

1902

The Preparation of Phenyl Ether

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Recommended Citation

Cook, Alfred N. (1902) "The Preparation of Phenyl Ether," *Proceedings of the Iowa Academy of Science*, 10(1), 113-122.

Available at: <https://scholarworks.uni.edu/pias/vol10/iss1/21>

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added and the water will be free from ammonia and suitable for Nesslerizing purposes."

In our experiments we have found that the water prepared by this method has been unsatisfactory, and probably due to the addition of potassium iodide. The presence of the iodide apparently destroys the sensitiveness of the Nessler reagent. While this method may be satisfactory under certain conditions, it has been found without value for work in this laboratory. The following method is suggested for the preparation of water free from ammonia and nitrogen as nitrates and nitrites.

Sodium peroxide is added to the water in an ordinary round bottom flask, in the proportion of one dram to each liter of water. Flasks of five or six liters in capacity are found to be very satisfactory. The contents of the flask is boiled for thirty minutes or longer, until it is estimated that the water is free from ammonia. The time for boiling and the amount of sodium peroxide will vary according to the amount of ammonia which may be present in the water. If it is desired to prepare water that is free from ammonia and nitrogen as nitrates and nitrites in order that one supply may serve for making standards for the determination of ammonia, nitrites and nitrates, the contents of the flask are transferred to a copper distilling vessel and distilled. The first portion of the distillate is rejected and the remainder kept in bottles in the usual manner.

THE PREPARATION OF PHENYL ETHER.

BY ALFRED N. COOK.

While ethyl ether, the common ether of the modern drug store, has been known for three and a half centuries, and has been used as an anesthetic for over fifty years, phenyl ether is of more recent origin. It has never been put upon the market and has never been put to

any so-called "practical use." Improved methods of preparation, however, may bring it within reach of the physiological chemist or the manufacturer, so that this substance or some of its immediate derivatives may, 'ere long, play an important part in the economy of men.

Phenyl ether was discovered by List and Limpricht¹ in 1854, while studying the products of the destructive distillation of copper benzoate. They did not identify it as phenyl ether, but assigned to it the empirical formula $C_{12}H_8O$, derived from the results of their analysis. Why this formula was assigned to it is difficult to see, for their analyses correspond much better with the formula now assigned to phenyl ether. Acting on the suggestion of Gearhardt, Limpricht² later assigned the formula $C_{12}H_{10}O$ and called the substance the ether of carboic acid. The compound was next studied by Rudolph Fittig³ and later Kekule⁴ in his Lehrbuch suggested, on the ground of Fittig's work, that it was monohydroxy diphenyl.

C. Lesimple⁵ prepared a compound which he supposed to be phenyl ether, by distilling phenyl phosphate with lime, but Hoffmeister,⁶ afterwards showed that it was diphenylene oxide.

C. Clem⁷ attempted, without success, to prepare phenyl ether by heating potassium phenolate and potassium benzoate.

Since the discovery of phenyl ether in 1854, perhaps thirty different German, English, and American chemists have given the subject more or less attention. The French have not yet entered the field.

Aside from the above method of List and Limpricht for preparing phenyl ether, six other direct methods have been employed, as follows:

Hoffmeister⁷ obtained a small yield by means of the diazo reaction with phenol, aniline, and sulphuric acid.

¹ *Annalen der Chemie* XC, 190.

² *Lehrbuch*, page 713, and *Annalen der Chemie* CXXV, 328.

³ *Annalen der Chemie*, CXXV, 328.

⁴ *Annalen der chemie*, CXXXVIII, 276.

⁵ *Berichte*, III, 747.

⁶ *Jr. fuer Pract. Chem.*, 1870, 147.

⁷ *Annalen der Chemie*, CLl, 194, and *Berichte* III, 747.

Hirsch⁸ used the chloride instead of the sulphate, and claimed to have obtained a yield equal in weight to 50 per cent of the aniline used. He suggests that the cause of the small yield obtained by Hoffmeister was due to the formation of phenol sulphonic acid.

Merz and Weith⁹ obtained a yield of six per cent of theory by heating phenol with zinc chloride, and also a small yield by heating phenol with aluminium chloride.

