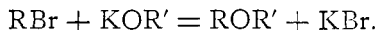


## DERIVATIVES OF PHENYLETHER. V.

BY ALFRED N. COOK.

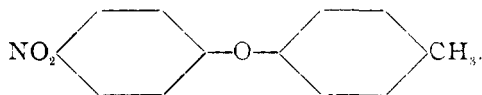
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For some time past I have been engaged in the study of the derivatives of phenylether, using a reaction that is of common application in both the fatty and aromatic series, that of treating a fatty or aromatic haloid with an alcoholate or phenolate of an alkali metal. An ether is formed and an alkali salt of a haloid acid is precipitated according to the following equation:



It has been found<sup>1</sup> that an aromatic bromide or chloride containing a nitro group in the ortho or para position reacts with great readiness upon potassium phenolates to produce derivatives of phenylether. During the past three years I have extended this method to the cresols. Success has attended each attempt to combine a potassium cresolate with a bromnitrobenzene, and each of the mother substances has yielded a number of derivatives.

### 4-NITRO-4'-METHYL PHENYLETHER,



This compound was prepared by the action of parabromnitrobenzene upon potassium paracresolate (prepared as described in a previous article.<sup>2</sup>) Equimolecular quantities of the two reacting substances were heated together in an oil-bath. Action began at 110°, as was shown by the agitation of the fused mass, and rose during the action to 125°. The phenylether could not be extracted from the precipitated potassium bromide with ethyl ether as had been previously done with its analogues, on account of its sparing solubility in that menstruum, and it was found that the substance could be separated from the parabromnitrobenzene not acted upon, and other substances, by simple fractional distillation under diminished pressure, instead of distilling them off with steam as had been previously done in analogous cases. The

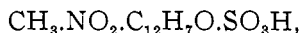
<sup>1</sup> *Ber. d. Chem. Ges.*, **29**, 1446 and 1878.

<sup>2</sup> *Am. Chem. J.*, **24**, 526.

method was afterwards found to give good results with other analogues, as has already been described in the two previous papers. The yield was about 1.25 grams of the nitromethylphenylether for every gram of the cresol used. After purifying as much as possible by repeated fractional distillation *in vacuo*, it was crystallized several times from hot alcohol.

4-Nitro-4'-methyl phenylether is a sulphur-yellow, crystalline substance which speedily turns brown on exposure to light, and melts at 66°. It is soluble in benzene, sparingly soluble in sulphuric ether, and insoluble in petroleum ether. It is much less soluble in cold than in hot alcohol which renders it very readily crystallized. It boils at 225° under a pressure of 25 mm. It has no taste but feels like sulphur when taken into the mouth. It had an odor of parabromnitrobenzene from which it could not be freed by fractional distillation and repeated crystallization from alcohol. An attempt to oxidize the side-chain to carboxyl by means of chromic acid in acetic acid solution was unsuccessful. The substance was entirely destroyed. An analysis gave 6.27 per cent. N; calculated, 6.11 per cent.

4-NITRO-4'-METHYL PHENYLETHER SULPHONIC ACID,



was prepared by the same method as its analogues described in previous papers. When a solution of the acid was evaporated to a small bulk it separated as a thick, red, syrupy liquid which, when dissolved in hot water, crystallized in light yellow needles which melted at 102°. A water solution is much yellower than the substance itself. 8.4 parts of the acid are soluble in 1000 parts of water at 80°. The purified acid is almost tasteless in the solid form, while the syrupy liquid has a sharp odor and taste, probably due to decomposition products formed during evaporation. Its composition was determined by the analysis of the barium salt.

