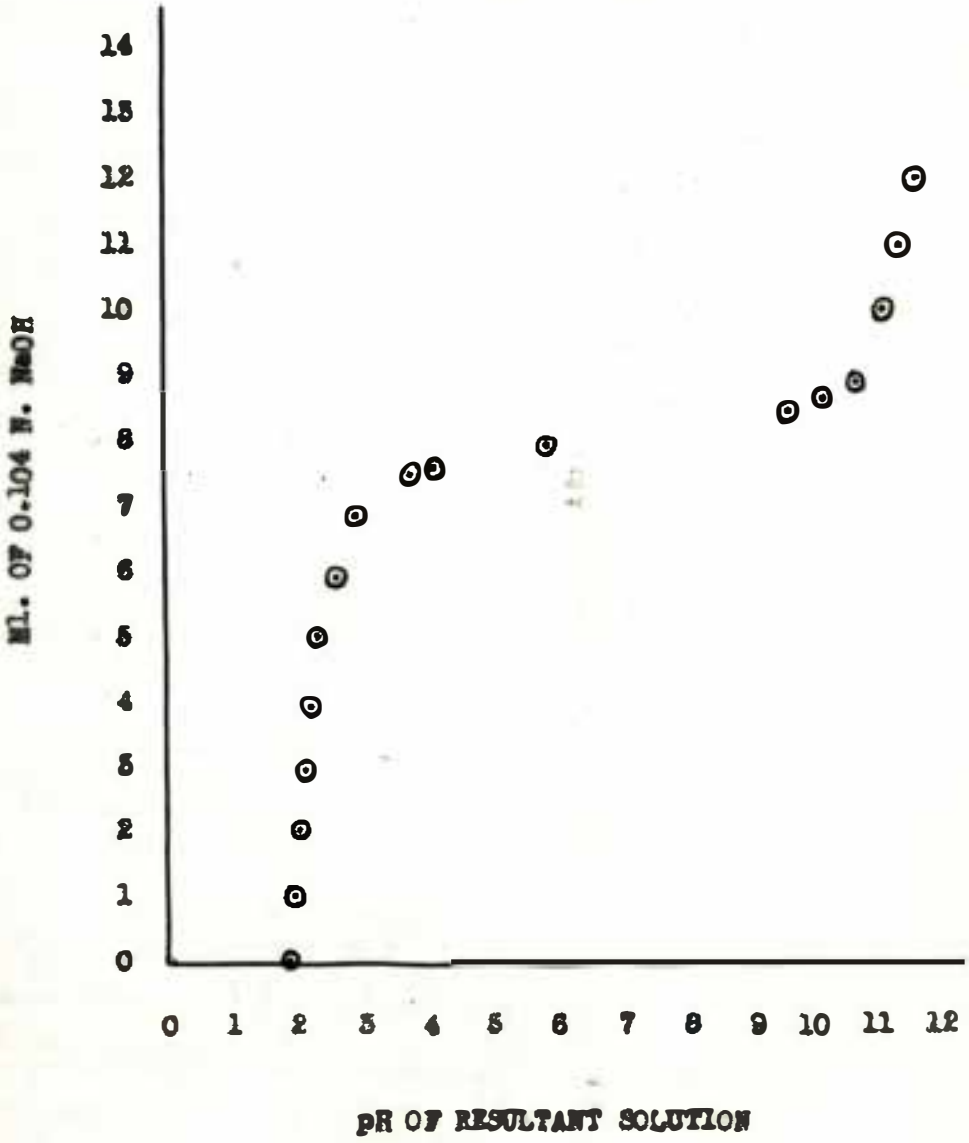
CONTAINING m-AMINOPHENOLPHALEIN



GRAPH II

TITRATION OF AN ACIDIC SOLUTION

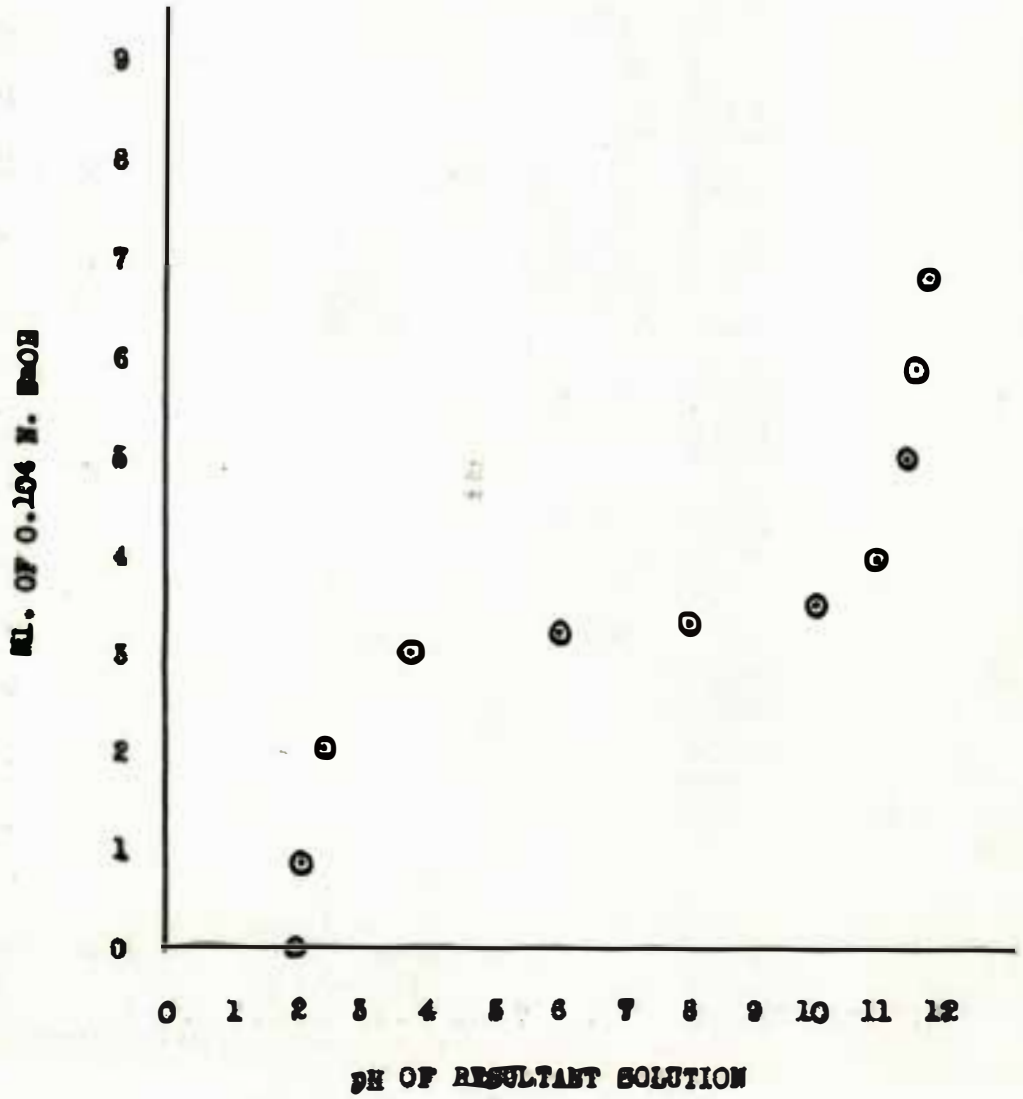
CONTAINING o-AMINOPHENOLMALEIN



GRAPH III

TITRATION OF AN ACIDIC SOLUTION

CONTAINING p-AMINOPHENOLMALEIN



Analysis:

Determination of Nitrogen:

The modified Kjeldahl-Dunning procedure (21) was used to determine the amount of nitrogen present in the indicator compounds.

