synthetically by a method analogous to that used by Borsche in the preparation of β-benzoyl-propionic acid.[1] One part anisole was added to 1 part succinic anhydride and 1.5 parts $AlCl_3$ suspended in 4 parts carbon disulfide. The mixture was heated on a water bath until hydrogen chloride was no longer evolved. The dark red semisolid addition product was decomposed with ice, when a white, insoluble product was obtained. The crude product was dried, and was finally purified by preparing ethyl-β-anisoyl propionate, recrystallizing it, and from it, regenerating the acid. This was then further purified by recrystallizing from acetone, from which it separated in large hexagonal prisms, m. p. 147°.

0.1354 and 0.1318 g. subs. gave 0.3141, 0.3058 g. CO_2; and 0.0623, 0.0614 g. H_2O; (recrys.) 0.1344 g. gave 0.3136 g. CO_2 and 0.0663 g. H_2O.

Calc. for $C_{11}H_{12}O_4$: C, 63.4%; H, 5.7%. Found: C, 63.2, 63.2, 63.6; H, 5.1, 5.1, 5.4.

The acid is sparingly soluble in most organic solvents, one part dissolving in 54 parts acetone, 48 parts ether, 36 parts ethyl acetate and 30 parts methyl alcohol. It is soluble in hot water, 15 parts of substance dissolving in 800 parts of solvent, from which about 90% crystallizes on cooling. Its solutions in methyl and ethyl alcohol, when saturated with hydrogen chloride, gave the corresponding esters. These melted at 47° and 52°, respectively. Both are very soluble in alcohol and ether, but may be readily purified by recrystallization from their respective alcohols, from which they crystallize in large colorless crystals. The acid contains hydrogen that is exceedingly sensitive to oxidizing agents, and its sodium salt reduces permanganate solution instantly in the cold. The products of this oxidation were anisic acid, and another acid product which was not fully studied. It was very soluble in water, from which, however, it was readily extracted by ether. The dried ethereal solution on evaporation deposited the acid in the form of large, glistening, white plates, but the substance was so extremely sensitive that its solution in ligroin decomposed with the deposition of carbon when evaporated on the water bath.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF SOUTH DAKOTA.]

THE MONONITRO PHENYL ETHERS.

BY HILTON IRA JONES AND ALFRED N. COOK.

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In 1873 Maikopar[2] made a dinitrophenyl ether by heating dinitrochlorobenzene, caustic potash and phenol in alcoholic solution. These substances react according to the following equation:

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[1] *Ber.*, **47**, 1110 (1914).

[2] *Ibid.*, **6**, 564 (1873).

$$(NO_2)_2C_6H_3Cl + KOH + HOC_6H_5 = (NO_2)_2C_6H_3OC_6H_5 + KCl + H_2O$$

Maikopar seems to have been the first chemist to use this general method, which has been brought into prominence by the work of Willgerodt, Haeussermann, Ullmann and Cook.

The presence of the negative nitro group makes it much easier to manufacture the nitrophenyl ethers than the corresponding non-nitro compounds. An increasing number of negative groups seems to enhance this effect. Thus picryl chloride and potassium phenolate give a much better yield than the phenolate with either *o*- or *p*-bromonitro benzene. The position of the nitro group in reference to the halogen also has a marked effect both on the stability of the substance and the yield as well as the ease of production. Thus, following the usual rule, a *m*-bromonitro benzene will scarcely react with potassium phenolate at all unless a catalytic agent be present, and the ortho compound reacts more easily than the para, the reaction going to completeness on the boiling water bath in case of the ortho compound, while it requires a temperature of 135 to 140° for the para. The yield of ether produced is greater in case of the ortho, though if it is freed from the other reaction products by distillation, it is liable to be less because of its greater instability and consequent decomposition at a higher temperature. Performed in this way we have obtained from the para compound 81% of the theoretical yield of ether, and from the ortho compound 67%. But if, instead of separating by distillation, the reaction compound is extracted with ether, sulfonated and converted into the potassium salt, the yield in case of the ortho compound was 85% of the theory, while the yield in case of the para compound was 82%. The para compound reduces much more easily than the ortho. It is sometimes very difficult to isolate these in pure form. These amino compounds in turn may be diazotized and converted into a large number of dyes, or the amino ethers may be coupled with other diazonium compounds with similar results. The ortho amino and diazonium compounds are much more unstable than the corresponding para compounds. The ortho aminophenyl ethers yield the more brilliant shades as well as the widest variety of colors. The shades of the sulfonated dyes seem somewhat less brilliant than the unsulfonated. The ortho nitrophenyl ethers are readily converted into the sulfonic acids by treatment with concentrated sulfuric acid in the cold. The para compounds sulfonate with greater difficulty, treatment with sulfuric acid on the boiling water bath being necessary. The para compounds are uniformly better crystalline than the ortho, less soluble and without exception melt and distil at higher temperatures. The *p*-nitrophenyl ether is beautifully crystalline and readily sublimes, while all efforts to reduce the *o*-nitrophenyl ether to a crystalline state by cooling far below zero have failed.

Experimental Part.

TABLE I.

General Outline.

