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THE CONDENSATION OF PHENOLS WITH MALEIC ANHYDRIDE

By

Leslie D. Kamstra

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.

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Introduction

The condensation of phenols with phthalic anhydride to give acid-base indicators is well known. The preparation of phenolphthalein was first reported by Baeyer in 1871 (1) using concentrated sulfuric acid as the catalyst. Baeyer reported the successful use of stannic chloride as the catalyst for the preparation of phenolphthalein in 1880 (2). Early reports of the condensation of resorcinol (3), p-chlorophenol (4) and o-cresol (5) with phthalic anhydride have also been made.

The reaction of phenols with coumarin (11), with diphenic acid anhydride (8) and with succinic anhydride (6) to form compounds comparable in structure to the phthaleins has been reported. Very little work was done however toward establishing the indicator properties of the products. Sisson (13) attempted to prepare a number of maleins and succineins from phenols and maleic anhydride and succinic anhydride respectively. While indicator properties were evident he obviously did not isolate pure compounds or study them in detail. Similar results were reported by Doss and Tewari (7) who could not have had pure products.

It seemed of interest therefore to repeat some of this work with the hope of obtaining the phenolmaleins in a pure condition and of making a more comprehensive study of their indicator properties.

Since an attempt to study all possible combinations of phenols and anhydrides might involve a problem of too great a scope, it was decided to choose the condensation of maleic anhydride with phenol, p-bromophenol and resorcinol, and to study the resulting products in an extensive manner.

The problem was initiated by the preparation of a known product similar to that of the proposed problem, as a means of bringing to light possible difficulties that might be encountered in the preparation of the unknown product. The preparation and purification of phenolphthalein was chosen for orientation.

Condensations Using Hydrated and Anhydrous Stannic Chloride as Catalysts

Preparation of the original product:

A. Test preparations

1. Five grams of maleic anhydride, ten grams of phenol and two grams of hydrated stannic chloride were heated for eight hours at 105-110° C.
2. Ten grams of maleic anhydride, twenty grams of phenol and four grams of hydrated stannic chloride were heated for eight hours at 105-110° C.
3. Fifteen grams of maleic anhydride, thirty grams of phenol and twenty grams of hydrated stannic chloride were heated for eight hours at 105-110° C.

In all the above cases a dark solid mass was produced which possessed indicator properties.

4. Separate mixtures of five grams of maleic anhydride, ten grams of phenol and two ml. of anhydrous stannic chloride were heated one half hour, one hour, two hours and four hours respectively.

The mixture possessed some indicator properties after one half hour, with increasing properties up to four hours, at which time a solid began to form similar to the product produced by hydrated stannic chloride at the end of eight hours. The mass in this case was less tarry with a carbon-like appearance.

5. A mixture of ten grams of maleic anhydride, twenty grams of phenol and six ml. of anhydrous stannic chloride was heated for eight hours. A dark carbon-like mass was produced similar to that produced after four hours.

The above procedure was repeated replacing phenol with p-bromophenol and resorcinol, respectively.

Determination of temperature and time for optimum yield of indicators:

A method suggested by Sisson (13) was modified by substituting a Model DU Beckmann Spectrophotometer for the Evelyn photoelectric colorimeter. The spectrophotometer has the advantage of more exact wave length adjustments. The method used was as follows:

0.25 gram of the anhydride, 0.5 gram of the phenol and 0.2 gram of anhydrous stannic chloride were placed in a series of pyrex testtubes. The phenol, in the case of phenolmalein, was melted (m.p. 42° C.) before being weighed because of the hygroscopic nature of phenol. Fourteen drops were found to weigh 0.5 gram. Anhydrous stannic chloride is fuming and corrosive and could not be weighed by ordinary methods. From the specific gravity of stannic chloride (2.2) the volume calculated to equal approximately 0.2 gram was .1ml. It was found advantageous to add the stannic chloride below the surface of material to prevent its escape before it could initiate the condensation reaction.

The tubes were subjected to the conditions indicated in Tables I. and II. and cooled to room temperature. Each sample was completely dissolved in 10 ml. of absolute alcohol. One ml. of this solution was pipetted into a centrifuge tube with 7 ml. of alcohol and 3 ml. of a saturated solution of sodium pyrophosphate. The pyrophosphate was added to remove the stannic chloride as insoluble phosphate to prevent its precipitation as the hydroxide when the solution was made alkaline. The contents of the centrifuge tube were shaken to allow the pyrophosphate to react completely, then centrifuged. One ml. of the centrifuged solution, 15 ml. of water and 1 ml. of 6 normal sodium hydroxide were added to a color-

TABLE I

DETERMINATION OF OPTIMUM TEMPERATURE

(Time 1 Hour)

Temperature	Time	Dilution	Wave Length μ	Optical Density	Relative Yield
phenolmalein					
107°	1 hour	1870	540	.415	.415
115°	1 hour	1870	540	.467	.467
125°	1 hour	1870	540	.505	.505
130°	1 hour	1870	540	.295	.295
-bromophenolmalein					
100°	1 hour	1870	310	.720	.720
107°	1 hour	1870	310	.910	.910
115°	1 hour	1870	310	.924	.924
125°	1 hour	1870	310	.925	.925
130°	1 hour	1870	310	.930	.930
140°	1 hour	1870	310	.927	.927
resorcinolmalein					
107°	1 hour	1870	540	.520	.520
115°	1 hour	1870	540	.525	.525
125°	1 hour	1870	540	.820	.820
130°	1 hour	1870	540	.570	.570

