

1900

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Recommended Citation

Cook, Alfred N. (1900) "Diphenyl Ether Derivatives," *Proceedings of the Iowa Academy of Science*, 8(1), 94-103.

Available at: <https://scholarworks.uni.edu/pias/vol8/iss1/15>

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The well which proved to be the source of the epidemic was the only one which was contaminated among the wells examined, yet we cannot but realize that there are distributed in the small towns and on the farms many such wells, which are in the condition of a gun which is not supposed to be loaded, but is liable to "go off" at any time with disastrous results.

There is no doubt that little or no attention is given to the water and milk supplies as long as Providence in some mysterious manner protects those who tempt her in many ways, but when the penalty is paid, it is a costly one, for instruction furnished by "experience" is in many cases very expensive.

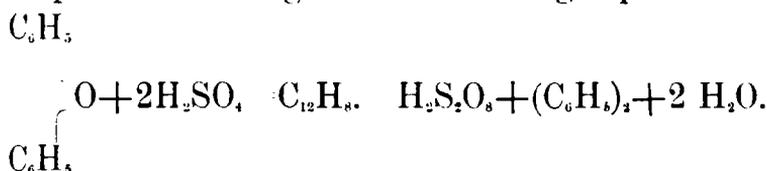
DIPHENYL ETHER DERIVATIVES.

ALFRED N. COOK.

- (1) HISTORICAL INTRODUCTION.
- (2) PREPARATION OF A NITRO-METHYL DERIVATIVE.
- (3) OXIDATION OF THE METHYL GROUP TO AN ACID AND THE PREPARATION OF SOME OF THE SALTS OF THE ACID.
- (4) REDUCTION OF THE NITRO GROUP TO FORM A BASE AND THE FORMATION OF THE PLATINUM SALT.
- (5) BIBLIOGRAPHY.

HISTORICAL:—In the year 1854, Dr. K. List and Dr. H. Limpricht (Ann. 90, 190) were studying the products of the destructive distillation of copper benzoate and succeeded in identifying the principal product as phenyl benzoate. During the process of purification they separated from this by fractional distillation a substance to which they assigned the formula, $C_{22}H_{10}O_2$, and called it phenyl oxide. (Dr. John Steinhaue had previously studied the products of the distillation of copper benzoate (Ann. 53, 91), but did not detect the substance in question). Limpricht

(Lehrbuch, p. 713), afterwards made a further study of the compound and assigned it to the formula $C_{12}H_{10}O$. Rudolph Fittig (Ann. 125, 328), in 1863, prepared from the above mentioned distillate by means of sulphuric acid a compound which he called diphenyl and assigned the formula, $C_6H_5.C_6H_5$, and made the supposition that the reaction took place according to the following equation:



Kekule (Lehrbuch. Vol. III, 19), opposed the formula of List and Limpricht on the ground of Fittig's work, and argued that it must be monohydroxy diphenyl ($HO.C_6H_5.C_6H_5$), which would have the same empirical formula.

C. Lesimple in 1867 (Ann. 138, 375), prepared a substance by distilling triphenyl phosphate with an excess of lime, which he called phenyl oxide, although his analysis shows that the per cent of hydrogen was .9 too low. The melting point also was 53° too high, but this he could not have known, as List and Limpricht's compound remained a liquid. (This was afterwards shown by Hoffmeister to be due to impurities.)

In view of all the uncertainty that existed, W. Hoffmeister in 1871 (Ann. 151, 191), set out to determine whether diphenyl ether had really been prepared or not. He repeated the experiments of List and Limpricht, but distilled off the compound in question from the phenyl benzoate with steam instead of separating by fractional distillation, and thus obtained the substance in a much purer state. It was then a crystalline solid, and had a melting point of 27° C. He showed that diphenyl could not be obtained from this crystalline compound by the action of sulphuric acid, but that it occurred as an impurity when diphenyl ether was made by the method of List and Limpricht, and Fittig had simply separated it. Kekule was therefore wrong with regard to the constitution of the compound. He also

showed that Lesimple (Ann. 159, 192), had made diphenylene oxide instead of diphenyl oxide.