A 0.7 to 3.5 gram sample of the indicator was decomposed in the presence of concentrated sulfuric acid and suitable catalysts to yield ammonium sulfate. The ammonia was then liberated by the addition of strong alkali and distilled into an excess of 0.1 normal acid. The excess acid was titrated with 0.1 normal base to determine the amount of ammonia liberated.

The weighed sample of the indicator and ten grams of potassium sulfate (to act as catalyst) was placed in a Kjeldahl flask. Twenty-five milliliters of concentrated sulfuric acid were added to the flask to dissolve the sample.

The Kjeldahl flask containing the indicator, catalyst and concentrated sulfuric acid was then placed on a digestion unit and the contents boiled until perfectly clear and light green in color. After the digestion was complete, the flask and contents were allowed to cool. When sufficiently cool, two hundred milliliters of distilled water were cautiously added to the acidic solution.

The required amount of 0.1 normal acid (100 milliliters) was measured out and placed in an Erlenmeyer flask. Several

drops of methyl red indicator were added to both the digested material and the 0.1 normal acid solution. The Erlenmeyer flask containing the 0.1 normal acid was connected to the distilling unit with the end of the exit tube well below the surface of the acid.

To the aqueous acidic solution containing the sample, several pieces of zinc shot were added to prevent bumping when the solution boiled. Sixty milliliters of Greenbank's solution (50 percent NaOH) were slowly added to the solution. The Greenbank's solution was not permitted to mix with the acidic solution, but poured so that it would settle to the bottom of the flask. This flask was connected to the distilling apparatus and shaken thoroughly. It was then placed on the preheated distilling unit and permitted to boil until approximately one hundred fifty milliliters of distillate had been collected.

The Erlenmeyer flask containing the distilled ammonia and the 0.1 normal acid was removed from the distilling unit and the distillation discontinued. The excess of acid was titrated with 0.1 normal base to determine the amount of ammonia distilled.

Since some of the reagents might contain dissolved ammonia, it was necessary to run a blank determination at the same time as the nitrogen determination was made. The blank sample contained the same reagents used in the nitrogen

determination, but without the indicator sample. The same procedure as described for the nitrogen determination was repeated on the blank.

From the values obtained from the titration of the excess standard acid samples and from the blank determinations, the amount of nitrogen present in the sample was calculated by using the following formula.

$$\text{Percentage N} = \frac{(\text{Vol. of Acid})(\text{N. of Base})(\text{At. Wt. N})(1000 \text{ ml.})}{(\text{Wt. of sample})\ (100)}$$

The results may be found in Table IV.

Carbon and Hydrogen Determinations:

The carbon and hydrogen determinations were made by the Clark Microanalytical Laboratory of Urbana, Illinois. These results may be found in Table V.

Table IV

Determination of Nitrogen

		Malein		
		m-Amino-phenol	o-Amino-phenol	p-Amino-phenol
Equivalents of Base	Sample 1	0.00150	0.00613	0.00208
	2	0.00192	0.00698	0.00401
Sample Weight (grams)	Sample 1	0.2274	0.9092	0.3025
	2	0.2888	1.0216	0.6012
Percentage of Nitrogen	Sample 1	9.208	9.442	9.629
	2	9.282	9.566	9.342
Average Nitrogen Determined		9.245%	9.504%	9.486%
Theoretical Nitrogen	$C_{16}H_{14}O_4N_2$	9.392%	9.392%	9.392%
	$C_{16}H_{12}O_3N_2$	9.996%	9.996%	9.996%