Graph I

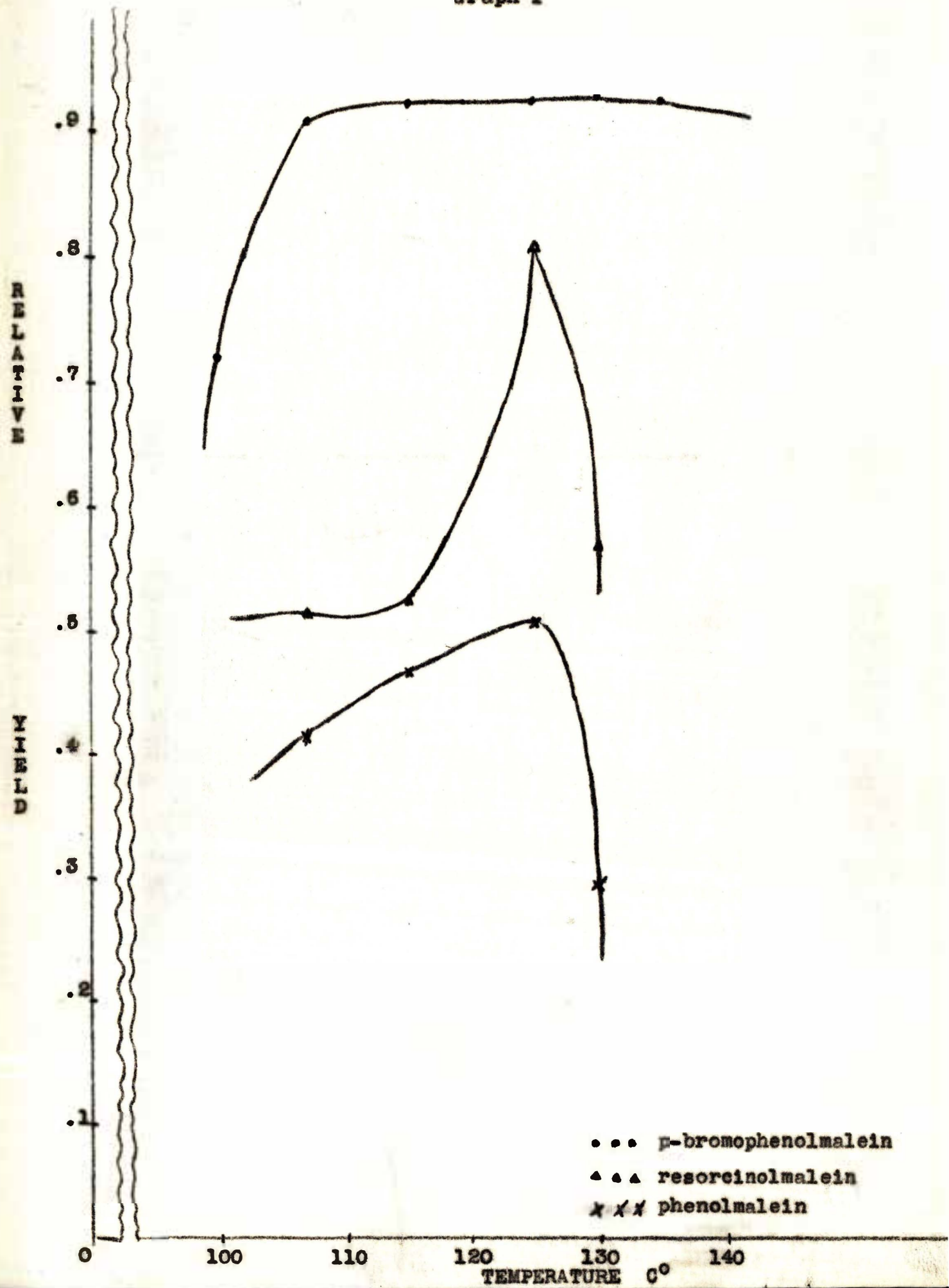
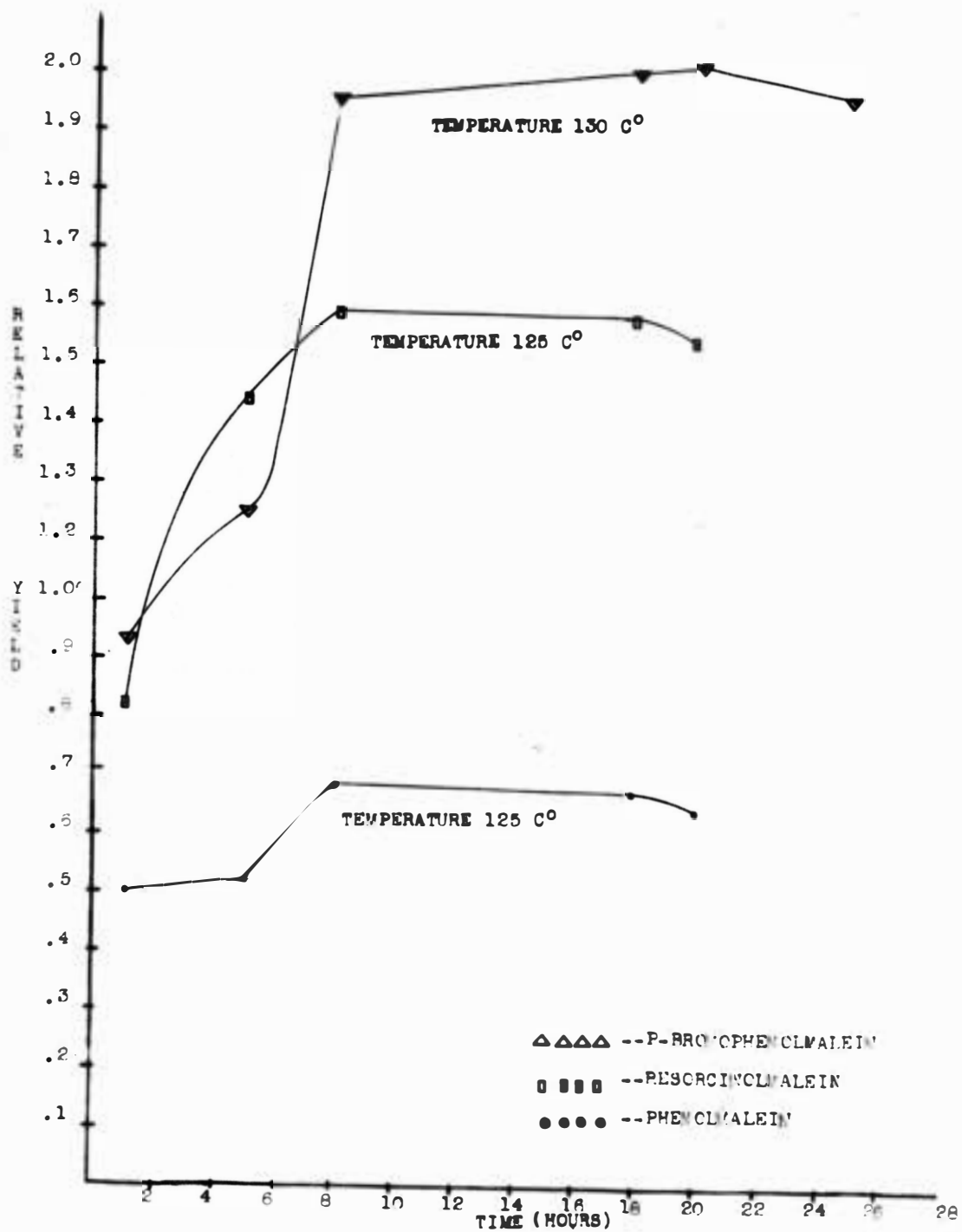