*The barium salt*,  $(\text{CH}_3\cdot\text{NO}_2\cdot\text{C}_{12}\text{H}_7\text{O}\cdot\text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$ , was prepared by the method described in previous papers. It crystallizes from a water solution in warts of a light yellow color which turn brown on exposure to light, if but slightly moist. The substance has a bitter taste and its water solution is yellow. 20.8 parts of the salt are soluble in 1000 parts of water at 15°, and

128.6 parts are soluble in 1000 parts of water at the temperature of the boiling water-bath. When heated in the air-bath at 100° it turns to a sulphur-yellow color and loses in weight corresponding to 1 molecule of water of crystallization. At this stage it is hygroscopic and when exposed to the air increases to its original weight. When heated to 168° it loses in weight corresponding to a second molecule of water and becomes white. At this stage it is not hygroscopic. The loss in weight is permanent. Two analyses of the salt desiccated over sulphuric acid resulted as follows :

	Calculated for (C <sub>13</sub> H <sub>10</sub> O <sub>6</sub> NS) <sub>2</sub> Ba + 2H <sub>2</sub> O.	I.	Found.	II.
Barium.....	17.36	17.29		17.21
Water at 100°.....	2.28	2.46		2.49
Water at 168°.....	2.28	2.23		2.33

The sodium salt, CH<sub>3</sub>.NO<sub>2</sub>.C<sub>12</sub>H<sub>7</sub>O.SO<sub>3</sub>.Na + 3½H<sub>2</sub>O, was prepared by precipitating the barium from a water solution of the barium salt with sodium carbonate. The water solution is more intensely yellow than that of the barium salt. On evaporating to a small bulk it crystallized out in radial aggregations of leaf-like crystals. It is soluble in alcohol and 62 parts of the salt are soluble in 1000 parts of water at 20° C. After desiccation over sulphuric acid it was heated in the air-bath to 100°, when it lost in weight corresponding to 3.5 molecules of water of crystallization. Two determinations of the water of crystallization resulted as follows :

	Calculated for C <sub>13</sub> H <sub>10</sub> O <sub>6</sub> NSNa + 3½ H <sub>2</sub> O.	I.	Found.	II.
Water.....	15.99	15.97		15.97

4-AMINO-4'-METHYL PHENYLETHER, NH<sub>2</sub>.C<sub>6</sub>H<sub>4</sub>OC<sub>6</sub>H<sub>4</sub>.CH<sub>3</sub>, was prepared from the hydrochloride salt mentioned below by precipitating from a water solution with ammonium hydroxide. It is a snow-white substance which is soluble in alcohol, insoluble in ether, and melts at 122°. It is soluble in hot water from which it crystallizes on cooling in white flakes.

The hydrochloride salt was prepared from the corresponding ether by reducing with tin and hydrochloric acid in alcoholic solution while warming on the water-bath, and precipitating the tin with hydrogen sulphide. It showed some tendency to decompose while evaporating to crystallization. It is very soluble in water

but does not crystallize from it successfully. It crystallizes readily from a hot solution of strong hydrochloric acid in long needles or glistening flakes.

The *hydrobromide* was formed by dissolving the free amino compound in hydrobromic acid. Its appearance is very much like the hydrochloride. The amino compound dissolves with some difficulty in dilute sulphuric acid to form the *sulphate*. It crystallizes out in glistening flakes. The *nitrate*, formed in a similar manner, crystallizes from the acid solution, on cooling, in flat needles.

The *platinum salt*,  $(\text{CH}_3\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\text{NH}_2)_2\text{H}_2\text{PtCl}_6 + \text{H}_2\text{O}$ , was prepared by adding a solution of chlorplatinic acid to a strong solution of the hydrochloride. It does not precipitate immediately, unless the solutions are very strong, but in a few minutes fine yellow crystalline needles are formed. When moist it turns brown in diffused light, but when dry the direct sunlight does not affect it. The melting-point is  $195^\circ$ . When heated to  $100^\circ$  in an air-bath it became dark colored and lost in weight corresponding to 1 molecule of water of crystallization. Analyses for platinum and water resulted as follows:

	Calculated for $(\text{C}_{13}\text{H}_{13}\text{NO})_2\text{H}_2\text{PtCl}_6 + \text{H}_2\text{O}$ .	I.	Found.	II.
Platinum.....	23.61	23.40		23.85
Water at $100^\circ$ .....	2.18	2.47		....

