

CONDENSATION OF MALEIC ANHYDRIDE WITH PHENOLS II¹

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The condensation of phenol, p-bromophenol, and resorcinol with maleic anhydride and a study of the pH range, color changes, and titration curves of the products were reported in the first paper in this series (1). References to earlier work in this field may be obtained from this paper. The color change with p-bromophenolmalein reported by Webster and Kamstra (1) was colorless to straw yellow and was not sharp. It seemed of interest, therefore, to continue the investigation using other halogenated phenols to determine whether a difference in position of the halogen might have an effect and whether chlorophenol or iodophenol might differ from bromophenol.

EXPERIMENTAL

p-bromophenolmalein:

The procedure of Webster and Kamstra (1) was repeated using fifteen grams of maleic anhydride, fifty-three grams of p-bromophenol, and twenty grams of anhydrous stannic chloride. The mixture was heated for twelve hours at 130-135° C. The product was added to about 600 ml. of distilled water and steam distilled for one hour. The residue was cooled to room temperature, filtered and the product extracted with ether. The ether was evaporated and the residue was recrystallized from an alcohol-carbon tetrachloride solution. Further purification was accomplished by chromatographic adsorption. The color, melting point, acid-base color change and pH range will be found in Table I. The analysis and molecular weight determination will be found in Table II.

TABLE I
PHYSICAL CONSTANTS OF COMPOUNDS

phenolmalein	color	m.p. °C	color in		pH range
			acid	base	
p-bromo	dark red	blackened at 195-200	at* colorless	red*	5.3-7.2*
p-chloro	light brown	blackened at 240-245	at colorless	yellow	6.4-8.2
o-chloro	violet	blackened at 210-215	at yellow	yellow-orange	4.5-6.5
m-chloro	light orange	blackened at 270-275	at yellow	yellow	-----
o-bromo	bright red	89-90	yellow	red	5.1-6.8
o-iodo	red	96-97	yellow	red	5.3-7.3

*Webster and Kamstra (1) reported the m.p. 188-190° C, straw color in basic solution and the pH range 8.5-10.5.

¹. Taken in part from Master's Degree Thesis of George W. Engstrom, South Dakota State College, 1953.

TABLE II
COMPOSITION AND MOLECULAR WEIGHTS OF COMPOUNDS

phenolmalein	% halogen		molecular calc.	weight found
	calc.	found		
p-bromo	37.51	36.34	426.1	418.0
p-chloro	21.03	19.98	337.2	332.1
o-chloro	21.03	20.68	337.2	336.0
m-chloro	21.03	14.75	337.2	272.8
o-bromo	37.51	36.81	426.1	424.3
o-iodo	48.81	49.68	520.1	528.3

p-chlorophenolmalein:

The mixture of fifteen grams of maleic anhydride, forty grams of p-chlorophenol, and twenty grams of anhydrous stannic chloride was heated to 150-160° C for twelve hours. The product was purified in the same manner as p-bromophenolmalein. The color, melting point, acid-base color change, and pH range will be found in Table I. Analysis and molecular weight determination will be found in Table II.

o-chlorophenolmalein:

The mixture of fifteen grams of maleic anhydride, forty grams of o-chlorophenol, and twenty grams of anhydrous stannic chloride was heated at 145-155° C for twelve hours. The product was purified in the same manner as p-bromophenolmalein. The color, melting point, acid-base color change, and pH range is recorded in Table I. Analysis and molecular weight determination will be found in Table II.

m-chlorophenolmalein:

A mixture of fifteen grams of maleic anhydride, forty grams of m-chlorophenol, and twenty grams of anhydrous stannic chloride was heated at 160-170° C for twelve hours. The product was purified in the same manner as p-bromophenolmalein. The color, melting point, acid-base color change, and pH range is recorded in Table I. Analysis and molecular weight determination is recorded in Table II.

o-bromophenolmalein:

This compound was prepared and purified in the same manner as p-bromophenolmalein. The color, melting point, acid-base color change, and pH range is recorded in Table I. Analysis and molecular weight determination is recorded in Table II.

o-iodophenolmalein:

A mixture of fifteen grams of maleic anhydride, seventy grams of o-iodophenol, and twenty grams of anhydrous stannic chloride was heated

at 110-120° C for twelve hours. The reaction mixture was heated with six hundred milliliters of distilled water at 70-90° C for about fifteen minutes. The mixture was cooled to room temperature, filtered, and extracted with ether. The ether was evaporated; the residue was purified by chromatographic adsorption using an acetone solution and eluted with a ten percent alcohol-water solution. The color, melting point, acid-base color change, and pH range is recorded in Table I. The analysis and molecular weight determination is recorded in Table II.

Determination of the Indicator Range:

The indicator range was determined by the method of Webster and Kamstra (1) except that a Beckman pH meter was used instead of the Macheth meter.

Analysis:

The Parr Bomb procedure (2) was used to determine the percent of halogen in the indicator compounds.

Determination of Molecular Weight:

A method originally proposed by Rost and modified by Shriner and Fuson (3) and Kamm (4) was used to determine the molecular weight. This was a method making use of the molal freezing point lowering of camphor.

DISCUSSION

The preparation of p-bromophenolmalein originally reported by Webster and Kamstra (1) was repeated. The results seem to indicate that a purer product has been obtained.

The para halogenated phenolmaleins were found to give the sharpest end points in acid-base titrations with the ortho derivatives somewhat less sharp. The meta chlorophenolmalein gave no color change but the analysis and molecular weight determination indicates that a pure product was not obtained.

The iodo and bromo derivatives produced brighter colors than the chloro derivatives in acid and basic solutions.

Further work is in progress.

BIBLIOGRAPHY

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4. Kamm, Qualitative Organic Analysis. Second Edition, John Wiley and Sons, Inc., New York, pp. 130-133 (1932).