Up to the present time diphenyl ether and its derivatives have been prepared by at least thirteen different methods, and have been studied by no less than twenty-five different chemists, among whom were Fittig and Kekule. While the methods are various, the yield in almost every case is remarkably small. The leading methods that have been used are as follows:

W. Hoffmeister (Ber. 3, 747) prepared diphenyl ether by warming diazo benzene sulphate and phenol, but the yield was very small. Hirsch (Ber. 23, 370) used the chloride instead of the sulphate and modified the method in some other respects and obtained a yield of 50 per cent of the aniline used.

Merz and Weith (Ber. 14, 187) obtained a small yield by heating phenol with zinc chloride, and also with aluminum trichloride.

Gladstone and Tribe (Jr. Chem. Soc., 41, 5 and ditto 49, 27) made various methyl phenyl ethers by distilling the corresponding aluminum cresolates.

Willgerodt (Ber. 12, 1278) obtained a large yield of the trinitro derivatives by heating pikryl chloride with one molecular equivalent of potassium hydroxide.

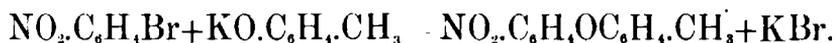
One of the most productive methods that has been used is that originated by Haeussermann and Teichmann (Ber. 29, 1446), and also independently by F. Ullmann (Ber. 29, 1878). The heated potassium phenolate and several of its derivatives with the various nitro halogen derivatives of benzene and obtained, as a rule, a good yield.

EXPERIMENTAL PART:—In approaching the study of diphenyl ether derivatives, it was suggested by Dr. H. W. Hillyer of the University of Wisconsin, that the method of Haeussermann and Teichmann might be extended to the Cresols, and in the following account it will be seen that this was accomplished with a good degree of success. It has seemed best to adopt the nomenclature of Haeussermann and Bauer (Ber. 29, 2083) as the simplest, and at the same time susceptible of very extended application.

2-nitro-4'-methyl phenyl ether——



This compound was prepared by the action of o-brom nitro benzene on potassium p-cresolate and the reaction takes place according to the following equation:



The potassium p-cresolate was made by treating one part of p-cresol with a molecular equivalent of potassium hydroxide dissolved in one part of water, evaporating to dryness on the water bath, with continual stirring and then drying in the air bath at 100° C. for half an hour. This method yielded a very good product, which was of a slight yellow color. An endeavor to prepare the cresolate by dissolving metallic potassium in the cresol, as did Haeussermann and Teichmann (Ber. 29, 1446), and F. Ullmann (Ber. 29, 1878), with phenol in making derivatives of diphenyl ether, yielded a dark tarry product which very materially effected the yield and purity of the diphenyl ether which was made from it. The above mentioned ether was made in the following manner: One part by weight of potassium p-cresolate was heated in a small Florence flask on a fusible metal bath with three parts of o-brom-nitro benzene to 125-130° C. when a vigorous action began, accompanied by a rise of temperature of several degrees. As soon as the action had ceased, which required about five minutes, the melt was cooled and extracted with ether. The above mentioned ether extract was washed with potassium hydroxide solution to remove any free cresol which might be present. The excess of o-brom-nitro benzene was distilled off with steam, and the phenyl ether was distilled under diminished pressure to free it from any remaining trace of ortho-brom nitro benzene, and the solid, and higher boiling substances which were extracted with the sulphuric ether. Under a pressure of 25 mm. o-brom nitro benzene boils at 150° C., while 2-nitro-4'-methyl phenyl ether boils at about 220° C.

under the same pressure. The yield was one gram of the ether for every gram of the cresol used. On crystallizing several times from alcohol it was completely purified and analysis yielded the following results:

	Carbon.	Hydrogen.	Nitrogen.
Calculated for $C_{12}H_{11}NO_2$..	68.04	4.88	6.11 per cent.
I	...68.12	4.75	6.28 per cent.
II	...68.20	4.77	6.32 per cent

The compound melts at 49° C. It distills with partial decomposition at ordinary atmospheric pressure. It is not volatile with steam. It is very soluble in hot alcohol, from which it crystallizes out in beautiful sulphur yellow, and apparently monoclinic crystals of sufficient size to be easily measured with the goniometer. It has no taste, but feels like sulphur when taken into the mouth. It is very soluble in ether, acetic acid, chloroform, benzene, toluene, aniline, nitro benzene, ethyl acetate, acetone, benzoyl chloride, brom benzene and carbon disulphide. It is sparingly soluble in petroleum ether, and insoluble in water and hydrochloric acid. It is dissolved by concentrated sulphuric acid with slight charring and by concentrated nitric acid with apparent oxidation, brown fumes being given off.

2-Nitro phenyl ether-4'-carbonic acid— $NO_2.C_6H_4.OC_6H_4.COOH$ —This acid was prepared by dissolving the above mentioned ether in glacial acetic acid (which had been prepared by distilling Kahlbaum's glacial acetic acid from chromic acid) warming on the steaming water bath and adding very slowly a cold solution of chromium trioxide in glacial acetic acid until a test portion failed to become turbid upon diluting with a large amount of a weak solution of sodium hydroxide. To accomplish this, three or four times the theoretical quantity of chromium trioxide was necessary. To a portion of the ether many times the theoretical quantity of chromium trioxide sufficient for oxidation was added and no trace of the acid could be found in the solution. The acid itself had thus probably become completely oxidized. When the oxidation of the ether was judged to be complete, the acid was precipitated from the acetic acid solution by diluting with a large amount of

water. It was purified by washing with water, dissolving in weak ammonia and filtering to remove any traces of the original mother substance, reprecipitating with hydrochloric acid and recrystallizing from dilute alcohol two or three times. The yield in the first experiment was 24 per cent of theory. Later experiments apparently yielded better results, but the resulting quantity of acid was not weighed. The pure acid melts at 182-3° C. It is of a light yellow color and has no taste. It is slightly soluble in hot water, from which on cooling it crystallizes out in tufts of radial needles. It is insoluble in petroleum ether, sparingly soluble in sulphuric ether, but is very soluble in warm alcohol and in dimethyl aniline, benzaldehyde, nitro benzene, toluene, glacial acetic acid and glycerine. The acid was analyzed by determining the amount of silver in the silver salt which yielded results as given below. In the second analysis the silver salt had darkened somewhat by being allowed to remain some time in contact with a solution of silver nitrate during the process of manufacture:

	Calculated for $\text{AgC}_{13}\text{H}_9\text{NO}_6$	I.	II.
Ag.	30.09	30.09	30.59

A portion of the acid was dissolved in dilute ammonium hydroxide, the excess of ammonia evaporated off and observations made as to the character of the precipitates yielded by various metallic salts, with results as follows:

Copper sulphate.....	light greenish blue.
Aluminum chloride.....	white.
Lead nitrate.....	white flocculent.
Manganese chloride.....	white.
Cobalt chloride.....	light pink.
Magnesium sulphate.....	white.
Ferric chloride.....	yellowish white.
Ferrous sulphate.....	light yellow.
Cadmium chloride.....	white crystalline.
Mercuric chloride.....	white.
Platinum tetrachloride.....	yellow.

Nickel, calcium, strontium and barium salts yielded no precipitate with the dilute solutions used. The solution was very dilute, and in some cases would undoubtedly have yielded a precipitate if it had been more concen-

trated as e. g., the barium salt. When the acid is dissolved in a solution of sodium, potassium or ammonium hydroxide a deep yellow colored solution is obtained.