NITRO-4-NITRO-4'-METHYL PHENYLETHER,  $(\text{NO}_2)_2\text{CH}_3\text{C}_6\text{H}_4\text{O}$ .

Strong nitric acid was added to a quantity of 4-nitro-4'-methyl phenylether when the temperature rose  $2^\circ$ - $3^\circ$  and the acid turned to a reddish color, the ether apparently dissolving slightly in the acid. On heating to  $80^\circ$ - $90^\circ$  a violent action began, dense brown fumes being given off, which subsided after a few minutes, and there resulted a deep orange-red liquid. On adding water a yellow oil was precipitated, which, on repeatedly being washed with water and kneaded with a glass rod, became viscous and finally solidified. It was purified by crystallizing from hot alcohol, from which it is deposited in radial aggregations of fine needles. Fuming nitric acid produces the same result, as was shown by the crystalline form, melting-point and analysis for nitrogen, but it acts more readily. Action began at  $60^\circ$  and rose of its own accord to  $75^\circ$ .

This dinitromethylphenylether is a very yellow compound which dyes the hands and paper yellow. Its alcoholic solution is intensely yellow, and when agitated with water colors it distinctly yellow. It has a slightly bitter taste, and melts at  $101^{\circ}$ . The mode of formation as well as the analysis for nitrogen would point to its being a dinitromethylphenylether. Found, 10.42 per cent. N; calculated, 10.22 per cent.

NITRO-2-NITRO-2'-METHYL PHENYLETHER.

This was prepared in the same manner as the preceding compound, from the corresponding nitromethylphenylether. It is a sulphur-yellow compound which crystallizes from hot alcohol in well-defined crystals that have very much the same appearance as those of 2-nitro-4'-methyl phenylether. It melts at  $98^{\circ}$ . An analysis for nitrogen gave 10.42 per cent.; calculated, 10.22 per cent.

NITRO-2-NITRO-4'-METHYL PHENYLETHER.

This was prepared by the same method as its analogues. It is light yellow in color and changes to a brownish hue on exposure to light. It was purified by crystallizing from alcohol and melts at  $100^{\circ}$ . An analysis for nitrogen gave 9.95 per cent.; calculated, 10.22 per cent.

NITRO-2-NITRO-3'-METHYL PHENYLETHER.

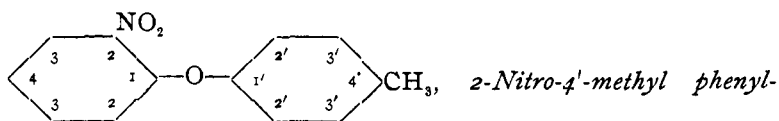
This substance was prepared from the corresponding nitromethylphenylether by the same method as its isomers that have been described. It is yellow and crystallizes from alcohol in radial aggregations of thin plates, which melt at  $106^{\circ}$ . An accident befell the analysis for nitrogen and there was not enough of the substance at hand to repeat it, but, judging from the fact that the other nitromethylphenylethers have yielded a dinitro derivative under the same conditions, it would seem likely that this is also a dinitromethylphenylether.

HEXANITRO METHYL PHENYLETHER,  $(\text{NO}_2)_6 \cdot \text{CH}_3 \cdot \text{C}_{12} \text{H}_9 \text{O}$ .

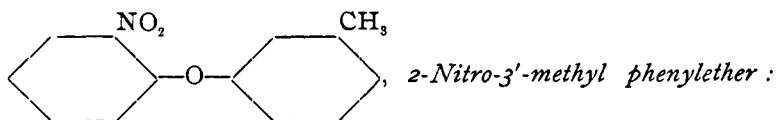
4-Nitro-4'-methyl phenylether was boiled with strong nitric acid for three-fourths of an hour. When the solution was poured into cold water a light yellow oil was precipitated which quickly

solidified. It was purified by crystallization from hot alcohol in which it is very soluble. It is also soluble in benzene, ether, and acetic acid, and sparingly soluble in water. It deflagrates like a nitrate when ignited in the flame of a lamp. Two analyses for nitrogen gave 18.15 and 18.88 per cent. N; calculated, 18.55 per cent.