TABLE II

DETERMINATION OF OPTIMUM TIME USING OPTIMUM TEMPERATURE

Temperature	Time	Dilution	Wave Length μ	Optical Density	Relative Yield
phenolmalein					
125°	1 hour	1870	540	.505	.505
125°	5 hours	1870	540	.525	.525
125°	8 hours	1870	540	.689	.689
125°	18 hours	1870	540	.670	.670
125°	20 hours	1870	540	.642	.642
p-bromophenolmalein					
130°	1 hour	1870	310	.930	.930
130°	5 hours	1870	310	1.255	1.255
130°	8 hours	1870	310	1.953	1.953
130°	18 hours	1870	310	1.991	1.991
130°	20 hours	1870	310	2.000	2.000
130°	25 hours	1870	310	1.952	1.952
resorcinolmalein					
125°	1 hour	1870	540	.820	.820
125°	5 hours	1870	540	1.454	1.454
125°	8 hours	1870	540	1.591	1.591
125°	18 hours	1870	540	1.580	1.580
125°	20 hours	1870	540	1.121	1.121

Graph 2



imeter tube, and the color intensity determined immediately to avoid fading of the red color of the indicator.

The Beckmann spectrophotometer was used with a wave length setting of 540 μ which gave maximum absorption for red colors and eliminated the brown color of impurities. A setting of 310 μ was determined as the wave length for maximum absorption of the color produced by p-bromophenolmalein since it was straw colored on the basic side. No brown colored impurities were present to interfere with the results from this indicator.

The results are listed in Tables I and II and are plotted on Graphs 1 and 2. The relative yield was indicated by reading the optical density which increased quantitatively with the increasing intensity of the sample color. Before the reading was taken the instrument was adjusted to zero by blocking the beam from the photo tube and balancing the galvanometer with the dark current adjuster. The one hundred per cent transmission reading was made, in which the beam fell on the phototube after passing through a blank containing absolute alcohol and the milliammeter was brought to balance by adjusting the slit width.

The true yield was determined only for optimum yields of the indicators and are found on Table III.

