sion that in its nitrogen compounds a bridged oxygen atom shows little tendency towards chemical action, and to apply this conclusion to the study of the valence-problem in other nitrogen-oxygen compounds.

SAN FRANCISCO, August, 1902.

DERIVATIVES OF PHENYLETHER. III.

BY ALFRED N. COOK AND CHARLES F. EBERLY.

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IN papers[1] previously published, accounts were given of the preparation of several derivatives of phenylether by the action of orthobromnitrobenzene upon ortho-, meta-, and paracresolates of potassium, and by reducing, oxidizing, and sulphonating the resulting compounds. During the past few months the work has been continued and extended to the reaction between the cresols and parabromnitrobenzene with results as given in this paper and two others that will follow.

4-NITRO-2′-METHYL PHENYLETHER, $NO_2.C_6H_4—O—C_6H_4.CH_3$.

This compound was prepared by the action of parabromnitrobenzene upon potassium paracresolate (prepared by a method described in a previous article).[2] The reaction is represented by the following equation:

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

Molecular equivalents of the two reacting substances were heated in an oil-bath to 135° C. An action began, as was shown by the agitation of the fused mass, which continued for some time as long as heat was applied. When it was ended the temperature was raised to 160° without inducing any further action. There remained a dark brown liquid and a copious precipitate of potassium bromide. The yield was very good.

The nitro methyl phenylether was separated from the parabromnitrobenzene not acted upon, and other constituents, by fractional distillation under diminished pressure. In a good vacuum it boils about 60° higher than parabromnitrobenzene and much higher than the other contaminating substances.

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[1] *Am. Chem. J.*, **24**, 525-529; This Journal, **23**, 806-813.

[2] This Journal, **23**, 806.

4-Nitro-2′-methyl phenylether is a tasteless, oily, reddish brown liquid which is soluble in organic solvents in general. It did not solidify when subjected to a temperature considerably below zero. An attempt to oxidize the side-chain with chromic acid in acetic acid solution was unsuccessful. The phenylether was entirely destroyed. Under a pressure of 27 mm. it boils at 220°-222°. Two analyses for nitrogen gave 6.36 and 6.45 per cent.. Theory requires 6.11 per cent.

4-NITRO-2′-METHYL PHENYLETHER SULPHONIC ACID,
$NO_2.CH_3.C_{12}H_7O.SO_3H$.

This compound was prepared by dissolving the corresponding ether in a small quantity of concentrated sulphuric acid by the aid of the heat of the boiling water-bath. The solution was then diluted with several volumes of water, the excess of sulphuric acid precipitated with lead chloride, and the excess of lead precipitated with hydrogen sulphide. On concentrating the solution to a small bulk a thick, syrupy, red liquid separated out. On redissolving in hot water and allowing to stand, however, it crystallized out in tufts of white needle-like crystals. After recrystallizing several times it melted sharply at 115°. It is soluble in acids, alcohol, and hot benzene, has a bitter taste, and the syrupy liquid previously mentioned has a sharp piercing odor. It also dyes the hands and cloth yellow while the crystalline substance does not do so. A weak, water solution of the acid did not give a precipitate with any of the metals. Its composition was determined by the analysis of the barium salt given below.

Barium Salt, $(CH_3.NO_2.C_{12}H_7O.SO_3)_2Ba$.—This salt was prepared by adding sufficient barium chloride to the diluted sulphuric acid solution of the ether to remove all of the sulphuric acid and change all of the free sulphonic acid to the barium salt. It is one of the least soluble salts that have been prepared, on account of which most of it was precipitated with the barium sulphate and had to be extracted from it with hot water, from which it crystallized out in yellow crystalline grains, on cooling. 13.27 parts of the salt are soluble in 1000 parts of hot water at the temperature of the boiling water-bath, and 3.77 parts are soluble in 1000 parts of water at 24° C.

It is therefore approximately twice as soluble as the corresponding salt of 2-nitro-2′-methyl phenylether and about half as soluble as the corresponding strontium salt. Two determinations of the barium after purification by recrystallization from water gave 18.38 and 17.89 per cent. barium. Calculated for $(C_{13}H_{10}O_6NS)_2Ba$, 18.18 per cent.

Copper Salt, $(NO_2.CH_3.C_{12}H_7.SO_3)_2Cu + 5?H_2O$.—The copper salt was prepared by treating a water solution of the barium salt with a molecular equivalent of copper sulphate in water. On concentrating the filtrate a greenish yellow powder was obtained which was desiccated over sulphuric acid. On being heated in the air-bath for some time at 100° it lost in weight and turned brown. On being allowed to come in contact with the air for a few hours it increased in weight and assumed its original color. The results of the determination of the water of crystallization were only fairly satisfactory, but corresponded nearest with 5 molecules.