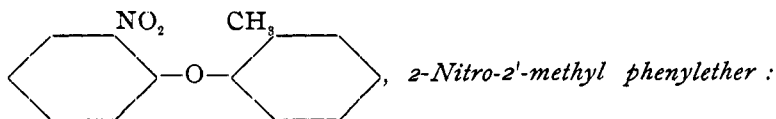
For the sake of greater clearness in comparison the graphic formulas of the six isomeric nitromethylphenylethers are given here:



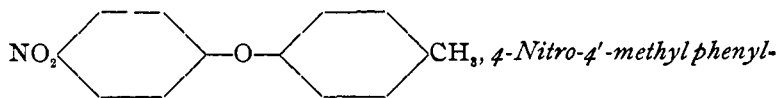
*ether* : melting-point,  $49^{\circ}$  ; free amino derivative unstable when moist.



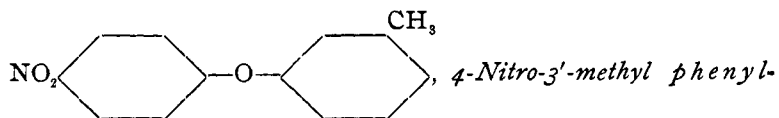
liquid ; free amino derivative very unstable when moist.



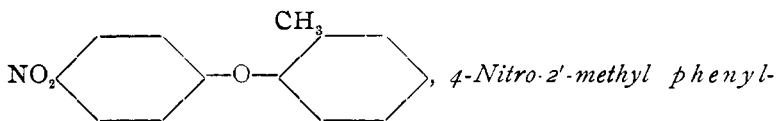
liquid ; free amino derivative very unstable when moist.



*ether* : melting-point,  $66^{\circ}$  ; free amino derivative perfectly stable when moist.



*ether* : melting-point,  $61^{\circ}$ – $62^{\circ}$  ; free amino derivative decomposes slightly when moist.



*ether*: liquid; free amino derivative partially decomposes when moist.

Three of the six isomers are liquids and three are solids. It will be observed that the nearer the nitro and methyl groups are together the greater is the tendency to be a liquid. Of the two intermediate compounds, 4-nitro-2'-methyl phenylether and 2-nitro-4'-methyl phenylether, one is a liquid and one is a solid.

The stability of the free amino derivatives was in proportion to the distance the methyl and amino radicals were apart. The free amino derivative, 4-nitro-4'-methyl phenylether, where the two groups are as far apart as possible, was found to be the most stable. It remained in contact with water for some time without showing any signs of decomposition. 2-Nitro-2'-methyl phenylether and 2-nitro-3'-methyl phenylether where the two groups are as near together as possible are the least stable. They decomposed within a few minutes after being liberated. 2-Nitro-4'-methyl phenylether, where the two groups are one stage further apart, was a little more stable, but it decomposed before it could be dried. The two remaining compounds decomposed only partially while being desiccated.

All of the solid mother-substances are yellow and the liquids are brownish red, due to the presence of the nitro group. Phenylether described by Hoffmeister,<sup>1</sup> and also jointly by Gladstone and Tribe,<sup>2</sup> is a colorless substance. So also are ortho-, meta-, and paracresyl ethers described by the latter chemists.<sup>3</sup>

All of the nitro phenylethers that were examined decomposed when boiled under ordinary atmospheric pressure but distilled unchanged in a good vacuum. This would seem to be due to the oxidizing action of the nitro group, since the original phenylether described by Hoffmeister as well as the ditolyl ethers described by Gladstone and Tribe distil unchanged under ordinary atmospheric pressure. The nitromethyl phenylethers

<sup>1</sup> *Ber. d. chem. Ges.*, 3, 748.