Silver-2-nitro-4'-phenyl ether carbonate— $\text{AgOOC}\cdot\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\cdot\text{NO}_2$ —The silver salt was prepared by dissolving a portion of the acid in dilute ammonium hydroxide, evaporating off the excess of ammonia and precipitating with silver nitrate. It separates out in pinkish curdy lumps. It is sufficiently soluble in water to yield a slight turbidity when hydrochloric acid is added to the solution. When pure and dry it is very stable and is not decomposed by direct sunlight, even when exposed for several hours. It is insoluble in inorganic solvents in general, and melts with decomposition at about 220°C . One part of the salt is soluble in 2180 parts of water at ordinary room temperature.

Barium-2-nitro-4'-phenyl ether carbonate— $\text{Ba} [\text{OO}\cdot\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\cdot\text{NO}_2] + 1\frac{1}{2}\text{H}_2\text{O}$.—The barium salt was prepared by adding a little more than the theoretical quantity of barium hydroxide to a strong water solution of the ammonium salt obtained as given above in the manufacture of the silver salt. The excess of barium was precipitated from the solution by passing in a stream of carbon dioxide. The salt crystallizes out from a hot water solution on cooling in pearly flesh-pink scales. One part of the salt dissolves in 122 parts of boiling water and in 948 parts of cold water. Before making an analysis it was dried over sulphuric acid for several days and then dried in the air bath for three or four hours at $100\text{--}110^\circ\text{C}$. Between 80 and 100 degrees it took on a much deeper hue, which seemed to be permanent and lost water corresponding to $1\frac{1}{2}$ molecules. Two analyses resulted as follows:

Calculated for $\text{Ba}(\text{C}_{18}\text{H}_8\text{NO}_5)_2 + 1\frac{1}{2}\text{H}_2\text{O}$.	I	II
Barium.....	19.37 per cent	19.32 per cent.
Loss of water....	7.64	7.03

2-amido-4'-methyl phenyl three— $\text{H}_2\text{N}\cdot\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\cdot\text{CH}_3$ —The amido ether was prepared by dissolving the previously described phenyl ether in alcohol and water and reducing with tin and hydrochloric acid while warming on the

water bath to 40 or 50 degrees. During the reduction the solution was sky blue, but when complete it usually changed to a pinkish color. The end of the reaction was determined by taking a test portion and diluting with several times its own volume of water. If any unreduced ether was present it would be precipitated, forming a white turbidity. The tin was removed from the solution by means of hydrogen sulphide and, on concentration on the water bath, the hydrochloride crystallized out in white needles, which were very stable when dry, but unstable in contact with water. The hydrochloride melts at 220° C. It is somewhat soluble in hot, but much less soluble in cold water, and insoluble in organic solvents in general. The constitution of the compound was ascertained by determining the platinum in the platinum salt, as given below.

An attempt to prepare the free base by precipitating it with an alkaline hydroxide from a water solution of the hydrochloride proved unsuccessful. It decomposed in the bell jar over sulphuric acid before it could be thoroughly dried.

4-Methyl-2'-amido phenyl ether chlor-platinate— $(\text{CH}_3\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\text{NH}_2)_2\text{H}_2\text{PtCl}_6 + 1\frac{1}{2}\text{H}_2\text{O}$ —The platinum salt was prepared by precipitating the amido hydrochloride in water solution with chlorplatinic acid. It is of a greenish yellow color and melts with decomposition at 150° C. The salt was dried for several days over sulphuric acid and then in the air bath at 100-110° C for three or four hours when it lost weight corresponding to one and one-half molecules of water. On being heated it assumes a much deeper tint, but on coming in contact with the air again it acquires its original color. It is very hygroscopic and gains weight very rapidly while being weighed. An analysis resulted as follows:

Calculated for $(\text{C}_{13}\text{H}_{13}\text{NO})_2\text{H}_2\text{PtCl}_6 + 1\frac{1}{2}\text{H}_2\text{O}$		Found.
Platinum.....	24.1 per cent	24.1 per cent.
Loss of water	3.28	3.03

A further study of diphenyl ether derivatives is being carried on in the chemical laboratory of Morningside Col-

lege, and as this paper is to be made the basis for future work a bibliography of diphenyl ethers is here appended.