Gladstone and Tribe¹⁰ obtained a good yield by distilling alluminium phenolate.

B. Jeitles¹¹ obtained phenyl ether by distilling calcium phenyl salicylate

Klepl¹² prepared phenyl ether by distilling para-phenoxy benzoic acid with caustic baryta.

Richter¹³ obtained phenyl ether by distilling sodium salicylate with triphenyl phosphate.

During the past three years, in company with some of my advanced students, I have been studying the preparation of derivatives of phenyl ether by means of a method which is of general application in both the fatty and aromatic series—that of heating a halogen-nitro-benzene with a potassium phenol. The results were published in part in the PROCEEDINGS OF THE ACADEMY, but mostly in other journals.

As I was about to begin the study of derivatives of phenyl ether by direct methods it was important to obtain the substance in considerable quantities. Having attempted to follow out several original ideas of my own without avail, I began to study the methods of those who had already prepared the substance and selected the method of Hoffmeister, as modified by Hirsch, and that of Gladstone and Tribe as the most promising.

⁸ Berichte XXIII, 370.

⁹ Berichte XIV, 187.

¹⁰ Jr. Lond. Chem. Soc. XLI, 5.

¹¹ Monats Hefte 17, 65.

¹² Jr. Pract. Chem. (2), 28, 193.

¹³ Jr. Pract. Chem. (2), 28, 201.

THE HIRSCH-HOFFMEISTER METHOD.

The method as carried out by Hirsch was as follows: A 90 per cent solution of phenol was warmed on a water bath in a flask fitted with a return condenser and the diazobenzene chloride solution added through the reflux condenser by means of a separating funnel with sufficient rapidity to cause an active, but not too violent, reaction. When all was added the temperature was finally raised to 90°. The resulting solution was salted out with a concentrated solution of sodium chloride and the liquid precipitate fractionated by distillation. The portion boiling above 200° C was dissolved in toluene and washed with a solution of sodium hydroxide. This solution on being fractionated yielded phenyl ether, boiling between 260° and 290° C, and a neutral oil in small quantity boiling between 320° and 350° C, which he supposed to be diphenyl phenyl ether, $C_6H_5-O-C_{12}H_9$, although he did not analyze it. He states that under certain circumstances he obtained a yield of phenyl ether equal in weight to 50 per cent of the aniline used. He did not, however, describe the circumstances under which he obtained it.

I carried out the process in all respects essentially like the above, except that no return condenser was found necessary, and that part of the distillate containing the phenyl ether was not dissolved in toluene for washing with caustic soda, but was washed directly with the sodium hydroxide solution. No loss of phenyl ether could have taken place, as the soda solution was very weak, and phenyl ether is almost entirely insoluble in water. It is soluble, however, in a very strong solution of sodium phenolate, but is precipitated on adding a considerable amount of water. The degree of dilution of the sodium phenolate solution would entirely prevent any appreciable loss by this method of washing. Three experiments were made, and in each case a large quantity of phenol was recovered.

First experiment:

AMOUNTS OF SUBSTANCES EMPLOYED.

Aniline	100 grams.
Concentrated hydrochloric acid.....	325 grams.
Water.....	900 grams.
Sodium nitrate, a sufficient quantity to diazotize the aniline.	
Phenol containing 10 per cent of water.....	550 grams.

When a portion of the diazo solution was added to the phenol, warmed to 65°C, nitrogen was evolved quite rapidly, and very rapidly at 85°. Most of the diazo solution was added at the higher temperature. When 100 c. c. of the diazo solution was added to the phenol solution it took only a few minutes to evolve its nitrogen.

On distilling, the phenol with one or two other substances came over below 210°, when the temperature rose rapidly to 260°, where the higher boiling substances began to come over. As a final result there were obtained a few grams of a substance having the odor of geraniums and boiling at 250°. This was undoubtedly phenyl ether. There was also obtained 40 grams of a crystalline solid, boiling between 275° and 280°. This substance was obtained by neither Hirsch nor Hoffmeister. No attempt was made to purify or analyze this substance or the one mentioned further on, as the chief object of this research was to obtain a considerable quantity of phenyl ether. The neutral oil mentioned by Hirsch, boiling between 320° and 350°C, and which he suggested to be diphenyl phenyl ether, was not obtained. A very small quantity of tar remained at the end of the first distillation.