I. The Unsulfonated Dyes.

Aminophenyl ether

$\uparrow$ NH_4OH

Amino hydrochloride $\xrightarrow[HCl]{NaNO_2}$ diazo Cl

+ *m*-Phenylenediamine
+ *o*-Nitraniline
+ *o*-Phenylenediamine
+ Benzidine
+ *o*-Toluenediamine
+ Dimethylaniline
+ β-Naphthylamine γ-disulfonic acid
+ β-Naphthol disulfonic acid
+ γ-Amidonaphthol sulfonic acid
+ α-Naphthylamine hydrochloride
+ α-Naphthol
+ β-Naphthol
+ Hydroquinone
+ *p*-Amidophenol
+ Phenol
+ Resorcin
+ Pyrocatechin
+ Salicylic acid

$\uparrow$ Sn + HCl (ppt. H_2S)

Ether $\rightarrow$ sulfonated ether —

+ $PbCO_3$ = Pb-sulfonate
+ $SrCO_3$ = Sr-sulfonate
+ $CaCO_3$ = Ca-sulfonate
+ $BaCO_3$ = Ba-sulfonate
+ $CuCO_3$ = Cu-sulfonate
+ Na_2CO_3 = Na-sulfonate
+ K_2CO_3 = K-sulfonate

Ba-sulfonate

+ Na_2SO_4 = Na-sulfonate
+ $CdSO_4$ = Cd-sulfonate
+ $AgSO_4$ = Ag-sulfonate

General Outline.

II. The Sulfonated Dyes.

Nitrophenyl ether
Potassium sulfonate

$\downarrow$ Sn + HCl (ppt. H_2S)

Aminophenyl ether
Potassium sulfonate $\xrightarrow[HCl]{NaNO_2}$ diazo chloride

+ *m*-Phenylenediamine
+ *o*-Nitraniline
+ *o*-Phenylenediamine
+ Benzidine
+ *o*-Toluenediamine
+ Dimethylaniline
+ β-Naphthylamine γ-disulfonic acid
+ β-Naphthol disulfonic acid
+ γ-Amidonaphthol sulfonic acid
+ α-Naphthylamine hydrochloride
+ α-Naphthol
+ β-Naphthol
+ Hydroquinone
+ *p*-Amidophenol
+ Phenol
+ Resorcin
+ Pyrocatechin
+ Salicylic acid

Potassium Phenolate.—In the earlier experiments of Maikopar[1] and Willgerodt,[2] an alcoholic solution of potassium hydroxide and phenol was employed. In one of his experiments he also used carbon bisulfide as a solvent. Haeussermann and Teichmann[3] were the first to use potassium phenolate with phenol as a menstruum. They made the potassium phenolate by treating phenol with metallic potassium in an atmosphere of hydrogen. For use in preparing various phenyl ethers, Cook[4] made potassium phenolate by dissolving both phenol and alkali in a small amount of water, evaporating to dryness on a water bath and heating to 100° in an air bath. In later experiments he made the potassium phenolate without the use of any water and showed[5] that better yields are obtained by using the phenolate made with KOH and phenol. Our recent work confirms this conclusion. We have found the most convenient way of preparing potassium phenolate is to take 50 g. of phenol and 35 g. of potassium hydroxide, purified by alcohol, and melt each separately with the smallest possible amount of heat. The molten hydroxide is then poured with active stirring into the molten phenol and the product heated on a low flame with constant stirring until it just begins to form a hard ball on the rod. It is removed and placed in a flask and tightly corked. It is best to powder it while hot. This method gives a snow-white product free from the objectionable charring which usually occurs. This method is applicable to the preparation of various phenolates except when they contain one or more nitro groups, in which case they ignite spontaneously.

o-**Nitrophenyl Ether.**—13.2 grams of potassium phenolate prepared as above are mixed with 20.2 g. of powdered *o*-bromonitro benzene, being one-tenth gram molecule of each, heated for two hours on a boiling water bath until the reaction compound is of a homogeneous reddish brown color and granular appearance. All the earlier workers in making the phenyl ethers by this method thought it necessary to use some substance as a menstruum—alcohol, carbon bisulfide or phenol. We now know that the use of any menstruum is in some cases unnecessary and in others harmful. The reaction product is not extracted with ether as was done by the early experiments, but distilled directly *in vacuo*. On redistillation the pure *o*-nitrophenyl ether is obtained, boiling at 195 to 197° under 45 mm. pressure[6] with partial decomposition. It boils without decomposition at 13 mm. pressure. A sample was seven times distilled and reduced to a temperature of —80° with solid carbon dioxide and ether. Under these

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[1] *Ber.*, **6**, 564 (1873).

[2] *Ibid.*, **12**, 762 and 1277 (1879); **13**, 887 (1880).

[3] *Ibid.*, **29**, 1446 and 2083 (1896); **30**, 738 (1897).

[4] *Am. Chem. J.*, **24**, 525 (1902).

[5] THIS JOURNAL, **25**, 60 (1903).

[6] Haeussermann and Teichmann give the boiling point as 205° at 45 mm. and Ullmann 185° at 55 mm.

conditions the liquid became very viscous, but showed no signs of crystallization. Ortho nitrophenyl ether has a pleasing, characteristic, ethereal odor. It is very soluble in alcohol, ether, benzene, xylene, toluene, carbon bisulfide and chloroform. It is but slightly soluble in ligroin and entirely insoluble in water. Its specific gravity at 21.5° is 1.2539. The ether shows the peculiar property of not wetting glass, but draws away from it like water from a glass that is oily. The surface tension was found to be 0.6225, as compared with water, and 44.882, absolute. The viscosity was 13.17, as compared with water, and 6.664, absolute. both being determined at 25°. The refractive index[1] at 20° is 1.575. The ether when freshly distilled is a golden yellow color, but shows signs of darkening on long standing.

