double potentiometer, with duplicate dials. One effective form of double potentiometer, which employs a master switch, can be arranged at the cost of a few knife switches and very little labor. An especially suitable instrument to arrange in this way is the combination potentiometer, all of whose dial switches are single, and free from contact resistance error.

(7) Another convenience especially easy to obtain with the thermo-element-potentiometer system is the power to take the last two figures of any reading directly from the galvanometer scale. It increases speed, simplifies manipulation, diminishes errors, and gives calorimetric data in a form specially convenient for further treatment.

(8) For high temperature measurements and much other thermo-element work not calorimetric, though the required precision may often be less, most of the features above described are desirable, especially the facility for simultaneous and direct readings.

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[Contribution from the Chemical Laboratory of the State University of Kentucky.]

A STUDY OF THE REACTION OF ALKALI SALTS OF SULFONIC ACIDS WITH ALKALI PHENOLATES BY DRY DISTILLATION.

By Edgar H. Nollau and Lloyd C. Daniels.

Received June 11, 1914.

By analogy to the reaction of alkali sulfonates with alkali hydroxides in the preparation of phenols, aromatic ethers should result from the distillation of sulfonates with phenolates. Results confirming this idea having been obtained with the simplest mixture of the kind, *viz.*, sodium benzenesulfonate and potassium phenolate, a study of the reaction was undertaken with a view to determining whether it is generally applicable. The trend of the proposed investigation is exhibited by the following mixtures that have been used:

1. Sodium benzenesulfonate and potassium phenolate.
2. Potassium toluenesulfonate and sodium phenolate.
3. Sodium xylenesulfonate and potassium phenolate.
4. Sodium sulfanilate and potassium phenolate.
5. Sodium toluidinesulfonate and potassium phenolate.
6. Sodium α-naphthalenesulfonate and potassium phenolate.
7. Sodium β-naphthalenesulfonate and potassium phenolate.
8. Sodium benzenesulfonate and potassium thymolate.
9. Sodium benzenesulfonate and mono-potassium resorcinate.
10. Sodium benzenesulfonate and di-potassium resorcinate.
11. Sodium methylsulfonate and potassium phenolate.

The problem was to find what radicals might be represented by R and R′ in the following general equation, and what substituent groups might be present in those radicals:

$$RSO_3M + MOR' = ROR' + M_2SO_3$$

The great variety of possible mixtures made it impossible to cover the whole field, but sufficient has been accomplished to show that the reaction is quite general. But few references could be found in the literature to methods for making aryl ethers of phenols and some of the methods that have been proposed result in rather poor yields. Following is a list of the methods, reference to which was found, with comments on their applicability and on the yields where the latter are stated in the original papers:

I. Action of phenol on diazobenzene sulfate; W. Hoffmeister,[1] yield, very poor. Applicable to the preparation of mixed ethers.

II. Action of anhydrous zinc chloride on phenols; Merz and Weith;[2] yield, usually 6–8%. Not applicable to the preparation of mixed ethers.

III. Distillation of aluminium phenolate; Gladstone and Tribe;[3] yield, about half of the phenolate distilled. Not applicable to the preparation of mixed ethers.

IV. Action of potassium metaphosphate on potassium phenolate (dry distillation); H. von Niederhauesern;[4] yield, less than 1%.

V. Action of phenol on a diazonium salt, phenol used to extract the diazonium salt from solution before the reaction; R. Hirsch;[5] yield, 50% of the aniline used. This is not a good yield considering the large quantity of phenol that must be handled.

VI. Action of halogen substitution products of aromatic hydrocarbons on potassium phenolates in the presence of reduced copper; Ullmann and Sponagel;[6] yields, very high. This method was applied to the preparation of a great variety of ethers and is the source of most of the data on this class of compounds. It is frequently necessary to introduce halogens by way of the corresponding amino compounds, however, and in some cases the corresponding sulfonic acids can be made directly.

VII. One application of the method here proposed was found after this investigation was undertaken. A salt of anthraquinone-α-sulfonic acid was distilled with potassium phenolate, resulting in anthraquinone-α-phenyl ether; R. E. Schmidt;[7] no details given. This same ether has been prepared by patented methods.[8]

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[1] *Ber.*, **3**, 747 (1869).