<sup>2</sup> *J. Chem. Soc.* (1882), p. 6.

<sup>3</sup> *Ibid.*, (1886), p. 25.

with the nitro group in the para position were not examined in this regard but it is quite possible that they would distil under ordinary atmospheric pressure unchanged. Paranitro phenylether described by Haeussermann and Teichmann<sup>1</sup> distilled unchanged at 320°. The boiling-points under diminished pressure lie quite close together, varying from 196° under a pressure of 30 mm. in case of 2-nitro-2'-methyl phenylether to 230°-233° under a pressure of 30 mm. in case of 4-nitro-3'-methyl phenylether.

All are darkened on exposure to light, but not in the same degree. 4-Nitro-4'-methyl ether seems to be the most sensitive to light.

According to Hoffmeister, chromic acid in acetic acid solution does not affect diphenylether on long-continued heating but I have found that it attacks all of the nitro methyl phenylethers in my hands. 2-Nitro-4'-methyl phenylether, however, first yielded a carboxyl acid by oxidation of the side-chain. Repeated attempts to obtain carboxyl acids with the other isomers were not successful.

All yield a monosulphonic acid derivative by warming with concentrated sulphuric acid on the water-bath. The nitromethylphenylethers differ from phenylether in that, as Hoffmeister found, it yielded a disulphonic acid derivative. They were similar in that they seemed to be capable of existing in two modifications. When a solution of one of the sulphonic acid derivatives is evaporated to a small bulk on the water-bath a thick syrupy liquid separates which is of a deep yellow or red color. (This was at first thought to be possibly due to the action of nitric acid, introduced by the addition of lead nitrate to precipitate the excess of sulphuric acid, but lead chloride was substituted with the same result.) If this is dissolved in hot water and allowed to stand, it deposits white or light yellow crystals which, in every case where the determination was made, melted above 100°. None of them were found to be deliquescent as Hoffmeister found his disulphonic acid derivative to be, but one was hygroscopic after desiccation over sulphuric acid. The sulphonic acid of 2-nitro-2'-methyl phenylether, which was the first derivative prepared, and

<sup>1</sup> *Ber. d. chem. Ges.*, 39, 1446.



which was reported in a previous paper, was obtained only in the syrupy form, but in view of what has been observed since with regard to its isomers, it is very probable that it would also have crystallized, if similar conditions had been supplied. Seven out of ten salts that were analyzed were found to contain water of crystallization, varying from 1 to 4 molecules. Water solutions of all of the acids and salts were more or less yellow whether the acids and salts themselves were yellow or not.

Orthobromnitrobenzene seems to act the most readily upon the potassium cresolates. Parabromnitrobenzene and the potassium cresolates require a continued application of heat for a longer or shorter period.

The specific gravities of 2-nitro-2'-methyl phenylether and 2-nitro-3'-methyl phenylether are about 8.5 per cent. higher than those of diphenylether and ditolyl ether as determined by Gladstone and Tribe and considerably less than that of paranitrophenylether as determined by Haeussermann and Teichman.<sup>1</sup>

There is a marked tendency to crystallize in radial aggregations or warty masses. This property is especially noticeable in the salts of the sulphonic acid derivatives. It was first noted in the barium salt of the disulphonic acid derivative of phenylether, by Hoffmeister.

All yielded a dinitro derivative with great readiness by simply heating with concentrated nitric acid, when they passed into solution. It is possible that some of these substances are identical, since their melting-points, as determined, lie quite close together, *e. g.*, nitro-2-nitro-4'-methyl phenylether, with a melting-point of 100°, and nitro-4-nitro-4'-methyl phenylether, with a melting-point of 101°. Only one of the mother-substances was boiled with concentrated nitric acid for any length of time. It yielded a hexanitro derivative.

Other work is contemplated for the coming year on two or three lines to extend our knowledge of phenylether and its derivatives.

MORNINGSIDE COLLEGE,  
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August 30, 1902.

<sup>1</sup> *Ber. d. chem. Ges.*, 29, 1448.