On fractionating the portion boiling below 210°, there was obtained a liquid not soluble in caustic soda, which boiled a few degrees higher and melted a few degrees lower than phenol. It crystallized in long needles on standing at room temperature. This substance was not mentioned by Hirsch. It would be easily overlooked, since it distills over with the phenol, but mostly with the last portion. However, it may not have been formed in his experiments since he kept the temperature considerably lower than in this experiment during the addition of the diazo solution to the phenol. While I

did not study the compound exhaustively, I think it likely has the formula, $C_6H_5N_2NH.C_6H_5$. I do not know that this compound has been obtained up to this time, but the corresponding para-toluidine compound is known. On fractionating the substance several times a portion weighing several grams was obtained, which boiled between 180° and 182° . On standing decomposition took place. When first prepared it had no odor and was colorless, but on standing for three months it became dark in color and had a strong odor of phenol. All but a few globules dissolved in caustic potassa. These globules had the characteristic odor of phenyl ether. There was not enough of this oil to collect and determine its melting point. The change took place in two portions, one in an open flask and the other in a full and tightly corked bottle. The action was not, therefore, due to the oxidizing action of the air.

Second experiment:

Quantities taken,

Aniline.....	100 grams.
Concentrated hydrochloric acid	200 grams.
Water	700 grams.
Phenol containing 10 per cent of water	500 grams.

The diazo solution was added slowly while the phenol solution was heated to 53° — 63° . This was the only difference between this trial and the preceding one.

Results were obtained as follows:

1. None of the substance boiling at 180° - 182° .
2. About eight grams of purified phenyl ether.
3. Much less of the crystalline solid.
4. A great deal of tar.

Third experiment:

Quantities taken,

Aniline	100 grams.
Water	1,000 grams.
Phenol containing 10 per cent of water.....	450 grams.
Concentrated hydrochloric acid, sufficient to diazotize the aniline.	

In this experiment the phenyl ether was distilled from the higher boiling substances with steam. The yield was

fifteen grams of the purified ether. This was much better than the results obtained by Hoffmeister, but much less than was claimed by Hirsch.

The process is long and tedious, and the returns so relatively small that it was thought best to give attention to other promising methods.

THE GLADSTONE-TRIBE METHOD.

Gladstone and Tribe obtained phenyl ether and two or three other compounds by distilling aluminum phenolate, prepared by acting on phenol with aluminum, in the presence of iodine as a catalytic agent. They estimated that one-half of the aluminum phenolate was decomposed by the action of heat into phenyl ether and aluminum oxide. That being the case, the distillation of aluminum phenolate would be an excellent method by which to prepare phenyl ether, providing the aluminum phenolate could be easily obtained.

Preparation of the Aluminum Phenolate.—Five hundred grams of phenol containing a gram or so of iodine in a flask fitted with a return condenser was heated over a direct flame, and the aluminum, in the form of strips, *very* slowly added. It was found necessary to obey this precaution very carefully, since, when considerable quantities of aluminum were added at a time, the action was so violent that the heat of reaction raised the phenol to its boiling point and volatilized it so rapidly that it projected from the tube uncondensed.

Properties of Aluminum Phenolate.—The solid substance is brittle and possesses a vitreous luster and conchoidal fracture. Prepared as given above, it is usually black, but sometimes gray. It is soluble in hot xylene, from which it separates as a gelatinous mass on cooling, and Gladstone and Tribe found it to be soluble in benzene. If bottled tightly it can be kept for a long time without undergoing any change, but if allowed to come in contact with the air it very soon loses its vitreous luster and crystalline grains appear throughout the surface of the fragments. It

becomes moist and smells strongly of phenol, whereas, when freshly prepared, it has no odor. Evidently either the oxygen or the moisture of the air (most probably the latter, but possibly both), acts upon it with the liberation of phenol and the formation of aluminum oxide. The reaction is probably represented by the following equation:



The phenol is probably simply held mechanically, and the crystalline grains are probably aluminum oxide.