TABLE III

PHENOL	ANHYDRIDE	YIELD %	MELTING POINT DEG. C°	pH RANGE	ACID COLOR	BASE COLOR
PHENOL	MALEIC	15.8	301	5.5-7.2	YELLOW	RED
P-BROMOPHENOL	MALEIC	33.2	188-190	8.5-10.5	COLORLESS	STRAW
RESORCINOL	MALEIC	56.4	275-276	5.0-6.5	YELLOW	ORANGE-RED

A standard was run using 0.2 gram of the purified sample and 400 ml. of water as the solvent for phenolmalein, 200 ml. of water as the solvent for resorcinolmalein and 400 ml. of absolute alcohol as the solvent for p-bromophenolmalein. The pH of the standard was adjusted to compare with the unknown sample so that both standard and known would be at the same concentration in the salt form. The standard pH for phenolmalein was 7.2; for p-bromophenolmalein 8.5; and resorcinolmalein 10.4. The reading of the known was compared with the reading of the unknown sample under optimum conditions and the actual gram per cent yield calculated, using the following equation

$$\text{Indicator Yield} = \frac{R_s}{R_u} \times m_s \times \frac{100}{v} \times \frac{D_u}{D_s}$$

ms--weight of sample
Ru--Beckmann reading
of unknown
Rs--Beckmann reading
of known
v--volume actually used
Du--dilution unknown
Ds--dilution known

Purification

A column of Merck aluminum oxide was prepared for separation of the product into its components. A suitable solvent for the mass was found by successive spot checks using two plates of glass separated by a thin even layer of alumina. If the solution produced rings when a drop of it was placed on the edge of the plate system, it was an indication of a suitable solvent that would develop layers in the column proper.

The most suitable solvent indicated was acetone. This solvent was used to dissolve the dark mass. The acetone solution upon being passed through the alumina column developed into a large orange layer and narrow yellow layer. When a mixture of 5 ml. of ethyl alcohol and 100ml. of acetone was passed through the column the layers were extruded and the acetone evaporated. The alcohol is less polar than acetone and thus improves the development of the layers. This theory was proposed by Williams (14). The residue from the orange layer was a semi-solid with indicator properties. The yellow layer produced yellow crystals when the acetone was allowed to evaporate slowly.

The orange layer was put into solution with acetone and again passed through the alumina column using fresh alumina. The orange layer produced a dark orange solid upon extrusion. From melting point indications and the odor of phenol it did

not appear to be a pure product. This method did not seem to be feasible with p-bromophenolmalein. A red layer proved to be of high purity in the case of resorcinolmalein.

Alternate purification method:

The black mass was dissolved in excess cold distilled water and boiled. After the solution was boiled for a few minutes a black mass separated and the solution became orange in color. The black mass was filtered and the filtrate was again boiled and filtered. This process was repeated until there was no further separation of black material. The resulting filtrate was then evaporated until the volume was about fifty mls. A solid separated from the super-saturated solution. The supernatant liquid was poured off and added to other impure samples. The solid was dried and prepared for further purification.

Reprecipitation:

Twenty nine different single solvents as indicated below were used as possible reprecipitating agents. None were successful.

1. water
2. ether
3. ethyl alcohol
4. allyl alcohol
5. benzyl alcohol
6. capryl alcohol
7. isobutyl alcohol
8. n butyl alcohol
9. tert. butyl alcohol

10. n heptyl alcohol
11. n hexyl alcohol
12. iso propyl alcohol
13. n amyl alcohol
14. iso amyl alcohol
15. tert. amyl alcohol
16. methyl alcohol
17. benzene
18. acetone
19. petroleum ether
20. carbon tetrachloride
21. chloroform
22. pentane
23. toluene
24. pyridine
25. acetic acid
26. carbon disulphide
27. dichloromethane
28. cyclohexane
29. chlorobenzene

Ten mixed solvents were attempted--with sudden cooling, slow cooling, centrifuging and seeding.

1. ethyl alcohol--carbon tetrachloride
2. water--ethyl alcohol
3. ethyl alcohol--petroleum ether
4. acetone--allyl alcohol, capryl, isobutyl, n butyl, n hexyl, methyl.
5. water--benzene
6. ethyl alcohol--benzene
7. water--petroleum ether
8. water--ether
9. water--acetone
10. water--carbon tetrachloride

Only the first was successful. Reprecipitation was successful using the following method:

Enough ethyl alcohol was added to put the impure indicator into solution when hot, then carbon tetrachloride was added until the solution became cloudy. The solution was heated again and allowed to cool slowly. Precipitation using this method was nearly complete.

Possible purification method:

Enough impure indicator was added to water until the water was saturated hot, then allowed to cool slowly. The supersaturated material separated on cooling with some purity, but precipitation was not complete. Melting points will be found in Table III.

Indicator Range Determination:

Two tenths gram of the indicator was dissolved in 100 ml. of distilled water and the visible range was determined using the McBeth pH meter. The solution was made acidic with HCl, then dilute NaOH was added slowly while the pH was taken from the McBeth pH meter. The range was checked by adding a dilute acid slowly to the now basic solution.

Kolthoff, Laitinen and others (10) believe that indicators behave like weak acids or weak bases, the dissociated and undissociated forms of which have different color and constitution. The quantitative equilibrium may be indicated by the following:

$$\frac{[H^+][I^-]}{[HI]} = K_I$$

K_I is the ionization constant of the indicator. The color of the indicator in solution may be determined by the ratio of $[I^-]$ to $[HI]$. Both forms are present at any pH. It was further proposed that it is incorrect to speak of transition point of an indicator since the transition occurs gradually over a wide range of H ion concentration. The phrase "visual

pH range" or "useful visual range" stems from the fact that the eye has a limited sensitivity to color observation. It is proposed that about 10% of the alkaline form of the indicator in the presence of the acid form can be detected as indicated by the following:

$$\frac{[I]}{[HI]} = \frac{1}{10} = \frac{K_1}{[H^+]} \quad [H^+] = 10^{-pK_1 - 1}$$

The eye observes the indicator to be completely in the alkaline form when in reality 90% of the indicator is in the alkaline form as indicated by the following:

$$\frac{[I]}{[HI]} = 10 = \frac{K_1}{[H^+]} \quad pH = pK_1 + 1$$

This theory indicates that most indicators will have a pH range of 2. A truer picture of the change of alkaline to acid form or vice versa, for phenolmalein, p-bromophenolmalein, resorcinolmalein and a known indicator, phenolphthalein, is indicated by graph 3, obtained from the data in Tables IV, V, VI, and VII.