The Free Sulfonic Acid, ($NO_2C_6H_4OC_6H_4SO_3H$).—The free sulfonic acid of *o*-nitrophenyl ether was prepared from the corresponding cadmium sulfonate (*q. v.*) by dissolving this salt in hot water, precipitating the cadmium with hydrogen sulfide and removing the water from the solution by distillation *in vacuo*. When the solution had been reduced to very small volume it was removed and placed in an evaporating dish in a vacuum desiccator over sulfuric acid. After a few hours the free sulfonic acid crystallized out in glistening white flakelets which grouped themselves together in radial systems resembling hoar frost. These crystals on exposure to the air soon liquefied, and if exposed to the light, lose their luster and darken. The crystals melt at 90° with decomposition. When a water solution of the acid is added to a soda solution, a brisk effervescence results. The free acid is unstable, very hygroscopic and extremely soluble. An analysis was not attempted because of this hygroscopic character.

The Sulfonic Acid Salts.—The sulfonic acid salts of *o*-nitrophenyl ether were prepared in two ways. First, the ether was sulfonated by treating with three volumes of concentrated sulfuric acid. This was warmed for thirty minutes on a water bath. The ether turns red during this process and complete solution takes place. As soon as the ether is completely sulfonated the reaction product is poured into a large excess of water. The whole is heated to boiling and completely neutralized with the carbonate of the metal whose salt is sought. The solution was filtered boiling hot and evaporated to crystallization. In a few cases the slight solubility of the salt has made it necessary to treat the solid residue once more with boiling water. The second method of making the salts is to treat the barium sulfonate with equal molecules of the sulfate of the metal whose salt is sought and evaporating to crystallization after filtering.

Nine salts have been prepared by these methods. In every case the

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[1] Determined by Professor A. L. Haines.

salts have crystallized in radial systems when pure. In many cases the salts at first have crystallized in thin plates and arranged themselves in the radial form only after repeated crystallization. The solubilities of the salts show wide variation, but appear to follow certain regularities, depending upon their position in the periodic system. The analysis of the salts for the metal gives in every case results which are slightly too high. The results for nitrogen seem to be uniformly too low. If this is actually caused by occlusion, it seems strange that repeated crystallization does not change the percentage. The following tabulation shows how the salts were prepared, their crystal form, solubility and analysis:

TABLE II.

Name of salt.	Method of preparation.	Nature of crystals.	Solubility in 100 cc. at 20° C.	Analysis.	
				Found.	Theory.
Barium	Carbonate on sulfonic acid	Thin glistening plates	0.51	Ba 19.01	Ba 18.95
Strontium	Carbonate on sulfonic acid	Friable warts	2.46	Sr 12.38	Sr 12.30
Calcium	Carbonate on sulfonic acid	Shiny scales	10.578	Ca 6.51	Ca 6.37
Sodium	Both methods were used	Glistening white granules	9.872	N_2 4.14	N_2 4.40
Potassium	Both methods were used	Radial aggregations of thin plates	4.02	K 11.80	K 11.73
Copper	Decomposition of the barium salt	Warty masses of thin scales	44.48	Cu 9.85	Cu 9.74
Cadmium	Decomposition of the barium salt	Large thin glistening plates	3.64	N_2 1.98	N_2 1.91
Silver	Decomposition of the barium salt	Thin plates which darken in the light very quickly	1.44	...	Ag 25.65
Lead	Both methods were used	Hard, brownish warts	8.20	...	N_2 1.69

All the salts were heated in an air bath first to 108° and then to 125° in an attempt to determine whether the salts contained water of crystallization or not. In only two cases did the loss seem to correspond to definite amounts of water of crystallization. The barium salt contained water equivalent to one-half molecule, and the copper salt an amount equalling exactly two molecules of water. The potassium salt lost no water at all on heating. The copper and the silver salts are both difficult to isolate in pure form, the former because of its extreme solubility, which made final evaporation in a vacuum desiccator necessary, and the latter because of its unusual sensitiveness to light. It was finally prepared in the dark by removing the water *in vacuo*. When so prepared it is of glistening whiteness, but it darkens somewhat even when kept in a deep red bottle. The crystals are slippery to the touch, somewhat like boric acid. The copper, silver, cadmium and lead salts are readily darkened by traces of hydrogen sulfide in the air, the lead salt being unusually sensitive. Practically every one of the salts darkens on exposure to the light and air, the sodium and potassium salts being the least affected.

o-Nitrophenyl Ether Sulfonyl Chloride.—The sulfonyl chloride of nitrophenyl ether was prepared by taking 2 g. of ortho nitrophenyl ether sodium sulfonate, powdering, and thoroughly mixing in a mortar with 4 g. of powdered phosphorus pentachloride. As no action took place at once, it was heated on a steam bath for some minutes when the color became darker and the whole assumed a waxy appearance. The reaction product was then added to ice water in a flask and shaken for some minutes, when the oil that first separated crystallized out. The sulfonyl chloride was separated from the water by filtration with suction. It was in the form of round granules. These are insoluble in water, but soluble in hot alcohol from which they crystallized on standing into beautiful, needle-like, white crystals.

o-Aminophenyl Ether Hydrochloride.—It is not easy to reduce ortho nitrophenyl ether to the corresponding amino compound by the ordinary methods, although if the alcoholic solution is boiled with tin and hydrochloric acid for eight hours, using a reflux, the reduction may be brought about. Complete reduction is determined by complete solution. As soon, therefore, as a few drops of the solution when removed and added to a large volume of water failed to leave behind an insoluble oil, the action was judged to be complete. The ether is best reduced, however, by the stannous chloride method first suggested by Ullmann.[1] By evaporating the menstruum long needle crystals of the tin salt separate out. These are dissolved in water which is slightly acid with hydrochloric acid and the tin completely removed by means of hydrogen sulfide. The filtrate must not be heated in contact with the air for the compound is easily oxidized. The water is therefore distilled off to small volume *in vacuo*. The crystals separate in large scales melting with decomposition at 154°. The free base may be liberated from the hydrochloride by treatment with ammonia. The crude oily mass left when the ether is evaporated is crystallized from xylene, giving crystals that decompose at 43 to 45° and darken on standing.

