

Summary

1. A number of new salts of phenolphthalein have been prepared and studied. They are always additive compounds of phenolphthalein and the base. Usually two or more molecules of crystal water are also present.

2. It has been demonstrated that most hydrated salts are colorless and become colored by loss of water. Loss of water can be effected by heat, pressure, friction or certain solvents and such loss of water is probably a dehydration from the carbinol form to the quinoid form. The colors of dehydrated salts, containing either chromogenic or non-chromogenic metals, differ widely.

3. The probable cause of color of phenolphthalein salts is the quinoid chromophore. Hydration and dehydration are important influences effecting changes in color. Isomerization, neutralization, addition, hydrolysis and ionization attend phenolphthalein phenomena, but precede or are incidental to the transforming of colorless carbinol forms to the colored quinoid form.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

THE PREPARATION AND PROPERTIES OF SOME SUBSTITUTED 2-METHYLTHIOPHENES

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In order to identify certain thiophene homologs in pyrolysis products, 2-methyl-5-ethylthiophene, 2-methyl-4-ethylthiophene and 2,3-dimethylthiophene were prepared for comparison. The preparation and properties of these compounds are reported here since these thiophene homologs were either unknown or imperfectly described.

2-Methyl-5-ethylthiophene was obtained in 40% yield by a modified Wolff reduction which consisted of heating the semicarbazide of 2-methyl-5-acetothienone with moist powdered potassium hydroxide. Steinkopf¹ has prepared this substituted thiophene in 10% yield by a Clemmensen reduction of 2-methyl-5-acetothienone, but he obtained insufficient material for determination of its physical properties.

The other two thiophene homologs were synthesized by the action of phosphorus sulfides on the proper substituted levulinic acids. While 2,3-dimethylthiophene has been prepared by Paal and Püschel² and by Grünewald,³ it is noteworthy that our specimen had a boiling point about 3° higher than reported by them. This observation was checked on a purer

¹ W. Steinkopf, *Ann.*, **424**, 22 (1923).

² Paal and Püschel, *Ber.*, **20**, 2559 (1887).

³ Grünewald, *ibid.*, **20**, 2586 (1887).

preparation obtained from 5-chloromercuri-2,3-dimethylthiophene. Table I summarizes the most significant data regarding these compounds.

TABLE I
SUBSTITUTED THIOPHENES

	2-Methyl- 5-ethyl-	2-Methyl- 4-ethyl-	2,3-Dimethyl- (a) From the mercurichloride	(b) from β -methyl- levulinic acid
Corr. boiling range, 760 mm.	159.8–160.4°	162–164°	140.2–141.2°	140.2–142.2°
F. p. range	–68.4 to –68.6°	–59 to –60°	–48.9 to –49.1°	
d_4^{20}	0.9663	0.9742	1.0021	1.0016
d_4^{30}	0.9577	0.9650	0.9919	
n_D^{20}	1.5073	1.5098	1.5192	1.5194
n_D^{30}	1.5024	1.5048	1.5140	
% S calcd.	25.42	25.42		28.59
% S found	25.47, 25.42	25.25, 25.34		28.44, 28.37
Mol. wt. calcd.	126	126		
Mol. wt. found	126, 125	127, 126		
M. R. calcd.	39.4	39.4	34.7	34.7
M. R. obs.	38.9, 38.9	38.7, 38.8	34.0, 34.0	34.0
Indophenin reaction	Red-brown	Green	Green	Green

The freezing points were measured with a toluene thermometer and are reliable to $\pm 1^\circ$. Molecular weights were determined cryoscopically in benzene. The indophenin tests were made by adding a drop of the substituted thiophene to a solution of isatin in sulfuric acid containing a trace of nitric acid, and the color reported is the one which developed after the mixtures had stood for five to fifteen minutes.