[2] *Ibid.*, **14**, 187 (1880).

[3] *J. Chem. Soc.*, **41**, T5 (1882).

[4] *Ber.*, **15**, 1123 (1881).

[5] *Ibid.*, **23**, 3705 (1890) and D. R. P. 58,001.

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

[7] *Ber.*, **37**, 94 (1894).

[8] D. R. P. 75,054, 77,818.

The apparatus used in this work was a flat, cylindrical iron retort, 15.5 cm., interior diameter, by 5 cm. depth. The cover of the retort was fastened down with bolts over an asbestos gasket. An iron pipe, 9 mm. in diameter by 50 cm. long, set in the cover with a street elbow, served as the outlet. An Allihn bulb condenser was used, since it was found that the clouds of vapor passed through a Liebig condenser. The apparatus was gas-tight so that distillations could be made at reduced pressure.

Experimental.

Diphenyl Ether, $C_6H_5OC_6H_5$.—An amount of solid potassium hydroxide, equivalent to 30 g. of the anhydrous compound, was dissolved in a small quantity of water and 51 g. of phenol were added to the solution. This phenolate solution and 85 g. of sodium benzenesulfonate were mixed in the retort. After thorough stirring, the mass presented the appearance of a thin white paste. On applying heat, water distilled over and was followed by a brown oil which was caught in a separate receiver. The distillation was continued at increasing temperatures as long as oil was formed.

The total oily portion of the distillate was 44 cc., which corresponds to a yield of about 50% of the theoretical. That it contained phenol was shown by a test with ferric chloride and by its distilling at 194.5–196°, but little above the boiling point of phenol and much below that of diphenyl ether (245°). It is believed, however, that only a small proportion of the product was phenol, because the ferric chloride test was faint, and the odor of the ether was predominant. The low boiling point was probably due to the formation of a constant boiling mixture. So much of the material was lost in unsuccessful attempts at finding a satisfactory method for purifying it that no valid estimate could be made of the relative amounts of substances present. Later in the course of the work, a good method for purifying the crude distillates was found and this method was used in the course of a detailed study of the best conditions for the preparation of diphenyl ether by this method. The results of this study will be stated at this point, though the experiments were made last in the course of the work.

The variations in conditions used were, distillation of a mixture of previously dried reagents, the addition of varying quantities of water to the mixture of dried reagents before distilling, the addition of iron filings to the mixture before distilling, and distilling at atmospheric and at reduced pressures. Several combinations of these different conditions were used, with the final decision in favor of preparing the phenolate just before using it and adding the sulfonate in the presence of enough water to keep the whole mass in solution. The use of iron filings apparently made no difference in the yield, indicating that the mixture was uniformly heated through and that probably the iron caused no reduction of the materials.

That the yield was increased by using considerable quantities of water in the mixture, indicates that in this way a better admixture of materials was obtained, either by reason of the evaporation of the solution of the mixed materials or by reason of one or both of the materials retaining water of hydration and remaining fused at the temperature at which the reaction begins. The pressure at which the distillations were made, made no difference in the yield.

The best yields obtained were close to 50% of the theoretical as crude product, and, of this, never less than 75% was obtained as pure ether.

The reason for using mixtures of sodium and potassium compounds instead of using both compounds as sodium or both as potassium salts, was that a mixture of lower melting point, and, therefore, of greater reactivity at low temperatures was expected to result in this way. A trial with sodium phenolate substituted for potassium phenolate seemed to confirm this idea both in point of temperature necessary to bring about the reaction and in point of yield. In all other experiments, the mixed salts were used.

Tolyl-p-phenyl Ether, $CH_3C_6H_4OC_6H_5$.—Fifty-two grams of potassium *p*-toluenesulfonate and 29 g. of sodium phenolate[1] were intimately mixed with one-third their bulk of iron filings and slowly distilled under reduced pressure. The crude product was a reddish brown oil with a slight green fluorescence. Yield, 49.7%. This was lost in the course of attempts to find a convenient method of purification and another distillation was made from 42 g. of the sulfonate and 23 g. of the phenolate. This was purified by steam distillation of the mixture with an excess of caustic potash solution and extraction of the distillate with ether. After drying the ether solution, it was distilled, yielding a colorless oil of a pleasant odor similar to that of diphenyl ether, boiling at 265° at 737.6 mm. Of the 51.7% of crude product obtained in the second distillation, only one-fifth was obtained as the pure ether. There is no doubt that more of it was present, but it distils so slowly with steam that enormous quantities of distillate had to be caught to get the quantity stated. If the method of purification worked out in the course of the next experiment had been known, no doubt much more could have been obtained as pure product.