The Unsulfonated Diazo Dyes.—In the preparation of these dyes, the solution of the ortho amino hydrochloride was prepared by boiling the ether with stannous chloride for an hour, or all night with tin and hydrochloride acid as has already been described. After the solution has been de-tinned by hydrogen sulfide, filtered and boiled for some time to remove all traces of the gas, the solution has a distinct and characteristic

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[1] *Ber.*, **29**, 1878 (1896).

odor resembling that of garlic. A weighed amount of ether having been taken, the solution was made up of such strength that each cubic centimeter contains one-tenth gram of the amino hydrochloride. In like manner the solution of the compound with which the diazotized body is coupled was made of known strength. In this way it was easy to mix correct molecular proportions by measuring the volumes. The *o*-aminophenyl ether hydrochloride solution was cooled with ice to 5° and diazotized with a cold solution of sodium nitrite. Upon evaporation the diazonium salt crystallizes for the most part in round, crystalline balls of reddish brown color. The crystals burn readily but do not explode when heated. Solutions containing equal molecules of the diazotized salt of *o*-aminophenyl ether and the substance to be coupled with it are mixed in the cold and boiled. The dyeing was done upon white nuns-veiling which had been mordanted with dilute tartar emetic solution. The dry dye was obtained in each case and crystallized from alcohol. Most of the dyes decompose when a melting point is attempted. While few of the dyes possess shades which might render them of commercial value in spite of the high cost, the opportunity for comparisons of shade which the preparation of the sulfonated and unsulfonated dyes of both the ortho and para series offers, makes their preparation and study of value. The value of this comparison is increased by the fact that the dye solution in every case is of exactly the same concentration, so that shades are strictly comparable. The abbreviations used in the following table are those employed in the Milton Bradley Color Standard supplied with Mulliken's "Identification of Pure Organic Compounds." It is impossible to give an accurate idea of the exact tone of the color without the dyed samples for comparison, and yet this Color Standard makes at least an approach to this possible. All the dyes of this series have been tested thoroughly for light and wash-fastness and in no case has one of them faded.

The *o*-Aminophenyl Ether Dyes—Sulfonated Series.—In the preparation of these dyes *o*-nitrophenyl ether potassium sulfonate was reduced with tin and hydrochloric acid. It is noticed that the introduction of the sulfonic acid radical makes the reduction of the nitro group much easier. The reduction is accomplished in this case within a half hour by using tin and hydrochloric acid and heating over a water bath. It is not possible, however, to determine the point of complete reduction in this case so easily as with the unsulfonated ether because the compounds before and after the reduction are both soluble. When reduction is complete, which is best told by a change of color, the solution is de-tinned and diazotized. The diazotized solution was then coupled with the same eighteen reagents as before and a new series of sulfonated phenyl ether dyes obtained. The shades of the dye on wool as well as those of the dry dyes are shown in Table III. The dye obtained in this case with

TABLE III.

Name.	Diazotized *o*-Aminophenyl Ether Hydrochloride Coupled with:			The Potassium Sulfonate of Diazotized *o*-Aminophenyl Ether Hydrochloride Coupled with:		
	Color on wool.	Color on dry dye.	Remarks.	Color on wool.	Color on dry dye.	Remarks.
m-Phenylene diamine	R-ORS_2	RS_2	A fine color resembling Bismark brown	ORS_2	RS_2	A brilliant tango brown
o-Nitraniline	Y-OY	OS_2	A fast lemon shade	OY	YOT_2	An intense orange-yellow
o-Phenylene diamine	YOS_1	Black		OYT_1	RS_2	
Benzidine	OYS_2	Black		YT_2	YO light	
o-Toluene diamine	YO medium	Black		OYT_2	ORT_2	
Dimethyl aniline hydrochloride	OY	YOS_1	An intense, brilliant yellow	VS_1 neut. or alkaline OT_1 acid	VS_2	The neutral or alkaline dye is an intense and permanent bluish purple
β-Naphthyl amine *γ*-disulfonic acid	YO	Black		O-YOT_1	Y light	
β-Naphthol disulfonic acid	RO	Black	A tango red	YOT_2	YOT_1	
γ-Amido naphthol sulfonic acid	OR	VRS_2		OR-ROT_1	ORT_2	A soft old rose shade
α-Naphthyl amine hydrochloride	ORS_1	RVS_2		ORS_1	VRT_2	
α-Naphthol	ROS_1	BGS_2		OR-RO	Y light	
β-Naphthol	RO-OT_1	Black		OT_1	Black	
Hydroquinone	OYT_2	Black		OYT_2	YO dark	
p-Amido phenol	R-ORS_2	Black		OS_2	Black	
Phenol	OYT_2	Black		OYT_2	OYT_1	
Resorcin	OS_1	ROS_2	A tango yellow	Y	Black	A very pure yellow
Pyrocatechin	OYS_1	VRS_2		YT_2	GBS_2	
Salicylic acid	YO-OYT_2	YOS_2		White	R dark	

dimethyl aniline hydrochloride is an unusually pleasing and brilliant bluish purple.