Experimental Part

2-Methyl-5-ethylthiophene.—2-Methyl-5-acetothienone semicarbazide was prepared by the method of Steinkopf. It melted at 224.5° (with decompn.); Steinkopf gives 225° . Fifty grams of the finely powdered potassium hydroxide and 35 g. of the semicarbazide were placed in a 500-cc. distilling flask, 5 cc. of water was added and the whole mass was thoroughly mixed. The flask was then heated with a free flame as long as liquid distilled over. The product from three runs was combined, steam distilled once to separate a small amount of yellow solid which accompanied the methylethylthiophene, dried and fractionated over sodium. The yield of pure material having the constants indicated in the table was 40%. This thiophene homolog has a very characteristic and pleasant odor, similar to that of *p*-ethyltoluene.

2-Methyl-4-ethylthiophene.— α -Ethyllevulinic acid was obtained by the procedure of Fittig and Young,⁴ and boiled from 161 – 166° (uncorr.) at 20 mm. Its semicarbazone had m. p. 171 – 172° with slight gas evolution; Gault and Solomon⁵ give 171 – 172° . The acid was converted to the sodium salt, which was dried over phosphorus pentoxide at 100° . The sodium salt was powdered, thoroughly mixed with twice its weight of sand, and the mixture was distilled from a retort heated with a free flame. The resulting distillate was washed with cold sodium hydroxide solution and fractionated over

⁴ Fittig and Young, *Ann.*, **216**, 39 (1883).

⁵ Gault and Solomon, *Ann. chim.*, [10] **2**, 205 (1924).

sodium, which separated a small amount of material boiling below 140°. The purified 2-methyl-4-ethylthiophene was obtained in 20% yield (based on ethyllevulinic acid).

2,3-Dimethylthiophene.— β -Methyllevulinic acid was obtained by the excellent method of Pauly, Gilmour and Will,⁶ and boiled from 130–132° (uncorr.) at 10 mm. On heating 30-g. portions of this acid with 35-g. portions of powdered phosphorus pentasulfide, a vigorous reaction took place and the product was distilled out as soon as the reaction slowed down. The crude product was worked up as before. The purified 2,3-dimethylthiophene was obtained in 20% yield.

As a check on the high boiling point observed, a specimen of 5-chloromercuri-2,3-dimethylthiophene was purified by crystallization until it melted with slight decomposition at 218.5–219.5 (corr.). Steinkopf⁷ gives the melting point of this compound as 213–214° (with decomposition). The 2,3-dimethylthiophene was recovered quantitatively from this mercury compound by heating with hydrochloric acid, and the specimen thus obtained boiled entirely in the range 140.2–141.2° (corr.). The constants of both specimens are given in the table.

Summary

The preparation and physical properties of 2,3-dimethylthiophene, 2-methyl-4-ethylthiophene and 2,5-methylethylthiophene are presented.

⁶ Pauly, Gilmour and Will, *Ann.*, **403**, 145 (1914).

⁷ Steinkopf, *ibid.*, **424**, 46 (1923).

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NATURAL AND SYNTHETIC RUBBER. IX. THE PRODUCTS OF DESTRUCTIVE DISTILLATION OF EBONITE

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Introduction

It has been shown that there is a definite relationship¹ between the rubber molecule and its pyrolysis products, and consequently the thermal decomposition of ebonite has been undertaken to throw light on the nature of the rubber sulfur complex.

It was relatively simple to correlate the pyrolysis products of raw rubber with the formula of the parent molecule, as the rubber formula had been previously established by oxidation. However, the formula of ebonite is still unknown, and cannot be arrived at by ordinary methods, because ebonite is amorphous, insoluble, non-volatile, completely saturated, and inert toward chemical agents. A correlation of its pyrolysis products may thus be the only way of establishing its formula.

The pyrolysis products of ebonite, the decomposition products of a mixture of rubber and sulfur, and the interaction of sulfur and the pyrolysis

¹ Midgley and Henne, *THIS JOURNAL*, **51**, 1215 (1931).