determination of other precipitates and, in the future, there is no reason why photometry should not take as important a place in chemical analysis as that now occupied by colorimetry.

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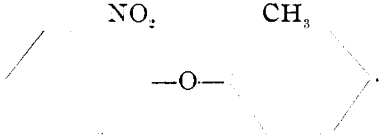
DERIVATIVES OF PHENYLETHER, II.

BY ALFRED N. COOK.

Received August 27, 1901.

IN a paper[1] published a few months since by A. N. Cook and H. W. Hillyer a number of derivatives of phenylether were described which had been prepared by acting on potassium paracresolate with orthobromnitrobenzene, and reducing and oxidizing the resulting compound. During the past six months the work has been extended to orthocresol and metacresol with results as described in the following pages:

2-Nitro-2'-Methylphenylether,



This compound was prepared by the action of orthobromnitrobenzene upon potassium orthocresolate. The reaction is represented by the following equation:

$$NO_2.C_6H_4Br + KO.C_6H_4.CH_3 = NO_2.C_6H_4OC_6H_4.CH_3 + KBr.$$

The potassium orthocresolate was prepared by heating on the water-bath, for several hours, molecular equivalents of orthocresol and potassium hydroxide dissolved in a little water, and then drying in the air-bath until thoroughly desiccated. On cooling, it solidified to a crystalline mass of a light brownish color. It is very hygroscopic.

In the preparation of the ether, molecular equivalents of potassium orthocresolate and orthobromnitrobenzene were heated in an oil-bath. At 137° C., a gentle ebullition began which increased for a few minutes, although the containing flask was removed from the bath, and then gradually subsided. The temperature also rose several degrees during the action. When the action had ceased there remained a copious precipitate of potassium bromide and a supernatant brownish-black liquid. When cool the liquid was

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[1] *Am. Chem. J.*, **24**, 525-529.

extracted with ether. The ether extract was washed with a weak water solution of potassium hydroxide to remove any free cresol which might be present. The orthobromnitrobenzene which remained unacted upon was distilled off with steam and the phenylether was distilled under diminished pressure.[1] Fourteen grams of the crude ether were obtained from 26 grams of orthobromnitrobenzene, or 40 per cent. of theory. Twenty-six per cent. of the orthobromnitrobenzene remained unacted upon.

When two molecular equivalents of the orthobromnitrobenzene were employed to one of potassium orthocresolate, a temperature of 170° C. was required to induce reaction and the yield was much less than with equimolecular quantities. When molecular equivalents of the two reacting compounds were heated with orthocresol as a menstruum, action began at 165° C. The temperature rose to 200° C. although the containing flask was removed from the bath. On cooling, a tarry mass resulted which could not be extracted with ether and no phenylether was obtained from it. Other solvents, such as nitrobenzene, that possess a high boiling-point were used, but no reaction took place, although the temperature was raised 65° C. above the point where they react, when heated together in equimolecular quantities. The first instance would be explained by the free cresol acting on the orthobromnitrobenzene or the resulting compound. The second would be explained on the ground that no ionization of the two reacting substances takes place in the solvents used. An endeavor to prepare the substance by substituting sodium orthocresolate for the potassium compound was also unsuccessful. A tar resulted from which nothing could be extracted with ether.

2-Nitro-2′-methylphenylether is a dark red liquid of 1.195 specific gravity at 20° C. It has an oily taste, and a fruity odor which is probably due to small traces of impurities. It is soluble in organic solvents in general, but is insoluble in water ; is not volatile with steam ; and when subjected to a temperature of 18° C. for several hours it did not solidify. It decomposes when boiled under ordinary atmospheric pressure, but distils unchanged at 194°–196° C. under a pressure of 14 mm. 0.6925 gram of the liquid, dissolved in 41.8 grams of absolute alcohol, gave a rise of the boiling-point of 0.095°. This gives 200.6 as the molecular

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[1] I am indebted to the kindness of Dr. H. W. Hillyer, of the University of Wisconsin, for distilling this compound for me under diminished pressure, as well as the 2-nitro-3′-methylphenylether mentioned farther on.

weight. Theory requires 229. Potassium dichromate in acetic acid solution does not oxidize the side-chain to carboxyl as in case of 2-nitro-4′-methylphenylether. The compound is burned completely when the temperature is but slightly raised. Analyses resulted as follows:

	Calculated for $C_{13}H_{11}NO_3$.	Found.	
		I.	II.
Carbon	68.12	67.97	68.22
Hydrogen	4.83	....	4.50

2-Amino-2′-Methylphenylether Hydrochloride, $CH_3.C_6H_4OC_6H_4.NH_2.HCl$.—The amido compound was prepared by dissolving the previously described phenylether in alcohol and reducing with tin and hydrochloric acid while warming on the water-bath. The action was allowed to continue until a test portion yielded no precipitate when diluted with a large amount of water. The tin was precipitated with hydrogen sulphide and the solution concentrated on the water-bath, when it assumed a slightly pink tint. The hydrochloride does not crystallize but simply separates out in the form of a snow-white wax which coheres readily when pressed together with the fingers. It is readily soluble in ether and alcohol, and moderately soluble in water. A water solution does not yield a chlorplatinate with hydrochlorplatinic acid. Of several attempts to prepare the amido derivative only one was successful. It would invariably decompose while concentrating on the water-bath. The specimen obtained, however, was perfectly stable. It was kept for several days, a part of the time in contact with water. In attempting to prepare the free base by precipitating with ammonia, it decomposed before it could be filtered.

2-Nitro-2′-Methylphenylether Sulphonic Acid, $NO_2.C_{12}H_7O.CH_3.SO_3H$.—The free acid was prepared by dissolving 2-nitro-2′-methylphenylether in concentrated sulphuric acid, diluting with a large amount of water, precipitating the excess of sulphuric acid with lead nitrate, and removing the excess of lead with hydrogen sulphide. The solution was then evaporated on the water-bath and the acid desiccated over sulphuric acid.

It is a reddish-yellow, sirupy liquid which becomes somewhat viscous on cooling, and has an intensely bitter taste. It is readily soluble in petroleum ether, glacial acetic acid, wood alcohol, ethyl alcohol, benzene, nitrobenzene, dimethyl aniline, glycerine, aldehyde, and benzaldehyde. One part of the acid is soluble in about 2.5 parts of water at 80° C. and considerably less soluble in cold water. A weak solution of the acid does not yield a precipitate with any of the metals. Its composition was determined by the analyses of some of its salts which are given below.

Barium Salt, $(NO_2.C_{12}H_7O.CH_3.SO_3)_2Ba$.—This salt was prepared by adding sufficient barium chloride to the diluted sulphuric acid solution of the ether to remove the excess of sulphuric acid and change all of the free sulphonic acid to the barium salt. Owing to the fact that the salt is only sparingly soluble in cold water, most of it was precipitated along with the barium sulphate and had to be extracted from it with boiling hot water, from which it crystallized on cooling in light, fluffy, radial aggregations of fine, cream-white needles. It is almost without taste. 7.45 parts of the salt are soluble in 1000 parts of boiling hot water and 1.2 parts are soluble in 1000 parts of water at 31° C. The water solution is almost colorless. This salt is the least soluble of any here described, and as a consequence the most easily purified. Two determinations of the barium after crystallizing the compound four times from hot water and drying at 150° C. resulted as follows:

I. 0.2394 gram of the substance yielded 0.0731 gram of barium sulphate.
II. 0.5112 gram of the substance yielded 0.1567 gram of barium sulphate.

	Calculated for $(C_{13}H_{10}O_6SN)_2Ba$.	Found. I.	II.
Barium	18.18	17.96	18.04

Strontium Salt, $(CH_3.C_{12}H_7O.NO_2.SO_3)_2Sr + 2H_2O$.—The strontium salt was prepared by the same general method as the barium salt. Strontium nitrate was used to precipitate the excess of sulphuric acid. Some of the salt was thrown down with the strontium sulphate and was extracted with hot water. It crystallizes from a hot water solution in crystalline grains except when allowed to crystallize very slowly, when the crystals resemble snowflakes in form. They are brownish yellow in color and about 2 mm. in diameter. The water solution of the salt is yellow. Twenty parts of the compound are soluble in 1000 parts of boiling hot water, and 6.8 parts are soluble in 1000 parts of water at 31° C. On being dried in the air-bath at 110° C. it lost in weight corresponding to two molecules of water.