p-**Nitrophenyl Ether.**—This compound was first made in 1896 by Haeussermann and Teichmann[1] by heating *p*-chloronitro benzene with potassium phenolate dissolved in phenol. It has been more recently made by Mailhe and Murat[2] by the nitration of phenyl ether. We first prepared the compound by the method described by Haeussermann and Teichmann and a very dark reaction product was obtained. On extraction with ether we got a dark-colored extract which on evaporation gave a mass of dark crystals. Recrystallizing once from alcohol, the melting point was 65°. Haeussermann and Teichmann gave 62°, Mailhe and Murat 56°. We next prepared the compound by heating *p*-bromonitrobenzene with potassium phenolate without a solvent for fourteen hours on a boiling water bath. In this process a large amount of sublimate gathered on the walls of the flask. These crystals were white, glistening and of long needle structure. They melted sharply at 123.5°. The reaction product was then distilled *in vacuo* boiling at 209° at 45 mm. The distillate on being recrystallized from alcohol melted at 118°. We questioned if the crystallized sublimate could be *p*-nitrophenyl ether. We, therefore, recrystallized the substance seven times with alcohol, and at last obtained a compound melting sharply at 123°. In our work we have obtained crystals melting all the way from 65° up. It seems certain, therefore, from these facts as well as from the analysis for nitrogen, which showed 12.21%, the theory being 12.3%, that the crystals obtained by sublimation were pure *p*-nitrophenyl ether, and that the true melting point of this compound is 123.5°. There is a marked difference between the stability of *o*- and *p*-nitrophenyl ether. The para compound may be distilled at ordinary pressure with little decomposition, the boiling point being 320°. It is insoluble in water, but slightly soluble in ligroin, but readily soluble in alcohol, ether, chloroform, benzene, acetone and other organic solvents.

p-**Nitrophenyl Ether Sulfonic Acid.**—The free sulfonic acid of *o*-nitrophenyl ether is prepared with the greatest difficulty by the decomposition of the cadmium salt, while on the other hand, the corresponding acid of the para ether is prepared with the greatest ease. It is much more difficult to sulfonate *p*-nitrophenyl ether, however, fuming sulfuric acid (33%) being required, while concentrated sulfuric acid in the cold sulfonates the ortho ether. To 10 g. of *p*-nitrophenyl ether are added 40 g. of the fuming sulfuric acid. The whole is heated on a water bath for one hour, or until the ether has entirely gone into solution. The reaction product is now poured into 250 cc. of cold water with constant stirring. The free acid crystallizes out at once. It is most conveniently purified by recrys-

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[1] *Ber.*, 29, 1446 (1896).

[2] *Compt. rend.*, 145, 715 (1912).

tallizing from hot water. The acid melts at 132°, and readily decomposes a soda solution. The crystals do not seem to be at all hygroscopic. An analysis of the acid for sulfur gave 10.79%, the theory being 10.85%.

The Sulfonic Acid Salts.—The sulfonic acid salts of *p*-nitrophenyl ether were prepared by neutralizing the acid with the carbonate of the metal, or by decomposing the barium salt with the sulfonate of the metal as in case of the salts of the ortho series. Because of the greater insolubility of the *p*-sulfonic acid and all its salts, a larger volume of water must be used, which should be boiling hot. The filtration by suction must be carried out rapidly and the precipitate thoroughly washed with boiling water. The para salts all have the same radial structure noted in the case of the ortho salts, but the crystals are better formed and larger. The para potassium sulfonate has one of the most beautiful crystal forms we have ever seen, crystallizing in concentric tufts as large as a pigeon's egg, and as delicate as a snow flake. The crystals are of glistening whiteness, and show little tendency to discolor on exposure to light and air. The following table shows the salts prepared, their crystal forms, solubilities, etc.:

TABLE IV.

Name of salt.	Method of preparation.	Nature of crystals.	Solubility in 100 cc. at 20° C.	Analysis.	
				Found.	Theory.
Barium	Carbonate on sulfonic acid	Small, glistening, white flakes	0.25	Ba 19.2	Ba 18.95
Strontium	Carbonate on sulfonic acid	White scales, smaller than Ba	1.312	Sr 12.42	Sr 12.30
Calcium	Carbonate on sulfonic acid	Very delicate radial flakes	3.280	Ca 6.50	Ca 6.37
Sodium	Both methods were used	Brownish, glistening scales	6.694	...	N_2 4.40
Potassium	Carbonate on sulfonic acid	Large warts of radial plates	1.902	...	K 11.73
Copper	Decomposition of the barium salt	Concentric bluish nodules	10.42	Cu 9.80	Cu 9.74
Cadmium	Decomposition of the barium salt	Shiny, radial plates	1.713	...	N_2 1.91
Silver	Decomposition of the barium salt	Thin, white flakes which darken quickly	1.221	...	Ag 25.65
Lead	Both methods were used	Brownish nodules	6.29	...	N_2 1.69

***p*-Aminophenyl Ether Hydrochloride.**—*p*-Nitrophenyl ether is much more easily reduced to the amino compound than is the corresponding ortho ether. The ether is dissolved in alcohol and boiled with tin and hydrochloric acid on a water bath for an hour or until an oil is no longer obtained, when a few drops of the substance are transferred to water. The alcohol is now evaporated and if necessary water added to keep the solution clear. The whole is de-tinned with hydrogen sulfide, filtered and the water evaporated *in vacuo.* When small volume has been reached, the hydrochloride crystallizes out in the distilling flask. The crystals are thin, irregular-shaped plates of glistening whiteness. They are perfectly stable either wet or dry and melt at 122°. The salt on analysis gave 16.34% chlorine, the theory being 16.03%.

The hydrochloride in water solution was neutralized with ammonia, which liberated the free amine as an oil. This was extracted with ether and recrystallized from alcohol. It melts at 95°. Haeussermann and Teichmann[1] give the melting point as 84°. Nollau and Daniels[2] give the melting point as 33° to 34°. Their product was undoubtedly impure. The body is stable in the air and can be distilled undecomposed. On treatment with chloroplatinic acid the amine gives a chloroplatinate which crystallizes in long reddish brown needles.