(1,2)-Xylyl-p-phenyl Ether, $(CH_3)_2C_6H_3OC_6H_5$.—One hundred and four grams of sodium xylenesulfonate (1,2,4) and 66 g. of potassium phenolate were distilled under reduced pressure. The crude product, a reddish brown, fluorescent oil, represented a yield of 20%. In subsequent distillations, the yield was 50%.

Up to this point in the work, the only method for purifying the products

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[1] For this and most of the subsequent experiments, the phenolate used was prepared in bulk, dried, and kept in a tightly stoppered bottle. The sulfonates were also thoroughly dried. Both were finely pulverized before being used.

that could be depended on, was to distil with steam from a mixture with a solution with caustic potash in excess. The pure substances distilled very slowly with steam, as has been mentioned, and the distillate was in the form of emulsions that would not settle. This necessitated extraction with large quantities of ether. Several attempts to find simpler methods for purification had resulted in failure and loss of material, when a very satisfactory method was found while working with this ether. The crude product was warmed with solid potassium hydroxide (83% KOH) and the mixture was distilled under reduced pressure in a Bendix distilling flask. The small amount of water present distilled over at very low temperature and was easily removed completely from the receiver. The ether then distilled at constant temperature.

The purified product was a nearly colorless oil, boiling at 104–105° (cor.) at 49.4 mm. It soon solidified into short, colorless needles, melting at 35–37°. Yield, over 75% of the crude product. The ether had a pleasant odor, resembling that of diphenyl ether mixed with a little xylene. No reference could be found in the literature to any previous preparation of this ether, so it was analyzed with the following results:

Calc. for $C_{14}H_{14}O$: H = 7.02, C = 84.89. Found: 7.50, 7.35, 7.11, and 84.89, 84.31, 85.11.

p-Amino-diphenyl Ether, $H_2NC_6H_4OC_6H_5$.—Ninety-seven and one-half grams of sodium sulfanilate and 66 g. of potassium phenolate, mixed with one-third their total bulk of iron filings, were distilled under reduced pressure. The crude product, a reddish brown oil, was distilled from mixture with solid caustic under reduced pressure in a Bendix flask. The pure product was a pale yellow oil which soon changed into beautiful white, shining flakes. This product, amounting to 33% (pure) of the theoretical, melts at 33–34° and boils at 84° under a pressure of 15.5 mm.

o-Aminotolyl-p-phenyl Ether, $CH_3(NH_2)C_6H_3OC_6H_5$.—Fifty-two grams of sodium toluidinesulfonate (1,2,5) and 33 g. of potassium phenolate, with one-third their total bulk of iron filings, were distilled under reduced pressure. The crude product amounted to a yield of 57% of the theoretical. It was purified as were xylylphenyl ether and amino-diphenyl ether, yielding a pale yellow oil amounting to about half the crude material. Boiling point, 102–104° at 67.4 mm. Unlike the amino-diphenyl ether, it did not solidify on standing, but darkens in the light. It has an odor similar to that of aniline, but not quite so disagreeable, when freshly distilled, and takes on a phenol-like odor on standing. No reference to the preparation of this compound could be found in the literature, so its nitrogen content was determined by the Kjeldahl method.

Calc. for $C_{13}H_{13}ON$: N = 7.02. Found: 7.18 and 7.22.

This was considered sufficient analytical data to establish its probable formula, since there was no apparent difference in the course of its preparation and that of its lower homolog just described, and the melting point of the simpler compound was as given in the literature.