Table III gives the yield, melting point, useful visible pH range and color changes of the indicators prepared.

Analysis

Determination of Carbon and Hydrogen

The per cent carbon and hydrogen in phenolmalein and resorcinolmalein was determined using a Sargent microcombustion apparatus.

TABLE IV

Titration of Resorcinolmalein with 0.1142 N NaOH

(0.2 gram in 100 ml. HOH)

NaOH ml	pH
	3
2	3.1
4	3.35
6	3.5
8	3.65
10	3.75
12	4.05
14	4.3
16	4.5
18	4.7
20	5
22	5.45
22.5	5.61
23	5.8
23.5	6.2
24	6.7
24.1	6.8
24.2	6.9
24.3	7.1
24.4	7.25
24.5	7.5
24.6	7.7
24.7	8.1
24.8	8.45
24.9	8.6
25	8.8
25.1	9
25.2	9.2
25.3	9.35
25.4	9.45
25.6	9.7
25.8	9.85
26	10.1
26.2	10.2
26.5	10.4
27	10.65
27.5	10.85
28	11
29	11.2
30	11.3
31	11.4
32	11.5

TABLE V

Titration of p-bromophenolmalein with 0.1142 N NaOH
(0.2 gram in 100 ml. HOH)

NaOH ml	pH
	2.55
1	2.55
3	2.57
6	2.65
7	2.75
8	2.8
9	2.9
10	3.05
11	3.15
12	3.3
13	3.4
14	3.55
15	3.65
16	3.75
17	3.85
18	3.95
25	4.55
30	4.75
40	5.65
42	6.15
42.5	6.35
43.2	6.9
43.5	7.45
43.6	7.85
43.7	8.6
43.8	9.7
43.9	10.3
44	10.4
44.1	10.65
44.2	10.75
44.3	10.9
44.6	11
45	11.1
45.5	11.25
46	11.35
47	11.4

TABLE VI

Titration of Phenolmalein with 0.1142 N NaOH
(0.2 gram in 100 ml. HOH)

NaOH ml	pH
	2.9
1	2.9
2	3.0
3	3.0
4	3.05
5	3.1
6	3.15
7	3.2
9	3.35
11	3.5
13	3.7
15	3.88
17	4.02
19	4.25
21	4.41
23	4.55
25	4.95
26	5.15
27	5.41
27.2	5.5
27.7	5.72
28	5.98
28.5	7.2
28.55	7.6
28.6	8.6
28.65	9.2
28.7	9.5
28.75	9.7
28.8	10.0
28.9	10.25
29.1	10.4
29.2	10.5
29.3	10.6
29.5	10.75
30	11
30.5	11.15
31.5	11.3
32.5	11.4
33.5	11.5