I. 0.2326 gram of the substance yielded 0.0104 gram of water and 0.0576 gram of strontium sulphate.

II. 0.2385 gram of the substance yielded 0.0108 gram of water and 0.0595 gram of strontium sulphate.

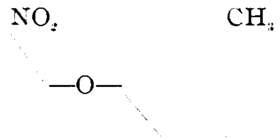
	Calculated for $(CH_3.C_{12}H_7O.NO_2.SO_3)_2Sr + 2H_2O$.	Found. I.	II.
Strontium	11.84	11.82	11.91
Water	4.87	4.47	4.53

Lead Salt, $(CH_3C_{12}H_7O.NO_2.SO_3)_2Pb$.—The same general method was used in the preparation of the lead salt as with the two preceding. Owing to the greater solubility, however, it was not necessary to digest the lead sulphate precipitate with hot water, but it was necessary to concentrate the solution in order to induce crystallization. Its water solution is a deep yellow. It crystallizes in well defined, yellow, crystalline grains. 81.7 parts of the salt are soluble in 1000 parts of boiling water, and 35 parts are soluble in 1000 parts of water at 31° C.

I. 0.3600 gram of the substance yielded 0.1001 gram of lead oxide.
II. 0.2816 gram of the substance yielded 0.0766 gram of lead oxide.

	Calculated for $(CH_3.C_{12}H_7O.NO_2.SO_3)_2Pb$.	Found. I.	II.
Lead	25.15	25.55	25.24

2-Nitro 3'-Methylphenylether,



was prepared by the same general method as the 2-nitro-2'-methylphenylether described in the preceding pages, from potassium metacresolate and orthobromnitrobenzene. The potassium orthocresolate was prepared in the same manner as the potassium orthocresolate. It is a light brown crystalline solid, when prepared by this method. It melts at about 55° C., and liquefies by absorption of water when allowed to remain in contact with the air.

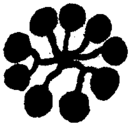
When the temperature of the two reacting substances was raised to 100° C. a gentle ebullition began which increased and the temperature rose to 145° C., although the containing flask was removed from the oil-bath. The action continued for about five minutes and then subsided. There remained a copious precipitate of potassium bromide and a supernatant brown liquid. The yield was almost quantitative in the first experiment but not so good in the second.

This compound is a red, oily liquid. From its appearance it could not be distinguished from 2-nitro-2′-methylphenylether. Its specific gravity is 1.208 at 27° C. It is not volatile with steam; it has an oily taste and a slight, fruity odor, probably due to small quantities of impurities; decomposes when boiled under ordinary atmospheric pressure, but under 30 mm. pressure it distils without decomposition at 223° C. It is very soluble in alcohol, ether, benzene, chloroform, acetic acid, and other organic solvents. It is insoluble in water. An attempt to oxidize the side-chain to carboxyl was unsuccessful. It seemed to burn completely. Owing to the small amount of the substance at hand I was unable to make an analysis, but its composition is sufficiently shown by the analysis of the barium salt of the sulphonic acid derivative.

2-Amino-3′-Methylphenylether Hydrochloride, $CH_3.C_6H_4OC_6H_4.NH_2.HCl$, was prepared in the same manner as the corresponding hydrochloride of 2-amino-2′-methylphenylether. It was more stable, however, during the process of preparation, only decomposing slightly when evaporating the water solution on the water-bath. It is a clear, viscous substance, very soluble in alcohol and ether, but quite sparingly soluble in water. A water solution does not yield a precipitate with hydrochlorplatinic acid. An attempt to prepare the free base was unsuccessful. It was precipitated from its water solution with ammonia, but it decomposed under the bell-jar over sulphuric acid before it could be thoroughly dried.

2-Nitro-3′-Methylphenylether Sulphonic Acid, $NO_2.C_{12}H_7O.CH_3.SO_3H$, was prepared by the same method as the corresponding derivative of 2-nitro-2′-methylphenylether. On concentrating the water solution it crystallizes in short, well defined, yellowish brown needles. It possesses a slightly bitter taste, and is soluble in alcohol, ether, and other organic solvents. Its water solution is yellow and dyes the hands yellow.

