tilled with steam to remove the alcohol and ethyl benzoate, the residue extracted with ether, and the ether-soluble oil distilled in a small Hickman type still. This gave a solid which was recrystallized from carbon tetrachloride. The properties of this and other sulfides are given in Table II. The solubilities are approximate values.

TABLE II

3,5-Dihydroxyphenyl alkyl sulfide	M. p., °C.	Sulfur, % Found	Sulfur, % Calcd.	Sol'y. in H_2O g./100 g. soln., 20°
Methyl	78–78.5	20.48	20.53	0.25
Ethyl	71–72	18.82	18.69	.14
n-Propyl	67–68	16.98	17.31	.08
n-Butyl	66	15.78	16.18	.06
n-Amyl	66	14.97	15.11	.01
n-Hexyl	Oil[a]	13.85	14.17	< .01

[a] All attempts to obtain this as a solid failed. It distilled from a bath kept at 250° at 1 mm. pressure.

The methyl and ethyl sulfides gave a red color with ferric chloride, the *n*-propyl a purple color and the *n*-butyl and *n*-amyl a green color.

Summary

1. Sodium *sym*-benzenetrisulfonate was found to be convertible into 3,5-dihydroxybenzenesulfonate in satisfactory yields but the reported preparation of phloroglucinol has not been confirmed.

2. A series of *n*-alkyl 3,5-dihydroxyphenyl sulfides has been synthesized and the phenol coefficients of these compounds are tabulated.

3. Monothiophloroglucinol has been prepared for the first time.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 5, 1937

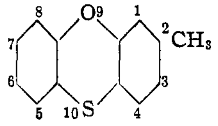
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Phenoxthin. II. Extension of the Ferrario Reaction

BY C. M. SUTER AND FRANK O. GREEN

Earlier[1] work in this Laboratory has shown that under the proper conditions the action of sulfur and aluminum chloride upon phenyl ether gives a good yield[2] of phenoxthin. This reaction which was first reported almost simultaneously by Ferrario[3] and Ackerman[4] for convenience may be referred to as the "Ferrario reaction."

The report of Ackerman[4] that *p*-chloro- and *p*-methylphenyl phenyl ethers are readily converted into the corresponding phenoxthins while *p*-bromophenyl phenyl ether and di-(*p*-bromophenyl) ether give only tarry products[1] made desirable an investigation of the behavior of other substituted aryl ethers toward sulfur and aluminum chloride. It has been found that the isomeric phenyl tolyl ethers and phenyl chlorophenyl ethers all give the corresponding phenoxthin derivatives in fair yields. With the chloro ethers the reaction is complete in about thirty minutes at 100° while the tolyl ethers require several hours. Long heating of the reaction mixtures containing the chloro ethers leads to decomposition with evolution of hydrogen chloride. The yield of the phenoxthin is higher when the directive influences of the ether oxygen and the methyl or chloro group coincide, *i. e.*, in the meta substituted ethers. It is assumed for the present that this reaction yields 2-substituted phenoxthins as in I rather than the 4-isomers (II) which are possible but not probable.



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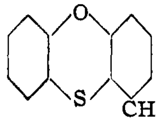

II

Additional attempts to convert 4-bromophenyl phenyl ether into the bromophenoxthin were unsuccessful. Reaction with sulfur and aluminum chloride is violent at 100° but the product was a mixture with an indefinite melting point from which no pure compound was isolated.

o-Methoxyphenyl phenyl ether gave no evidence of undergoing the Ferrario reaction at 100°. It is probable that the *m*-methoxy compound would react satisfactorily but this was not investigated. 3-Phenoxyphenoxthin was found to evolve hydrogen sulfide slowly when heated at 40° with sulfur and aluminum chloride. At higher temperatures decomposition set in with evolution of hydrogen chloride. No "diphenoxthin" was isolated.

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(1) Suter, McKenzie and Maxwell, THIS JOURNAL, **58**, 717 (1936).

(2) A slight modification of the directions given in ref. 1 improves the yield. By fractionating the reaction mixture containing unchanged phenyl ether and phenoxthin at 4 mm. through a 50-cm. punched-in lagged column 87% yields of crude material are obtained consistently. The approximate boiling point of phenoxthin at atmospheric pressure given in ref. 1 is low. Pure phenoxthin distils at 311° (745 mm., corr.) with slight decomposition.

(3) Ferrario, *Bull. soc. chim.*, **9**, 536 (1911).

(4) Ackerman, German Patent 234,743, *Frdl.*, **10**, 153 (1913).

A preliminary investigation of the chlorination of phenoxthin gave unexpected results. From the monochlorinated fraction, b. p. 212° (28 mm.), was isolated a compound m. p. 81–82° (sulfone m. p. 178–179°) which is not identical with any one of the three chlorophenoxthins made by the Ferrario reaction and hence is presumably 4-chlorophenoxthin. None of the expected 3-chloro compound has so far been separated from the chlorination products. This anomalous[1] substitution will be investigated further and reported in detail later.