The *p*-Aminophenyl Ether Dyes.—The amino hydrochloride was diazotized and coupled with various reagents. The same eighteen were used here as in the case of the ortho dyes and in just the same concentration. Nuns-veiling was dyed in each case and samples of the pure, dry dye obtained. The para dyes are much more stable, less soluble and better crystalline than the ortho dyes. Most of them can be obtained in pure form by crystallization in alcohol. Several of these melt sharply and without decomposition. Most of the dyes decompose somewhat, however, as they melt. While the shades obtained with these para dyes are in a few cases not so brilliant as the corresponding ortho dyes, the fact that *p*-nitrophenyl ether is so much more easily and cheaply prepared and also more easily reduced to the amino compound would tend to make them at least commercially of much greater importance. There is also the added fact that the *p*-aminohydrochloride is perfectly stable both when in solution and when dry, whereas the ortho compound must not be heated when exposed to the air. The four dyes made by coupling the diazotized amine with meta phenylene diamine, dimethyl aniline hydrochloride, β-naphthyl amine, gamma disulfonic acid and α-naphthol, might easily become of commercial importance. Table V is exactly similar to the tables of the ortho dyes. The dye concentration and the color notation are the same as in the preceding tables.

The *p*-Aminophenyl Ether Dyes — Sulfonated Series. — *p*-Nitrophenyl ether potassium sulfonate is used as the basis of these dyes. It is reduced with tin and hydrochloric as before and the reduction is accomplished very easily and in short time. The solution of the sulfonated amino hydrochloride, after being de-tinned and filtered, is diazotized with sodium nitrite solution and coupled with the same eighteen reagents as

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[1] *Ber.*, 29, 1446 (1906).

[2] THIS JOURNAL, 36, 1885 (1914).

TABLE V.

Name.	Diazotized *p*-Amino Phenyl Ether Hydrochloride Coupled with:			The Potassium Sulfonate of Diazotized *p*-Aminophenyl Ether Hydrochloride Coupled with		
	Color on wool.	Color of dry dye.	Remarks.	Color on wool.	Color of dry dye.	Remarks.
m-Phenylene diamine	OR	RS$_2$	From YO to R depending upon concentration	RS$_2$	Black	A soft, dark brown
o-Nitraniline	YT$_1$	Dark gray, neutral		OY	YOS$_1$	
o-Phenylene diamine	YO	VR		YO	RS$_2$	
Benzidine	OYS$_2$	R dark		OYS$_1$	YO dark	
o-Toluene diamine	OT$_1$	RS$_2$		YOT$_2$	Black	
Dimethyl aniline hydrochloride	OY alk. VRT$_1$ acid	VRS$_2$		VBS$_1$ alk. GB acid	BVS$_2$	A brilliant bluish violet
β-Naphthyl amine γ-disulfonic acid	YO	Dark gray, warm	A brilliant tango	YOS$_1$	R medium	
β-Naphthol disulfonic acid	ORT$_1$	ROS$_2$		YT$_1$	OS$_1$	
γ-Amido naphthol sulfonic acid	RT$_1$	Black		YOS$_1$	R dark	
α-Naphthyl amine hydrochloride	VRS$_2$	VBT$_2$		ROS$_2$	BG medium	A tango brown
α-Naphthol	OS$_1$	Black		YT$_2$	OYT$_2$	
β-Naphthol	YOS$_1$	BVT$_2$		GYT$_1$	GYT$_2$	
Hydroquinone	OYT$_1$	Black		GYT$_2$	Gray, dark green	
p-Amido phenol	OYS$_1$	Black		OYS$_2$	Black	
Phenol	OYS$_2$	Black		Cream	YOT$_2$	Dyes a light cream
Resorcin	YOS$_1$	Dark gray, warm		YT$_2$	Black	
Pyrocatechin	YS$_2$	Gray, dark green		Cream	Black	Dyes a light cream
Salicylic acid	OYT$_2$	Gray, dark warm		YOS$_1$	RS$_2$	

before. The same concentrations are used. The presence of the sulfonic acid group renders the dyes more soluble, less intense and harder to isolate in the crystal form. The para sulfonated dyes differ from the others prepared in being explosive when heated. Indeed many of the sulfonic acid salts of *p*-nitrophenyl ether are very explosive. Table V of sulfonated dyes obtained from *p*-aminophenyl ether is exactly comparable with the other tables and furnishes opportunity for the accurate study of the variation in shade produced by varying the position of the diazonium group and the introduction of the potassium sulfonate group.

Summary.

1. A new method has been devised for preparing potassium phenolate applicable to all non-nitrophenols.

2. The properties of *o*- and *p*-nitrophenyl ethers have been more fully determined and numerous errors corrected.

3. Eighteen new sulfonic acid salts of *o*- and *p*-nitrophenyl ether have been prepared and studied.

4. Seventy-two diazo dyes have been made and studied. These were equally distributed between the sulfonated and unsulfonated series of both the ortho and para ethers.

5. The effects of the positions of the groups upon the properties of the compounds and the colors of the dyes have been carefully studied and the following points have been observed:

a. *o*-Nitrophenyl ether and all its compounds are more soluble than the corresponding para bodies and do not crystallize so well.

b. *p*-Nitrophenyl ether and all its derivatives are more stable than the corresponding ortho compounds. This is especially noticeable in the case of the amino hydrochloride and the free sulfonic acid.

c. *o*-Nitrophenyl ether is more easily sulfonated, harder to reduce and its amino body is easier to diazotize than the para body.

d. The *o*-aminophenyl ether dyes tend mostly to the reds and browns, though a few purple and yellow dyes have been produced.

e. The ortho dyes are more brilliant than the para.

f. The sulfonated dyes are more soluble and less brilliant than the unsulfonated.