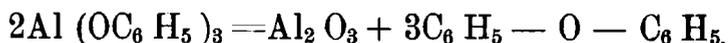
When distilled it did not melt down as fresh aluminum phenolate does, but remained in the powdery form in which it was placed in the flask, throughout the distillation, nor did the particles run together in the least. It apparently distilled at a lower temperature than fresh aluminum phenolate. From 123 grams of the substance there resulted 89 grams of the distillate and 34 grams of a powdery residue, which was poured from the flask as so much sand. On redistilling this distillate a portion came over below the boiling point of phenol, which had the characteristic odor of benzene. Most of the substance, however, came over at 179° — 180° , the boiling point of phenol. There were no higher boiling substances formed. The *odor* of phenyl ether which is so conspicuous in the phenol that results from the destructive distillation of aluminum phenolate, was not observed. The process of distillation evidently simply separated the mechanically held phenol with a little dissolved benzene from the aluminum oxide and other residue.

The distillation of the aluminum phenolate was carried out in a distilling flask containing from 100 to 200 grams of the substance. The products of distillation are a very small quantity of benzene (which, however, may have resulted from the reducing action of the nascent hydrogen on the phenol during the process of manufacture of the aluminum phenolate, and may have been simply held mechanically in the impure aluminum phenolate), a varying amount of phenyl ether, and some higher boiling substances not yet identified. Gladstone and Tribe purified

and analyzed one of them which boiled at 280° and melted at 97° , and which they supposed, from the results of their analysis, to be diphenyl ketone, but this substance, according to Watts' Dictionary of Chemistry, page 474, boils at 305° , and melts at 48° . It is safe to say, however, that none of these higher boiling substances have yet been identified.

The degree of heat employed should be as low as possible in order to obtain a large yield of phenyl ether. There is also obtained a relatively larger amount of tarry residue. When a high degree of heat is employed the aluminum phenolate decomposes mostly into phenol and the higher boiling substances. There results, however, much less of the tarry residue. By heating the flask as uniformly as possible at the close of the operation and carrying the distillation as far as possible, a porous residue remains, which can quite readily be removed from the flask when cool; otherwise a hard asphalt-like residue remains, which it is impossible to remove without sacrificing the flask.

Gladstone and Tribe estimated from their results that one-half of the aluminum phenolate decomposed, on heating, into aluminum oxide and phenyl ether, according to the following equation:



While the reaction probably goes on according to this equation it would seem from their results as well as my own, that this is too high an estimate. From having carefully gone over the work a number of times it would seem that about one-fourth of the aluminum phenolate is decomposed into aluminum oxide and phenyl ether at a low heat. While this method did not yield quite the results hoped for on reading the article of Gladstone and Tribe, it still proved to be a very good method, and is much more easily and quickly carried out than the Hirsch-Hoffmeister method, and the materials are cheap. From 1,227 grams of aluminum phenolate I obtained over 200 grams of pure phenyl ether boiling between 249° — 251° ,

and which crystallized readily at room temperature. This is undoubtedly the best and cheapest method that has yet been used for the preparation of phenyl ether.

“The preparation, properties, and products of the destructive distillation of aluminum phenolate” are now being investigated in company with an advanced student in the chemical laboratory of Morningside College, and will be published as a separate paper at some future date.

THE SIOUX CITY WATER SUPPLY. II.

BY ALFRED N. COOK AND W. J. MORGAN.

It is designed to continue the examination of Sioux City waters each year for a series of years, and thereby collect valuable data which may be of service in the future. It is yet too soon to draw many general conclusions with sufficient certainty. It will be observed by comparison with last year's results that the analyses of the city water resulted much better this year. The albuminoids ammonia and nitrates have been very much reduced, and the free ammonia entirely disappeared.

The analysis of the Missouri river water suffers by comparison with that of last year, but the specimen was taken near the Floyd monument, which is below the city. The specimen of last year was taken at the combination bridge and was consequently not contaminated with Sioux City sewage.

The specimen from the Sioux river was taken at the boat landing, Riverside park.

The results here given are the average of two or more duplicates. The figures indicate parts per million. All analyses were made in May or the first part of June, 1902.