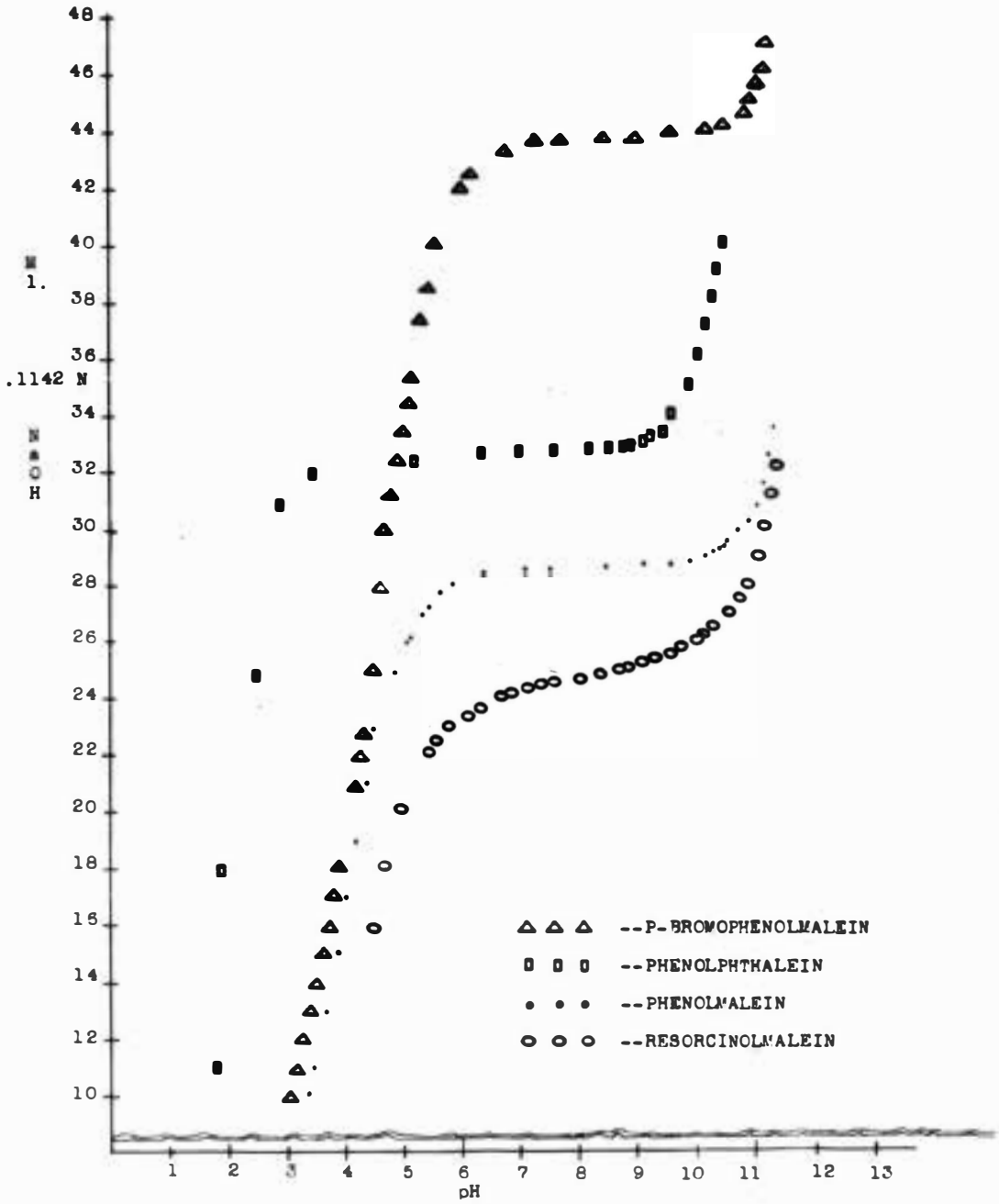
TABLE VII

Titration of Phenolphthalein with 0.1142 N NaOH

(0.2 gram in 100 ml. ethyl alcohol)

NaOH ml	pH
	1.4
1	1.45
2	1.5
4	1.6
11.	1.8
18	2.0
25	2.5
31	3
32	3.5
32.5	5.3
32.55	6.5
32.6	7.1
32.65	7.7
32.7	8.3
32.75	8.6
32.8	8.9
32.85	9.0
33	9.1
33.1	9.3
33.2	9.4
33.3	9.45
33.5	9.55
34	9.75
35	10.00
36	10.15
37	10.3
38	10.4
39	10.5
40	10.6

Graph 3



About 0.02 gram of indicator was placed in the boat which was placed in the combustion tube. The combustion products passed through a series of packings which removed constituents other than carbon and hydrogen. A continuous flow of oxygen and cupric oxide packing assured oxidation of carbon to carbon dioxide and hydrogen to water. The water was collected in a tared tube packed with anhydrone, (magnesium perchlorate) and the carbon dioxide was collected in a tared tube packed with a commercial mixture called ascarite. The tubes were reweighed and the per cent hydrogen and carbon calculated by the following:

$$\text{Per cent Hydrogen} = \frac{\text{Wt. H}_2\text{O} \times .119}{\text{Wt. of sample}} \times 100$$

$$\text{Per cent Carbon} = \frac{\text{Wt. CO}_2 \times .27289}{\text{Wt. of sample}} \times 100$$

The results are found in Table VIII.

Determination of Bromine in p-bromophenolmalein

The Parr Bomb procedure was used to determine bromine in this indicator.

The indicator sample (about 0.1 gram) was fused with potassium nitrate, sodium peroxide and cane sugar to give an ionized halogen which was precipitated and weighed as silver bromide. The per cent bromine was calculated using the following:

$$\text{Per cent Bromine} = \frac{\text{Wt. of AgBr} \times .42555}{\text{Wt. of sample}} \times 100$$

The results are found in Table VIII.

Determination of Molecular Weight

A method originally proposed by Rast and modified by

TABLE VIII
DETERMINATION OF HYDROGEN

WEIGHT HOH GRAMS		WEIGHT (H) GRAMS		WEIGHT SAMPLE GRAMS		% (H)		THEORETICAL % (H)
PHENOLMALEIN								
TRIAL 1.	TRIAL 2.	TRIAL 1.	TRIAL 2.	TRIAL 1.	TRIAL 2.	TRIAL 1.	TRIAL 2.	
.0078	.0077	.000864	.000855	.0194	.0210	4.46	4.07	4.47
RESORCINOLMALEIN								
.0062	.0067	.000688	.000743	.0198	.0213	3.478	3.49	3.99 or 3.62

DETERMINATION OF CARBON

WEIGHT CO ₂ GRAMS		WEIGHT (C) GRAMS		WEIGHT SAMPLE GRAMS		% (C)		THEORETICAL % (C)
PHENOLMALEIN								
TRIAL 1.	TRIAL 2.	TRIAL 1.	TRIAL 2.	TRIAL 1.	TRIAL 2.	TRIAL 1.	TRIAL 2.	
.0499	.0538	.01352	.01462	.0194	.0210	70.19	69.91	71.4
RESORCINOLMALEIN								
.0459	.0487	.0125	.01329	.0198	.0213	63.26	62.39	68.1 or 63.6

DETERMINATION OF BROMINE

WEIGHT AgBr GRAMS		WEIGHT (Br) GRAMS		WEIGHT SAMPLE GRAMS		% (Br)		THEORETICAL % (Br)
P-BROMOPHENOLMALEIN								
TRIAL 1.	TRIAL 2.	TRIAL 1.	TRIAL 2.	TRIAL 1.	TRIAL 2.	TRIAL 1.	TRIAL 2.	
.1412	.2614	.0661	.1109	.1501	.2872	40.05	38.72	37.5 or 39.1

Shriner and Fuson (12) and Kamm (9) was used to determine the molecular weight. This is a method making use of the molal freezing-point lowering of camphor.