CHRONOLOGICAL BIBLIOGRAPHY OF THE PHENYL ETHERS.

1. 1845 Ettling and Stenhouse, *Ann.*, **53**, 77 and 91.
First subjected copper benzoate to destructive distillation.

2. 1855 List and Limpricht, *Ann.*, **90**, 209.
Obtained diphenyl ether from the destructive distillation of copper benzoate and called it "phenyl oxide."

3. 1862 Fittig, *Ann.*, **125**, 328.
Obtained diphenyl ether in the same way and separated diphenyl from it by treatment with sulfuric acid.

4. 1866 Lesimple, *Ann.*, **138,** 375.
   Obtained a substance which he erroneously considered phenyl oxide by distilling phenyl phosphate with lime.
5. 1870 Clemm, *J. prakt. Chem.*, **1,** 161.
   Attempted to prepare trinitrophenyl ether from picryl chloride and sodium phenolate in alcoholic solution, but failed.
6. 1871 Hoffmeister, *Ann.*, **159,** 191, and *Ber.*, **3,** 747 (24, 123).*
   Prepared phenyl ether by treating diazobenzene sulfate with phenol. Carefully studied the compound and settled questions that had been in dispute.
7. 1873 Maikopar (article by Wredon), *Ber.*, **6,** 564 (26, 1026).
   First manufactured a nitrophenyl ether by treating a nitro halogen benzene with an alkaline phenolate in alcoholic solution.
8. 1879 Willgerodt, *Ber.*, **12,** 762 (36, 716).
   Made a dinitrophenyl ether by using dinitrochlorobenzene and potassium phenolate in carbon bisulfide solution. Probably same compound as in (7).
9. 1879 Willgerodt, *Ber.*, **12,** 1277 (36, 923).
   Made a trinitrophenyl ether from picryl chloride using phenol, alcohol and water as a menstruum.
10. 1880 Willgerodt, *Ber.*, **13,** 887 (38, 642).
   Made a tetranitrophenyl ether by heating dinitro potassium phenolate and dinitrochlorobenzene in sealed tubes.
11. 1881 Merz and Weith, *Ber.*, **14,** 187 (40, 264).
   Prepared phenyl ether by heating phenol with zinc chloride at 350°; yield, 5%; and also by heating phenol with aluminum chloride; yield, 10 to 12%. (See also *Ber.*, **12,** 1925.)
12. 1882 Boehmer, *J. prakt. Chem.*, **24,** 449; also *Ber.*, **15,** 83 (42, 1, 396).
   Made phenol bromophenyl ether by the action of hydrobromic acid on diazophenol nitrate or sulfate.
13. 1882 Niederhaeusern, *Ber.*, **15,** 1119 (42, 1, 1211).
   Prepared diphenyl ether by heating sodium phenolate with sodium metaphosphate and obtained methylene diphenyl oxide as a by-product.
14. 1882 Richter, *J. prakt. Chem.*, [2] **23,** 349 (42, 1, 618).
   Distilled phenyl phosphate with sodium salicylate and obtained oxydiphenyl ketone which on reduction yielded phenyl ether.
15. 1882 Gladstone and Tribe, *J. Chem. Soc.*, **41,** 5.
   Made aluminum phenolate, cresolate and thymolate and distilled these obtaining phenyl ether and some of its derivatives.
16. 1883 Klepl, *J. prakt. Chem.*, [2] **28,** 201 (46, 1, 446).
   Prepared *p*-phenoxy benzoic acid by passing carbonic anhydride over *p*-hydroxy benzide. He obtained phenyl ether by distilling *p*-phenoxy benzoic acid with baryta.
17. 1884 Richter, *J. prakt. Chem.*, [2] **23,** 293 (46, 1, 324).
   Obtained phenyl ether by distilling phenyl phosphate and sodium salicylate.
18. 1884 Willgerodt and Huetlin, *Ber.*, **17,** 1764 (46, 1, 1328).
   Prepared four nitrophenyl ethers by treating di- and trinitrochlorobenzenes with potassium *o*- and *p*-nitrophenolates in alcoholic solution.
19. 1884 Buch, *Ber.*, **17,** 2638 (48, 1, 147).
   Made ditolyl ether as a by-product of heating *p*-cresol with zinc chloride.

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* The numbers in parenthesis refer to the location of the abstract in the Abstract Volume of *The Journal of the London Chemical Society.*

20\. 1886 Gladstone and Tribe, *J. Chem. Soc.*, **49**, 25.
Made *m*- and *p*-cresyl ethers by the dry distillation of aluminum cresolates.

21\. 1888 Graebe, *Ber.*, **21**, 501 (54, 1, 447).
Prepared *o*-phenoxy benzoic acid.

22\. 1890 Hirsch, *Ber.*, **23**, 3705 (60, 1, 437).
Decomposed diazobenzene with phenol; yield, 50% of the weight of the aniline used.

23\. 1896 Haeussermann and Teichmann, *Ber.*, **29**, 1446 (70, 1, 533).
Made several nitrophenyl ethers and their derivatives by heating the chloronitro benzenes with potassium phenolate and phenol.

24\. 1896 Ullmann, *Ber.*, **29**, 1878 (70, 1, 605).
Makes *o*-nitro- and aminophenyl ethers.

25\. 1896 Haeussermann and Bauer, *Ber.*, **29**, 2083 (70, 1, 676).
Continued the work of Haeussermann and Teichmann using the same methods.

26\. 1896 Jeitles, *Monatsh.*, **17**, 65 (70, 1, 434).
Obtained a diphenyl ether by the distillation of calcium *o*-phenoxy benzoate.