The Sodium Salt was prepared by treating a water solution of the barium salt with a molecular equivalent of sodium carbonate in water. It crystallized as a fine yellow powder which melted at 233°. It is very soluble in water and the solution is much more yellow than the salt itself.

The Potassium Salt, prepared in an analogous manner with the sodium salt, crystallized from a concentrated water solution in small, yellow flakes which melted at 205°.

4-AMINO-2′-METHYL PHENYLETHER, $CH_3.C_6H_4OC_6H_4.NH_2$.

The free amino compound was prepared from the amino hydrochloride described below by precipitation with ammonium hydroxide. It is soluble in alcohol and benzene, insoluble in ether, and melts at about 60°. Its composition was determined by the analysis of the hydrochloride.

The Amino Hydrochloride was prepared by reducing 4-nitro-2′-methyl phenylether with tin and hydrochloric acid in alcoholic solution while warming on the water-bath. The tin was precipitated with hydrogen sulphide and the filtrate concentrated to crystallization on the water-bath when it assumed a pink tint. It crystallized in long needles and scales, but was recrystallized with difficulty, owing to decomposition. It melted at 182°-183°, and is soluble in alcohol, but insoluble in benzene and ether. Two analyses of the hydrochloride for chlorine gave 15.15 and 14.88 per cent. Calculated, 15.08 per cent.

The Nitrate was prepared by dissolving the free amino derivative in dilute nitric acid. On cooling, it crystallized in flaky crystals which melted with decomposition at 153°-155°. It is soluble in alcohol and water, but insoluble in organic solvents in general.

The Sulphate, prepared in the same manner as the nitrate, separates from a water solution on cooling in warty crystals. It melts with decomposition at 155°-160°.

The Hydrobromide, prepared in an analogous manner with the two preceding, is soluble in water and alcohol, but insoluble in organic solvents in general. It crystallizes from a water solution in warty aggregations like the sulphate, and melts with decomposition at 200°-204°.

The Platinum Salt was prepared by precipitation from a water solution of the hydrochloride with a solution of chlorplatinic acid. It is a light brown substance which melts with decomposition at 180°-190°. A specimen which had been desiccated over sulphuric acid, when heated in the air-bath at 100°, lost in weight, but increased to its original weight when allowed to remain in contact with the air for some time. Our substance was not of sufficient purity, on account of the difficulty of purifying the hydrochloride from which it was made, to determine the number of molecules of water of crystallization with a high degree of accuracy, but it is probably one.

DINITRO METHYL PHENYLETHER, $(NO_2)_2.CH_3.C_{12}H_7O$.

In the first article on the "*Derivatives of Phenylether*" attention was called to the fact that nitric acid acted on the nitro-methyl derivatives of phenylether, but until the present no attempt was made to study the reaction. On simply mixing the two substances the temperature was slightly raised and the nitric acid assumed a reddish color. On warming, a violent action set in with the evolution of dense brown fumes, the temperature rose to 90°, and the phenylether passed completely into solution. Continued application of heat did not, apparently, cause any further action. The resulting solution was of a deep red color. On diluting with water there was precipitated a yellow oil. On repeated washing with water and kneading with a glass rod it became viscous and finally solidified, and after repeated crystallization from hot alcohol it melted at 125°.

Nitro-4-nitro-2′-methyl phenylether is a yellow crystalline substance which is soluble in sulphuric ether, petroleum ether, benzene, nitrobenzene and aniline. An attempt to obtain an amino derivative by reducing with tin and hydrochloric acid was unsuccessful, owing to its decomposing when an attempt was made to evaporate the solution to crystallization. The results of the analysis for nitrogen together with its mode of formation, would lead us to the conclusion that it is a dinitro methyl phenylether. Two analyses for nitrogen gave 10.55 and 10.35 per cent. Calculated, 10.22 per cent.

MORNINGSIDE COLLEGE,
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THE DETERMINATION OF MANGANESE IN IRON AND STEEL.

BY JOHN V. R. STEHMAN.

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WALTERS,[1] has shown that ammonium persulphate in the presence of a small amount of silver nitrate can be employed to advantage in place of lead peroxide, for the oxidation of manganese in the colorimetric method.

The writer has been using lead peroxide as an oxidizing agent and titrating the permanganic acid, with a standard solution of sodium arsenite after first filtering free from lead oxides, through an asbestos filter.[2]

In attempting to replace the lead peroxide by the ammonium salt and titrating as before, the silver salt, of course, caused trouble. If, however, the silver salt is thrown out of solution before titration is begun, as insoluble silver chloride, the determination of the permanganic acid by a standard solution of sodium arsenite may be readily accomplished.

The silver salt can be precipitated by a solution of sodium chlo-

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[1] *Age of Steel*, November, 1901 ; This Journal, **24**, R. 12.

[2] Blair's "Analysis of Iron," third edition.