The method is as follows: Into a small tared test-tube about one inch long, was placed approximately 20 mg. of the indicator. About 200 mg. of d-camphor was added and the tube was weighed accurately again.

The tube was stoppered with a cork through which a blunt section of a size two knitting needle had been passed and used as a stirrer. The tube was placed in a melting-point bath at 150° C. In less than a minute the mass was melted and mixed, then allowed to cool and solidify quickly.

The mass was removed to a watch glass, mixed again and some of it was placed in a thin-walled melting point tube, and forced into a compact mass about 2 mm. in height by means of a smaller flat-bottomed melting point tube.

The melting-point was determined in the usual manner. The melting-point of the camphor alone was also determined.

Since there was disagreement as to the exact constant, a known was run (phenolphthalein) and the constant appeared to be best represented at the value 39.7. The molecular weight was determined using the following:

$$\text{Molecular Weight} = \frac{39.7 \times w \times 1000}{\Delta \times W}$$

w = weight of compound
 W = weight of camphor
 Δ = depression of melting-point

The results are found in Table IX.

TABLE IX

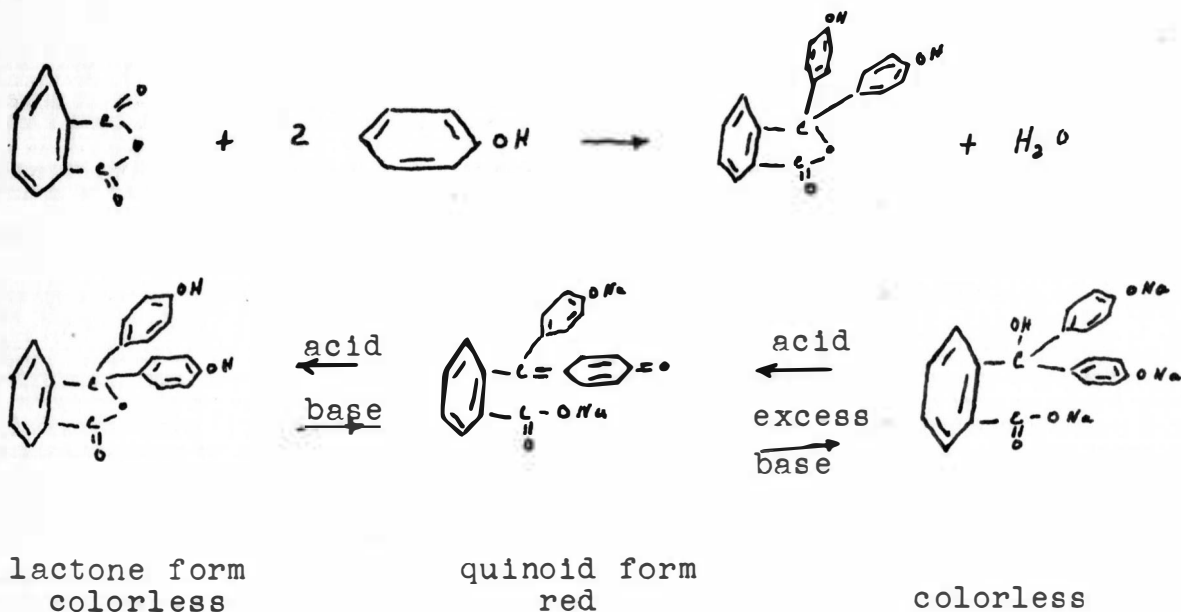
MOLECULAR WEIGHT DETERMINATION

SAMPLE GRAMS	CAMPHOR GRAMS		DEPRESSION OF M. P.		MOLECULAR WEIGHT		MOLECULAR WEIGHT THEORETICAL	
	TRIAL 1.	TRIAL 2.	TRIAL 1.	TRIAL 2.	TRIAL 1.	TRIAL 2.	TRIAL 1.	TRIAL 2.
PHENOLMALEIN .0381	.0678	.8134	.4744	11	21	267.4	270.2	268.7
P-BROMOPHENOLMALEIN .0397	.0473	.2689	.4926	14	9	436.6	426.2	426.07
RESORGINOLMALEIN .0181	.0233	.2614	.2861	9	10.6	306.4	307.6	306.26
PHENOLPHTHALEIN .0495	.0466	.6290	.6373	10	11	310.6	312.3	318.51