Table V

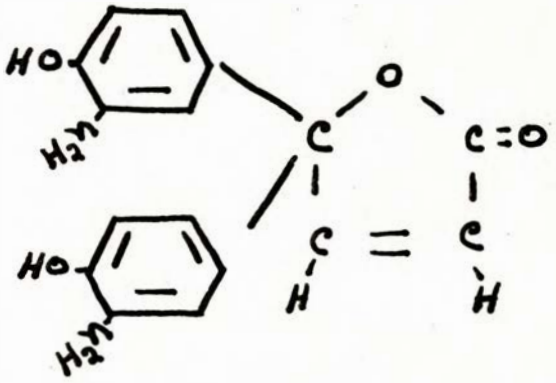
Determination of Nitrogen and Hydrogen

		Malein	
		o-Amino-phenol	p-Amino-phenol
Percentage of Carbon		66.60	65.04
Theoretical Carbon	$C_{16}H_{14}O_4N_2$	64.42	64.42
	$C_{16}H_{12}O_3N_2$	68.56	68.56
Percentage of Hydrogen		4.50	4.03
Theoretical Hydrogen	$C_{16}H_{14}O_4N_2$	4.73	4.73
	$C_{16}H_{12}O_3N_2$	4.31	4.31

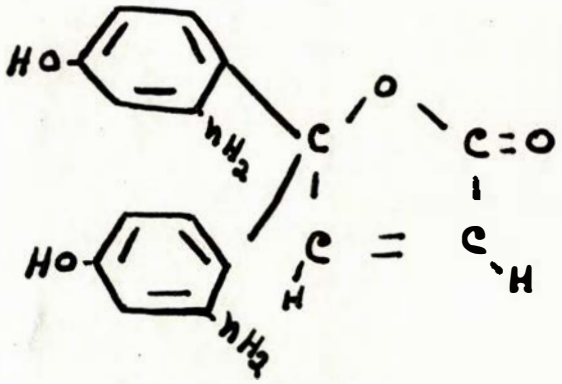
Discussion of Results:

In the preparation of the aminophenolmaleins there are three possible structural forms which may be obtained. These forms are:

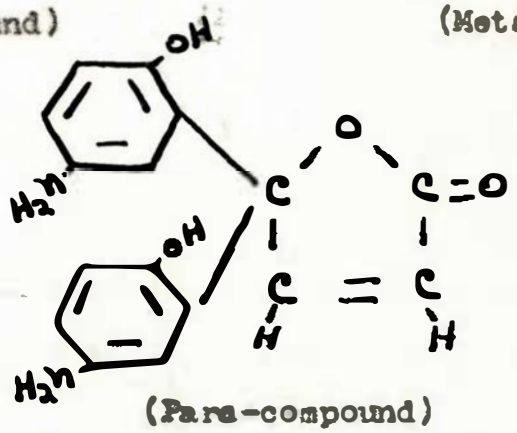
Form A



(Ortho-compound)

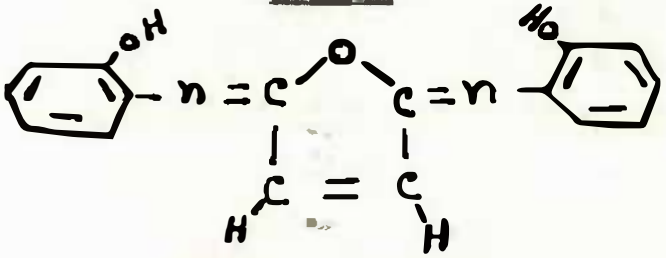


(Meta-compound)

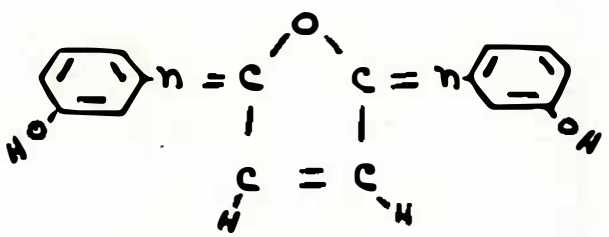


(Para-compound)

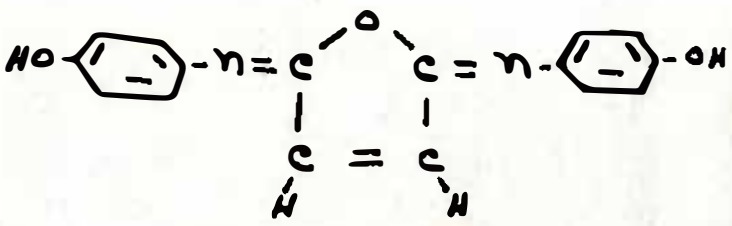
Form B



(Ortho-compound)