The Barium Salt, $(NO_2.C_{12}H_7.CH_3.SO_3)_2Ba + 2H_2O$, was prepared in the same manner as the barium salt of 2-nitro-3′-methylphenylether sulphonic acid. It separates from a weak water solution in crystals about 2 mm. in diameter which resemble snowflakes in appearance, but with a heavier structure. They are light brown in color and are composed of little balls connected to



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the central portion by ligaments as shown in the accompanying drawing. Eleven parts of the salt are soluble in 1000 parts of water at 82° C. and 6.1 parts are soluble in 1000 parts of water at 35° C. When dried in the air-bath at 100° C. for an hour it lost in weight corresponding to two molecules of water.

I. 0.2583 gram of the substance yielded 0.0110 gram of water.

II. 0.2363 gram of the substance yielded 0.0098 gram of water and 0.0683 gram of barium sulphate.

	Calculated for $(CH_3.C_{12}H_7.NO_2.SO_3)_2Ba + 2H_2O$.	Found. I.	Found. II.
Barium	17.36	....	17.01
Water	4.05	4.26	4.15

2-Nitro-4'-methylphenylether Sulphonic Acid, $NO_2.C_{12}H_7O.CH_3.SO_3H$, was made from the corresponding ether previously described[1] by the same method as the analogous compounds already described in this paper. The heat of the boiling water-bath was necessary to induce solution of the ether in the concentrated sulphuric acid. No charring was produced as stated in a previous article.[2] The substance then used, as was afterwards known, was not quite pure. On decomposing the lead salt with hydrogen sulphide and concentrating the water solution, the acid crystallizes out in well-defined crystals of a reddish brown color and a slightly bitter taste. After being desiccated over sulphuric acid it increases in weight rapidly on coming in contact with the air. Its water solution is very yellow. It is readily soluble in alcohol, ether, benzene, glacial acetic acid, and other organic solvents. Ninety-eight parts of the acid are soluble in 1000 parts of water at 31° C. Its water solution does not give a precipitate with any of the metals. Its composition was determined by analyzing the barium salt.

Barium Salt, $(NO_2.C_{12}H_7O.CH_3.SO_3)_2Ba + 5H_2O$.—The barium salt was prepared in the same manner as its analogues. Its solubility in water is the highest and the number of molecules of water of crystallization the greatest of any of the salts described. On account of its greater solubility it was the most difficult to purify by recrystallization. It crystallizes out in yellowish brown warts about $\frac{1}{4}$ inch in diameter on the average. It is insoluble in organic solvents in general, but is soluble in both methyl and

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[1] *Am. Chem. J.*, **24**, 526.

[2] *Loc. cit.*, p. 527.

ethyl alcohol containing a very little water. 691 parts of the salt are soluble in 1000 parts of water at 80° C. and 147 parts are soluble in 1000 parts of water at 27° C. On being heated in the air-bath at 100°-110° C. it becomes somewhat lighter in color and loses in weight corresponding to five molecules of water of crystallization.

0.1792 gram of the substance yielded 0.0167 gram of water and 0.0499 gram of barium sulphate.

	Calculated for $(NO_2.C_{12}H_7O.CH_3.SO_3)_2Ba+5H_2O$.	Found.
Barium	16.25	16.35
Water	9.54	9.33

This study is being continued and extended to the reaction between parabromnitrobenzene and the cresols.

MORNINGSIDE COLLEGE,
SIOUX CITY, IOWA,
August 10, 1901.

OPTICAL ROTATIONS OF CERTAIN TARTRATES IN GLYCEROL.

BY J. H. LONG.

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NEARLY all active substances exhibit different rotations in different solvents. In some cases the causes of these variations, are known while in other and numerous instances no satisfactory explanation of the variable activity has yet been given. The several important factors in this variation in specific rotation have been grouped by Landolt as follows:

a. Electrolytic dissociation in aqueous solution.
b. Formation or breaking down of molecular aggregations.
c. Presence of complex so-called crystal molecules in solution.
d. Formation of hydrates or corresponding bodies with solvent.
e. Hydrolysis.

It was pointed out by Landolt, and confirmed by Oudemans, that in dilute solutions the molecular rotations of salts of active acids are independent of the base combined with the acid, and that in salts of active bases the molecular rotations are independent of the inactive acid. This is well illustrated by the following table in which $[M]_D$ refers to the molecular rotation.