The colors produced when the various substituted phenoxthins are dissolved in concentrated sulfuric acid have been noted. The 1-chloro- and 1-methylphenoxthins give a purple color not visually distinguishable from that produced by phenoxthin while the two other methyl and the three other chloro compounds give a blue color.

Experimental

Aryl Ethers.—The tolyl phenyl ethers were obtained in 50–70% yields by heating the potassium cresoxides with bromo or iodobenzene at 160–190° for about six hours in the presence of 0.2 g. of copper powder according to the procedure of Ryan and Drumm.[5] These compounds have already been reported in the literature.[6] The products used in the phenoxthin preparations had the following properties: *o*-tolyl, b. p. 123–124° (9 mm.), d^{25}_{25} 1.049, n^{25}_{D} 1.5710; *m*-tolyl, b. p. 154–155° (25 mm.), d^{25}_{25} 1.051, n^{25}_{D} 1.5711; *p*-tolyl, b. p. 125–126° (9 mm.), d^{25}_{25} 1.049, n^{25}_{D} 1.5701.

The chlorophenyl phenyl ethers have not been prepared in a pure state previously. Mailhe and Murat[7] chlorinated phenyl ether and obtained a mixture of isomers. Various attempts to separate a pure compound from this mixture have been unsuccessful.[8] *o*-Chlorophenyl phenyl ether was obtained in 40% yield from *o*-iodochlorobenzene and potassium phenoxide in the presence of copper by heating at 160–180° for four hours. Heating potassium *o*-chlorophenoxide with bromobenzene at 170° gave chiefly diphenylene dioxide instead of the ether. *m*-Chlorophenyl phenyl ether was obtained in exactly the same way as the ortho isomer. *p*-Chlorophenyl phenyl ether was prepared in 55% yield by heating potassium phenoxide and *p*-bromochlorobenzene at 170–175° for four hours. A 7% yield of *p*-diphenoxybenzene,[6] m. p. 74°, was also isolated. The properties of the chlorophenyl ethers are listed in Table I.

TABLE I

Chorophenyl phenyl ethers	d^{25}_{25}	B. p., °C.	Mm.	n^{25}_{D}	Anal. Cl, % Calcd.	Found
o-Chloro	...	152–153 (m. p. 39–40)	15	....	17.34	17.51
m-Chloro	1.192	168–169	30	1.5867	17.34	17.06
p-Chloro	1.193	161–162	19	1.5865	17.34	17.75

Chloro and Methyl Phenoxthins.—Conversion of the substituted ethers into the corresponding phenoxthins was effected by mixing the reactants in the ratio of 1.3 moles of the ether, 1 mole of sulfur and 0.5 mole of anhydrous aluminum chloride in a round-bottomed flask equipped with an air condenser and heating on the steam-bath for the time shown in Table II. The mixture was poured into water and after hydrolysis was complete the water layer was decanted, the oil dissolved in ether and the solution dried with calcium chloride. Fractionation of the residue after removal of the solvent readily separated the unchanged diaryl ether from the phenoxthin. The 1-methyl and 1-chlorophenoxthins are oils at room temperature while the other compounds are solids. The results are summarized in Table II.

TABLE II

Phenoxthin derivatives	Reaction time at 100°, hrs.	Yield, %	M. p., °C.	Anal. S, % Calcd.	Found
1-Methyl	4	46	Oil,[a] b. p. 186–187 (14 mm.)	14.97	14.87
2-Methyl	4.25	77	83–84	14.97	14.61
3-Methyl	7.5	49	38–39	14.97	14.89
1-Chloro	0.5	50	Oil,[b] b. p. 192–193 (7 mm.)	13.66	13.80
2-Chloro	.6	71	59–60	13.66	13.49
3-Chloro	.6	65	88–89	13.66	13.71

[a] d^{25}_{25} 1.213, n^{25}_{D} 1.6403. [b] d^{25}_{25} 1.401, n^{25}_{D} 1.6618.

3-Phenoxyphenoxthin.—To 19 g. (0.2 mole) of phenol was added 7 g. (0.12 mole) of potassium hydroxide and the mixture distilled until all the water was removed. The excess phenol was returned to the flask, 28 g. (0.1 mole) of 3-bromophenoxthin and a trace of copper powder were added and the mixture heated in an oil-bath at 185–195° for eight hours. The mixture was then cooled and washed with water and the oily layer dissolved in ether, dried and fractionated. After removing a little phenol and bromophenoxthin, the product distilled at 230–235° (7 mm.). The yield was 17 g. or 58% of the theoretical amount. After crystallization from ethyl alcohol the melting point was 81–82°.

Anal. Calcd. for $C_{18}H_{12}O_2S$: S, 10.97. Found: S, 11.18.