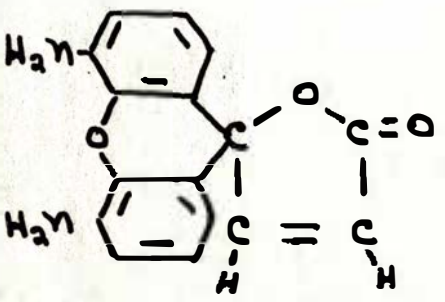


(Meta-compound)

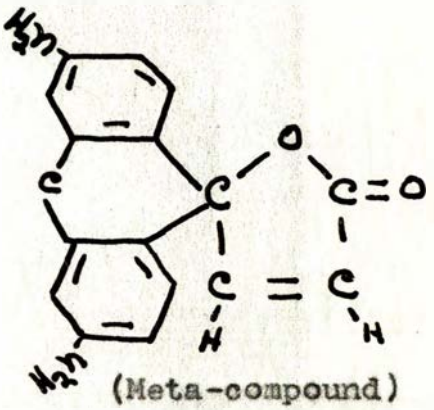


(Para-compound)

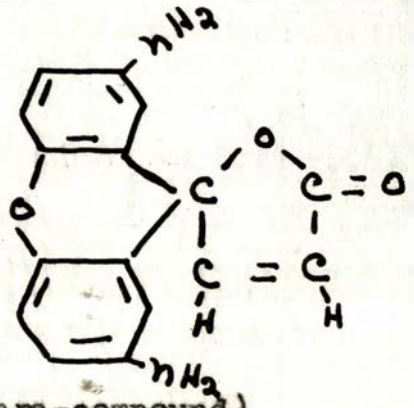
Form C



(Ortho-compound)



(Meta-compound)



(Para-compound)

The true aminophenolmalein structure is illustrated in form A, the iminophenolmalein structure in form B and the cyclic ether structure in form C. The amino (form A) would have a molecular formula of $C_{16}H_{14}O_4N_2$, while the imino and cyclic ether (forms B and C) would have a molecular formula of $C_{16}H_{12}O_3N_2$. The difference between the two molecular formulas, is one molecule of water.

Dass and Tewari (11) reported that the compound they prepared was the meta-amidophenolmalein, but conclusive evidence was not given to substantiate this report. Their conclusions were based simply on carbon, hydrogen and nitrogen determinations.

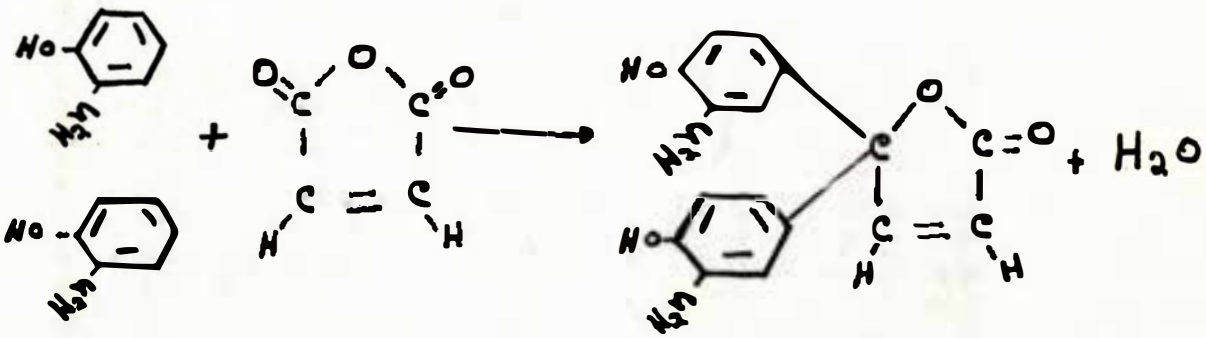
The meta compound was soluble in basic solution but insoluble in dilute or concentrated hydrochloric acid. If the compound had a true amine structure (form A) or cyclic ether structure (form C), it should have been soluble in acidic solutions. Thus, on the basis of solubility tests and carbon, hydrogen and nitrogen determinations, evidence was obtained which would indicate that this compound should be classified as an imino with a structure similar to form B. More accurate studies of the compound must be performed before the true structure will be definitely determined.