Thymyl-phenyl Ether, $CH_3(C_3H_7)C_6H_3OC_6H_5$.—An amount of potassium hydroxide equivalent to 14 g. of the anhydrous compound, 37.5 g. of thymol, and 45 g. of sodium benzenesulfonate were dissolved together in a small quantity of water and distilled. The water distilled off first, and was followed by a yellowish brown oil. This latter was redistilled as usual and the resultant colorless oil had a strong odor like that of thymol with a faint modification toward that of diphenyl ether. Its boiling point was found somewhat lower than that given for this compound by Ullman and Sponagel,[1] 289° as compared to 297°, but it all distilled within a degree.

It was suggested that the identification of this compound as thymyl-phenyl ether was not complete in view of its low boiling point. The quantity of it formed was too small to permit of further experiments with it, so the experiment was repeated, with the difference that it was purified by distillation with steam, extraction of the steam distillate with ether, and distillation of the residue after removal of the ether. The residue from the ether solution amounted to nearly 10 cc., of which 6 cc. distilled below 290° (only two or three drops came over below 287°) and the remainder came over between 294° and 295°, leaving a slight brown stain in the distilling bulb. The color of the distillate, however, was much darker than that of the residue from the ether and its odor was much sharper.

If thymyl-phenyl ether is formed by the reaction, it is decomposed by the high temperature, and the quantity obtained is too small to admit of clear identification.

Anisole, $CH_3OC_6H_5$.—An amount of potassium hydroxide equivalent to 14.3 of the anhydrous compound and 23.5 g. of phenol were dissolved together in the retort and 29 g. of sodium methylsulfonate were added. The sulfonate used was prepared by the method given in German patent No. 55,007.[2] The behavior during distillation differed, in this case, from the others only in that a larger part of the oil came over with the aqueous portion of the distillate. The crude product had a pronounced odor of anisole and measured up to a yield of 100% of the theoretical. It was purified by distillation with steam from caustic mixture—the oil separating readily from the water. After drying with calcium chloride, the ether was distilled and found to come over completely between the temperatures 149–152°. The yield of pure anisole (volume of the oil separated from the steam distillate) was 55%.

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[1] *Loc. cit.*

[2] Lessar-Cohn, *Arbeitsmethoden für Organisch-Chemische Laboratorien, 4te Aufl. spez. Tl.*, p. 1324.

Attempts were made to prepare the mono- and diphenyl ethers of resorcin and the phenyl ethers of α- and β-naphthols. The work is as yet incomplete.

Summary.

1. Dry distillation of alkali salts of sulfonic acids with alkali phenolates is a convenient method for the preparation of aryl ethers of phenols. Though the yields are considerably less than those obtained by the method of Ullman and Sponagel, the compounds used can, in some cases, be more directly prepared.

2. The reaction probably proceeds according to the equation:

$$RSO_3M + R'OM = R'OR + M_2SO_3,$$

in which equation, the symbol R may represent the phenyl radical and its homologs, provided no long side-chain is present, or a methyl group. The symbol R′ represents a phenyl radical or an aminophenyl radical. The presence of a long side-chain in this radical interferes with the reaction's proceeding normally or causes decomposition of the product.

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[Contributions from the Sheffield Chemical Laboratory of Yale University.]

RESEARCHES ON PYRIMIDINES. LXXII. THE SYNTHESIS OF 4-HEXYLURACIL AND ITS RELATIONSHIP TO URACIL-GLUCOSIDE.

By Treat B. Johnson.

Received June 26, 1914.

1. Pyrimidine-Nucleosides: The Structure of Uridine.

The elucidation of the structure of nucleic acids obviously involves the determination of the constitution of *nucleosides*. The latter are characteristic purine-carbohydrate and pyrimidine-carbohydrate combinations, which result by partial hydrolysis of these naturally occurring acids. We have practically no knowledge regarding the nature of the carbohydrate linkings in these compounds, and, consequently, we are unable to express structually their exact constitution. One important fact, however, seems to have been very definitely established by the results already obtained, namely, that the two nitrogen cycles—the purines and pyrimidines—are not joined to the carbohydrates in a similar manner. The experimental data, thus far obtained, suggest that the sugar, in the case of the purine-nucleosides, is very probably linked to the purine at a nitrogen atom occupying either the 7- or the 9-position of the purine ring. Such hexose combinations have recently been synthesized by Emil Fischer[1] and it is interesting to note that his synthetical glucosides agree

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[1] Fischer and Helferich, *Ber.*, 47, 210 (1914).