Phenoxthin Dioxides.—All of the phenoxthin derivatives prepared were converted into the corresponding sulfones by oxidation with excess hydrogen peroxide in glacial acetic acid on the steam-bath. The time of heating was thirty

TABLE III

Phenoxthin-10-dioxide	M. p., °C.	Anal. S, % Calcd.	Found
1-Methyl	141–142	13.02	13.16
2-Methyl	138–139	13.02	13.12
3-Methyl	134–135	13.02	13.32
1-Chloro	148–149	12.02	12.00
2-Chloro	152–153	12.02	11.60
3-Chloro	158–159	12.02	11.86
3-Phenoxy	112–113	9.89	10.03

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[5] Ryan and Drumm, *Sci. Proc. Roy. Dublin Soc.*, **19**, 461 (1930).

[6] Ullmann and Sponagel, *Ann.*, **350**, 83 (1906).

[7] Mailhe and Murat, *Compt. rend.*, **154**, 601 (1912).

[8] Smith and McKenzie, This Laboratory, unpublished results.

minutes except for the 3-phenoxyphenoxthin where it was five hours. The melting points and analyses of these sulfones are given in Table III. A check on the completion of the oxidation was made in each case by treating a small portion of the product with concentrated sulfuric acid. The sulfones give no color while the phenoxthins and the sulfoxides give colored solutions.

Summary

1. It has been shown that the three methyl and the three chloro derivatives of diphenyl ether are converted into phenoxthins by heating with sulfur and aluminum chloride. The properties of these compounds and the corresponding sulfones are listed.

2. Preliminary examination of the chlorination products of phenoxthin indicates that substitution occurs to some extent ortho to sulfur.

EVANSTON, ILLINOIS RECEIVED OCTOBER 8, 1937

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Chemiluminescence of Phthalhydrazide Derivatives[1]

BY CARL N. ZELLNER AND GREGG DOUGHERTY

The brilliant chemiluminescence of 3-aminophthalhydrazide was first investigated by Albrecht,[2] who found that various oxidizing agents, such as ferricyanide and hypochlorite, in alkaline solution, were effective in bringing about light emission. During the course of the present work, Huntress[3] has described a convenient method of preparing 3-aminophthalhydrazide, and methods of demonstration of the chemiluminescence. The reader may refer to these articles for references to previous work on other oxidation reactions accompanied by chemiluminescence.

In the present work, the relative chemiluminescence of a number of phthalhydrazide derivatives was measured by means of a photronic cell and galvanometer, and effects of structure on the intensity of the light emitted upon oxidation were noted. Measurements were made on the rate of oxidation of derivatives with different groups substituted in the benzene ring, and in the hydrazide ring. Also, the effect of hydroxyl ion and of inhibitors on the rate was noted.

Measurement of the Relative Chemiluminescence.—The apparatus consisted of a Weston photronic cell, a sensitive high-resistance galvanometer (Leeds and Northrup, internal resistance 896 ohms, and sensitivity of 128.35 mm. per microvolt) and a resistance connected in series. The reaction tube was directly in front of the photronic cell, and both were enclosed in a box, the inside walls of which were white. In the reaction tube was a stirrer, driven at constant rate. Table I shows the relative chemiluminescence of some phthalhydrazide derivatives in terms of cm. displacement of the beam, the scale being 1 meter from the galvanometer. Measurements were carried out at two different concentrations, namely, 0.001 and 0.004 molar solutions of phthalhydrazide, in 0.25% sodium hydroxide solution (20 cc.), to which 2 cc. of 0.2 N sodium hypochlorite was run in. The brilliant luminescence of 3-aminophthalhydrazide itself could only be measured by using 700,000 ohms resistance, connected in series. The displacement of the galvanometer beam was then 22 cm. for an 0.004 M solution in 0.25% sodium hydroxide solution. No resistance was used in the measurement of the compounds shown in the following table.

TABLE I

RELATIVE CHEMILUMINESCENCES OF SOME PHTHALHYDRAZIDE DERIVATIVES

Phthalhydrazide derivative	Cm. disp. 0.001 M	Cm. disp. 0.004 M
3-Series		
3-Hydroxy[a]	38.0	65.0
3-Acetamido	28.0	31.5
3-Acetamidoacetyl	11.5	26.5
3-Chloro[a]	4.0	3.5
3-Benzamidodiacetyl	0.8	1.1
α-3-Acetamido-N-methyl	.0	0.4
4-Series		
4-Acetamido	9.0	11.0
4-Acetamidoacetyl	8.5	10.0
4-Benzamidodiacetyl	0.2	0.2
α-4-Acetamido-N-methyl	.0	.2

[a] Not analytically pure.

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[1] From a thesis submitted by C. N. Zellner in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Princeton University, September, 1934. Original manuscript received March 13, 1937.

[2] Albrecht, Dissertation, Kaiser Wilhelm-Institut, 1928; *Z. physik. Chem.*, **136**, 321 (1928).

[3] Huntress, THIS JOURNAL, **56**, 241 (1934); *J. Chem. Ed.*, **11**, 142 (1934).