The ortho compound was insoluble in dilute base but soluble in concentrated base and concentrated acid. The solubility indicates that this compound should have a

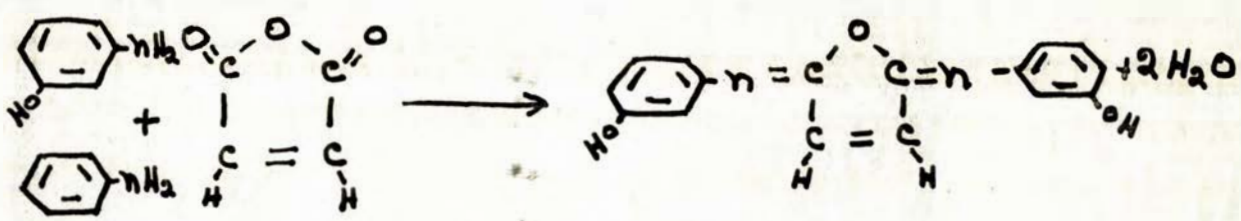
structure similar to form A, since this is the only form which will be soluble in both acidic and alkaline solutions. The carbon, hydrogen and nitrogen determinations tend to substantiate this belief. More accurate studies must be performed before this structural form for the ortho compound is definately proven.

The para compound was insoluble in acidic solutions and soluble in basic solutions. It is therefore proposed that structurally it is similar to the meta compound and its structure is of form B. The carbon, hydrogen and nitrogen determinations tend to favor this proposal.

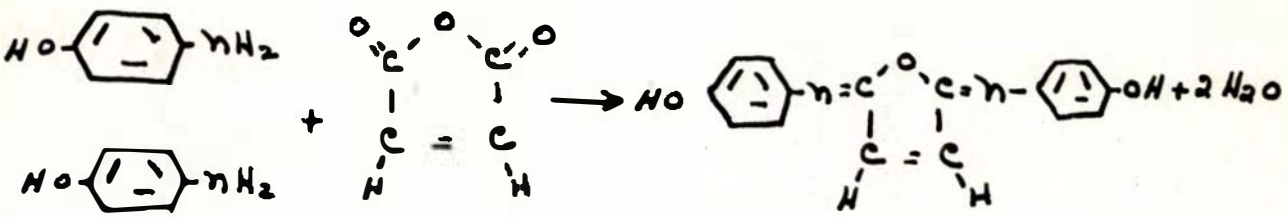
The proposed reactions for the preparation of these compounds are represented below.



(Ortho-aminophenolmalein)



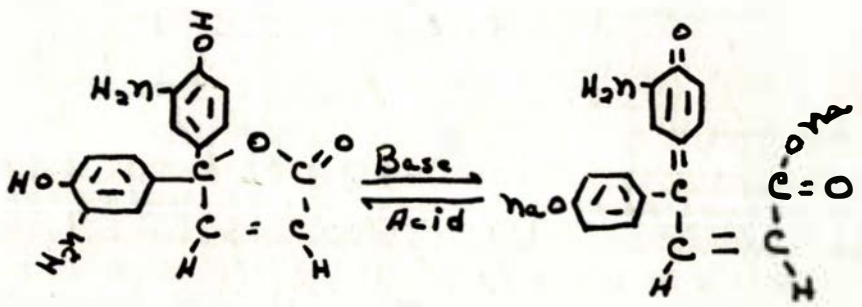
(Meta-iminophenolmalein)



(Para-Iminophenolmalein)

The ortho compound was the only one of the three compounds prepared which did undergo a color change with changes in pH. The ortho compound was colorless in solutions of pH values from 2 to 11 and changed to a straw or yellow color in solutions having pH values from 11 to 14. This would show primarily that the compound will act as an indicator.