27\. 1897 Haeüssermann and Bauer, *Ber.*, **30**, 738 (72, 1, 333).
Continued their former work and prepared numerous compounds.

28\. 1898 Peratoner and Ortoleva, *Ital. Gazetta*, **28**, [1] 197 (74, 1, 643).
Obtained chlorine derivatives of phenyl ether by treating with sulfonyl chloride.

29\. 1900 Cook and Hillyer, *Am. Chem. J.*, **24**, 525 (80, 1, 144).
Prepared 2-nitro-4'-methylphenyl ether and several derivatives.

30\. 1901 Cook and Frary, *Am. Chem. J.*, **28**, 486 (84, 1, 163).
Prepared 4-nitro-3'-methylphenyl ether and several derivatives.

31\. 1901 Haeussermann and Schmidt, *Ber.*, **34**, 376 (82, 1, 126).
Prepared azoxyphenyl ether by electrolytic reduction of the nitro compound and the corresponding amino compound by using the tin cathode.

32\. 1901 Cook, THIS JOURNAL, **23**, 806 (82, 1, 92).
Prepared 2-nitro-2'-methylphenyl ether and 2-nitro-3'-methylphenyl ether and several derivatives.

33\. 1902 Cook and Eberly, THIS JOURNAL, **24**, 1200 (84, 1, 250).
Prepared 4-nitro-2'-methylphenyl ether and several derivatives.

34\. 1903 Cook, THIS JOURNAL, **25**, 60 (84, 1, 337).
Prepared 4-nitro-4'-methylphenyl ether and several of its derivatives.

35\. 1904 Cook, THIS JOURNAL, **26**, 302 (86, 1, 400).
Describes the properties of phenyl ether.

36\. 1904 Ullmann, *Ber.*, **37**, 853 (86, 1, 417).
Made phenoxy benzoic acid using copper as a catalyst.

37\. 1905 Ullmann and Sponagel, *Ber.*, **38**, 2311 (88, 1, 644).
Made phenyl ether using copper as a catalyst and increased the yield from 0.9% to 87%.

38\. 1905 Cook, THIS JOURNAL, **28**, 608 (90, 1, 495).
Studied aluminum phenolate and its use in the preparation of phenyl ether.

39\. 1905 Reverdin and Dressel, *Ber.*, **38**, 1593 (88, 1, 51).
Prepared some new nitrophenyl ethers.

40\. 1905 Kipper, *Ber.*, **38**, 2490 (88, 1, 648).
A study of the Friedel and Crafts reaction on phenyl ether.

41\. 1906 Cook, *Am. Chem. J.*, **36**, 543 (92, 1, 126).
The distillation of aluminum *m*-cresolate; the preparation of *m*-tolyl ether and its derivatives.

42. 1906 Ullmann and Sponagel, *Ann.*, **350**, 84 (92, 1, 38).
A study of the yields obtained with various halogen benzene and alkaline phenolates in the presence of finely divided copper.

43. 1906 Ullmann and Stein, *Ber.*, **39**, 622 (90, 1, 258).
Made various methoxy and hydroxy phenyl ethers.

44. 1910 Cook, THIS JOURNAL, **32**, 1285 (98, 1, 731).
A study of the bromination of phenyl and tolyl ethers.

45. 1910 Sabatier and Mailhe, *Compt. rend.*, **151**, 492 (98, 1, 669).
Manufactured phenyl ether and its homologs by the use of thorium oxide as a catalytic agent.

46. 1910 Bonneaud, *Bull. soc. chim.*, [IV] **7**, 776 (98, 1, 669).
A study of the action of bromine in the presence of aluminum bromide, on the phenyl ethers and their homologs.

47. 1910 Farbf. v. Friedr. Bayer & Co. (98, 1, 312, 373).
A description of the preparation of dyes from some diazotized aromatic amino ethers.

48. 1911 Cook, THIS JOURNAL, **33**, 254.
An addenda to No. (44) containing omitted material.

49. 1911 Borsche and Rautscheff, *Ann.*, **379**, 152 (100, 1, 329).
A study of the reaction of chloronitro benzene in which they prepared 2:6-dinitrophenyl ether.

50. 1912 Mailhe and Murat, *Bull. soc. chim.*, **154**, 122–3 (1912, 1–183).
Made a study of the decomposition of phenyl ether by hydrogen in the presence of heated nickel.

51. 1912 Mailhe and Murat, *Compt. rend.*, **154**, 601 and *Bull. soc. chim.*, [IV] **11**, 288 (102, 1, 254).
A study of the halogen derivatives of phenyl and ditolyl ethers.

52. 1912 Mailhe and Murat, *Compt. rend.*, **154**, 715 (102, 1, 346).
A study of the nitration of phenyl ether.

53. 1912 Mailhe, *Compt. rend.*, **154**, 1240 (102, 1, 548).
A description of the dyes obtained by treating diazotized *p*-amino phenyl ether with various compounds.

54. 1912 Sabatier and Mailhe, *Compt. rend.*, **155**, 260 (102, 1, 767).
An extension of previous studies, several new compounds being produced.

55. 1914 Nollau and Daniels, THIS JOURNAL, **36**, 1885 (106, 1, 1129).
A study of the reaction of the alkaline salts of sulfonic acids with the alkaline phenolates resulting in the preparation of various aromatic ethers.

56. 1915 Cook and Sherwood, THIS JOURNAL, **37**, 1835 (108, 1, 877).
Made a number of new derivatives of phenyl ether.

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[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.[1]

IX. ETHYL ISOTHIOCYANACETATE.

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Organic combinations containing the primary halide grouping $ClCH_2$-

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