BIBLIOGRAPHY.

(1) Ann. 90, 209.—List and Limpricht obtained diphenyl ether as one of the products of the destructive distillation of copper benzoate.

(2) Ann. 125, 328.—Rudolph Fittig obtained diphenyl from the above mentioned distillate.

(3) Ann. 138, 375.—C. Lesimple obtained a compound by distilling phenyl phosphate with lime, which he called phenyl ether.

(4) Ann. 159, 191, and Ber. 3, 747.—W. Hoffmeister prepared phenyl ether by treating diazo-benzene sulphate with phenole and made a thorough study of the compound.

(5) Ber. 23, 3709.—Hirsch varied Hoffmeister's method and greatly increased the yield.

(6) Ber. 6, 564.—Maikopar made a dinitro derivative by acting on dinitro chlor benzene with an alcoholic solution of potassium hydroxide and phenol.

(7) Ber. 13, 887.—Willgerodt prepared a tetra nitro-derivative by heating dinitro-potassium phenolate with dinitro-chlor benzene in a sealed tube.

(8) Ber. 14, 187.—Merz and Weith prepared pheny ether by heating phenol with zinc chloride, and also aluminum chloride (see also correspondence, Ber. 12, 1925.)

(9) Ber. 15, 1123.—Niederhausern prepared methylene diphenyl-oxide by distilling sodium phenolate with sodium meta-phosphate.

(10.) Ber. 17, 1764.—Willgerodt and Huetlin prepared derivatives by acting on potassium phenolates with dinitro-chlor benzene and pikryl chloride.

(11) Ber. 17, 2638.—Bausch prepared a dimethyl derivative by heating para-cresol with zinc chloride.

(12) Ber. 29, 1446.—Hæussermann and Teichman prepared various derivatives by acting on halogen-nitro benzene derivatives with potassium or sodium phenolates.

(13) Ber. 29, 1878.—F. Ullman, independently from the above mentioned investigators, made a few compounds by the same method.

(14) Ber. 29, 2083, and *Ibid*, 30, 738.—Haeussermann and Bauer continued the work begun by Haeussermann and Teichman and prepared numerous compounds.

(15) Jr. Chem. Soc. (Lond.), 41, 5, and *Ibid*, 49, 27.—Gladstone and Tribe prepared phenyl ether and derivatives by distilling aluminum phenolate, aluminum thymolate, and aluminum cresolates.

(16) Chem. News, 42, 3.—See No. 15 above.

(17) Chem. News, 42, 146.—See No. 8 above.

(18) Jr. Pr. Chem. 1, 143.—See No. 4 above.

(19) Jr. Pr. Chem. (2) 28, 273.—Klepl prepared carbonyl phenyl oxide by the action of triphenyl phosphate on sodium salicylate.

(20) Jr. Pr. Chem. (2) 28, 193.—Klepl prepared phenyl ether by distilling para-phenoxy benzoic acid with caustic baryta.

(21) Jr. Pr. Chem. (2) 28, 201.—Richter prepared diphenyl oxide by distilling sodium salicylate and triphenyl phosphate.

(22) Monats Hefte, 17, 65.—B. Jeitles distilled calcium phenyl phosphate and obtained, among other things, diphenyl ether.

(23) Gazzetta, 28 (1), 197.—G. Ortoleva and A. Paratoner treated diphenyl ether with sulphonyl chloride and obtained chlorine derivatives. (Abstract in Journal of the London Chemical Society, 1898.)