Since ortho-aminophenolmalein shows indicator properties, the following change in structure is proposed to represent the change in color.



Ortho-aminophenolmalein does not become colorless in the presence of excess base.

The para and meta compounds did not undergo a change of color but a change in intensity of color was noticed. These compounds could not be used as indicators.

Summary:

In this research project two new compounds, ortho-aminophenolmalein and para aminophenolmalein, have been prepared and tested for indicator properties. Only the ortho-aminophenolmalein exhibited indicator properties.

Meta-aminophenolmalein, which had been prepared previously, was prepared and tested for indicator properties. This compound did not show indicator properties.

On the basis of their solubility in acidic or basic solutions, an attempt was made to predict the structure of the various compounds. The results show that the ortho compound has a true aminophenolmalein structure and the para and meta compounds have iminophenolmalein structures.

Suggestions for Further Work:

It would be of interest to determine whether the meta- and para-aminophenolmalein could be prepared by some similar condensation reaction. However, to obtain the correct compound it might be necessary to protect the amino group on the benzene ring by acetylation or some similar method. Better results might be obtained if a catalyst other than sulfuric acid were used.

It would be interesting to determine how large an anhydride and phenolic compound would react to give the phenolic anhydride condensation reaction.

Literature Cited

1. Remick, A., Electronic Interpretations of Organic Chemistry, 2nd Edition, John Wiley and Sons Inc., New York, 457-460 (1949).

2. Baeyer, Ber. 4, 659 (1871); 9, 1230 (1876).

3. Baeyer, Ann. 202, 68 (1880).

4. Kirk, R. & Othmer, D., Encyclopedia of Chemical Technology, Interscience Encyclopedia Inc. New York, 10, 370-373 (1953).

5. Baeyer, Ber. 4, 558, 662 (1871); Ann. 183, 3 (1876).

6. Baeyer & Caro, Ber. 8, 152 (1875).

7. Baeyer & Fraude, Ann. 202, 154 (1880).

8. Krishna, J. Chem. Soc. 119, 1420 (1921).

9. Dutt, J. Chem. Soc. 123, 225 (1923).

10. Briggs & Pope, J. Chem. Soc. 123, 2934 (1923).

    Dutt, J. Chem. Soc. 1132-8 (1926).

    Dutt, Proc. Indian Acad. Sci. 14A, 158-64 (1941).

11. Dass & Tewari, Proc. Indian Acad. Sci. 13A, 68-76 (1941).

12. Sisson, L., The Condensation of Phenols with Succinic and Maleic Anhydrides, Thesis, South Dakota State College, (1941).

13. Mehrotra, Tewari & Dube, J. Indian Chem. Soc. 24, 165 (1947).

14. Webster & Kamstra, The Condensation of Phenols With Maleic Anhydride, Proc. S.D. Acad. Sci. 30, 40-9 (1951).

15. Webster & Engstrom, The Condensation of Maleic Anhydride With Phenols, Proc. S.D. Acad. Sci. 33, 54-5 (1954).

16. Kolthoff, I. & Laitinen, H., pH and Electro Titrations, 2nd Edition, John Wiley and Sons Inc., New York, 23-5 (1941).

17. Kolthoff, I & Furman, N., Indicators, John Wiley and Sons Inc., New York, 235-9 (1926).

18. Bernthsen, Chemiker Ztg., 1956 (1892).

19. Friedlander, J. Am. Chem. Soc. 41, 1031 (1919).

20. Engstrom, G., The Condensation of Phenols With Maleic Anhydride, Thesis, South Dakota State College (1953).

21. Methods of Analysis of the Association of Official Agricultural Chemists, 4th Edition, George Banta Publishing Company, Menosha, Wisconsin, 24-5 (1935).