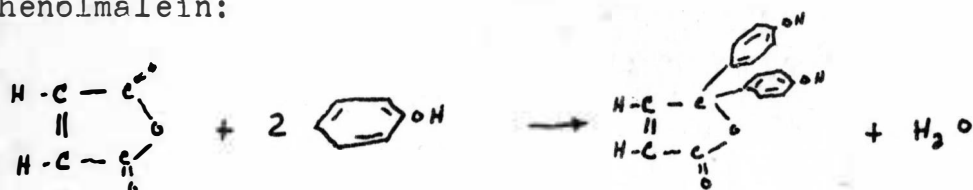
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Discussion of Results

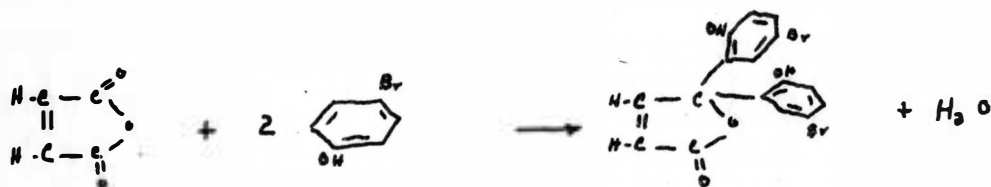
It appeared logical that the condensations of these aliphatic anhydrides with phenols should act similarly to the proposed action of phenolphthalein, a condensation product of phthalic anhydride and phenol, as follows:



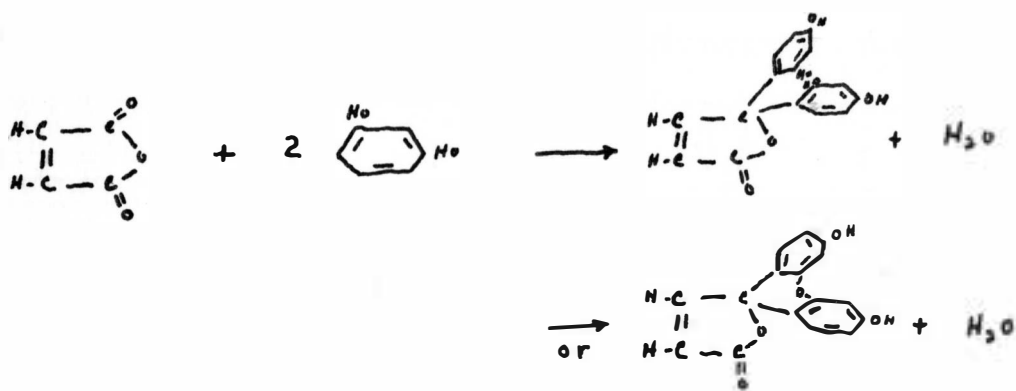
With due consideration of experimental error the analysis of carbon, hydrogen (bromine in p-bromophenolmalein) and molecular weight, gave evidence in favor of the supposition that condensation products of maleic anhydride, with phenol, p-bromophenol and resorcinol, respectively, would give similar compounds, with similar reactions. Thus the structure of the indicators prepared from maleic anhydride should be as follows:
phenolmalein:



p-bromophenolmalein:



resorcinolmalein:



oxygen bridge form

The colorless form in acid medium was not observed except in the case of p-bromophenolmalein. Phenolmalein exhibited the fading property upon addition of excess base. It seemed probable that resorcinolmalein could be in the form with an oxygen bridge similar to fluorescein, which follows:



especially since it exhibited a green fluorescence in alkaline or alcohol solution. The results from analysis gave added evidence in favor of the above structure. Therefore in the case of resorcinolmalein the oxygen bridge structure was indicated.

The use of anhydrous stannic chloride as a catalyst replacing sulfuric acid or hydrated stannic chloride, seemed to be advantageous since it gave increased yields and produced less tarry impurities. If a controlled method of adding this fuming catalyst could be devised it would perhaps shorten the time of condensations.

The greater yield of resorcinolmalein can be attributed to the previously suggested oxygen bridge structure. The yield of phenolmalein and p-bromophenolmalein is fair to good considering the steps by which purity was obtained.

The transition range of resorcinolmalein and phenolmalein are sharp enough to be usable in titrations. It would take more skill to observe the same changes using p-bromophenol-

malein. The titration curves of the indicators compared favorably to a known titration curve as far as amount of base and acid needed to carry it through the useable visible pH range is concerned.

The color shades through which the indicators passed in going through the visible pH range are shown by Plates I, II, and III. The color of the indicator upon addition of excess acid or base is also indicated on Plates I, II and III.

Suggestions for Further Work

The condensation products using other anhydrides than maleic and other phenols than phenol, p-bromophenol and resorcinol, would be of interest to determine how general are the condensation reactions of aliphatic anhydrides with phenols.

Special consideration should be given to condensation reactions of resorcinol and aliphatic anhydrides since investigation thus far seems to indicate products with sharp color changes and good yields with minimum difficulty of purification.

The results using anhydrous stannic chloride as a catalyst seem to merit further use with other condensation reactions.

Summary

1. Three new indicators, phenolmalein, p-bromophenolmalein, resorcinolmalein, have been prepared, purified and analyzed, and the molecular weight determined.
2. A study has been made of the pH range, color changes and titration curves of phenolmalein, p-bromophenolmalein and resorcinolmalein.

Plate I



Plate II



Plate III



3. The use of anhydrous stannic chloride as a catalyst in the condensation reaction of maleic anhydride with phenol, resorcinol and p-bromophenol, gave favorable results.

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