

## DERIVATIVES OF PHENYL ETHER.

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In previous papers by a number of authors it has been shown that under varying conditions of temperature and sometimes in solution in various solvents, the sodium and potassium salts of a variety of phenols react with halogen nitro benzenes (o & p) yielding nitro derivatives of phenyl ether. In this paper the study is extended to the reaction between mono-and-di-nitro brom benzene and the alkaline salts of thymol and carvacrol.

**Potassium Thymolate**—When this substance was prepared by dissolving thymol in a solution of caustic potash in water, according to the common mode of procedure in preparing like salts, on evaporating to dryness a tarry like mass was obtained which gave a very inferior yield of methyl-propyl-dinitro phenyl ether. The best mode of procedure was found to be as follows: An alcoholic water solution of caustic potash was prepared and titrated against standard acid to determine its strength. A measured quantity was evaporated until practically all of the alcohol was believed to be driven off to prevent the formation of a derivative of phenetol. Potassium phenolate of good quality was thus obtained. The office of the alcohol was probably to prevent oxidation by the exclusion of the air on account of its rapid vaporisation.

**3-Methyl-6-Propyl-2'-4'-Dinitro Phenyl Ether** ( $\text{CH}_3$ ,  $\text{C}_3\text{H}_7$ ,  $\text{C}_6\text{H}_3\text{OC}_6\text{H}_3$  ( $\text{NO}_2$ ) $_2$ ) was prepared by mixing equivalent quantities of the two reacting substances and warming on the water bath. A vigorous action ensued accompanied by several degrees rise in temperature. A brown oil resulted which was extracted with hot alcohol and crystallized from that menstruum several times when it melted at  $64^\circ \text{C}$ .

An analysis for nitrogen yielded the following results: Found I 8.93%; II 8.96%. Calculated: 8.86%.

The compound is of a sulphur yellow color and crystallizes in concentric clusters of radiating needles so characteristic of the derivatives of phenyl ether. It is soluble in ether, petroleum ether, benzene, acetone, carbondisulphide and other organic solvents. An attempt to oxidize the side-chain by dissolving in glacial acetic acid and treating with a strong solution of chromic acid while warming on the water bath proved unsuccessful. Likewise an attempt to reduce the nitro group and obtain a free base was unsuccessful on account of the instability of the substance. This is generally, though not universally, characteristic of other nitro derivatives of phenyl ether.

Very few of the nitro-methyl derivatives of phenyl ether readily, likewise, yield a carboxyl derivative by oxidation.

**3-Methyl-6-Propyl-2'-4'-Dinitro Phenyl Ether Sulphonic Acid (SO<sub>3</sub>H, CH<sub>3</sub>, C<sub>3</sub>H<sub>7</sub>, C<sub>6</sub>H<sub>2</sub>OC<sub>6</sub>H<sub>3</sub>, NO<sub>2</sub>, NO<sub>2</sub>)** was prepared by dissolving the mother substance in concentrated sulphuric acid by warming on the water bath, diluting with water, neutralizing with lead carbonate, precipitating the dissolved lead with hydrogen sulphide, and evaporating to crystallization. It crystallizes out in pearly, feathery crystals. The substance is very soluble in both hot and cold water, but practically insoluble if a little sulphuric acid is present. The composition of the acid is sufficiently shown by the analysis of the lead and barium salts given below.

**The Barium Salt (NO<sub>2</sub>, NO<sub>2</sub>, C<sub>6</sub>H<sub>3</sub>OC<sub>6</sub>H<sub>7</sub>, CH<sub>3</sub>, SO<sub>3</sub>)<sub>2</sub> Ba, +4½ H<sub>2</sub>O)** was prepared by dissolving the mother substance in sulphuric acid, diluting with water, neutralizing with barium carbonate and evaporating the filtrate to crystallization. On account of the sparing solubility of the salt in cold water it was necessary to extract the precipitated barium sulphate with hot water. It crystallizes in radial masses so characteristic of phenyl ether derivatives. On heating in the air bath to 110°C it lost in weight corre-

sponding to five molecules of water of crystallization. The following analysis for barium and water was carried out on the air dried salt:

Calculated for	Found	
	I	II
<b>C<sub>32</sub>H<sub>30</sub>O<sub>16</sub>N<sub>4</sub>S<sub>2</sub>Ba, 5H<sub>2</sub>O</b>		
Barium .....	14.95%	15.02%
Water .....	9.90%	9.86%

**The Lead Salt (NO<sub>2</sub>, NO<sub>2</sub>, C<sub>6</sub>H<sub>3</sub>OC<sub>6</sub>H<sub>2</sub>, CH<sub>3</sub>, C<sub>3</sub>H<sub>7</sub>, SO<sub>3</sub>, Pb)** was prepared in a similar manner to the barium salt, using lead carbonate for neutralization. Like the barium salt it was carried down with the lead sulphate and had to be extracted with hot water from which it readily crystallized on cooling. An analysis yielded the following results: Calculated, 20.79%; found, 20.95%. The potassium and sodium salts were prepared by adding the sodium and potassium carbonates to solutions of the barium salt, but no analyses were made. They crystallize very readily from concentrated water solutions.

**2-Methyl-5-Propyl-2'-Nitro Phenyl Ether (CH<sub>3</sub>, C<sub>3</sub>H<sub>7</sub>, C<sub>6</sub>H<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>, NO<sub>2</sub>)** was found to be best prepared by the action of o-brom-nitro benzene on sodium carvacrolate. At first an attempt was made to use the potassium salt by dissolving the carvacrol in a small amount of water containing an equivalent of caustic potash and evaporating on a boiling water bath and drying at 110°C, but without success. There remained a thick, black syrup on cooling which did not prove to be very reactive, and the yield of the phenyl ether derivative was very small.

Potassium carvacrolate was also prepared with alcohol as a solvent as in case of potassium thymolate, but the yield of the phenyl ether derivative obtained from it was very small.

Much better results were obtained by using the sodium salt of carvacrol which was obtained as a gray crystalline mass somewhat less hygroscopic than the potassium salt. It was mixed with a molecular equivalent of brom-nitro benzene and heated on an oil bath to 135°C before the reaction was induced, maintained at that temperature for some time and then distilled under diminished pressure. After distill-

ing off the unchanged nitro brom benzene, the ether came over at a somewhat higher temperature. This substance is a rather viscous, light brownish red liquid and after long standing becomes brown and then almost black, without losing its mobility. It boils at 222°C under 20 mm. pressure. It is seemingly miscible with alcohol and ether in all proportions. Analysis for nitrogen yielded 4.6%; calculated, 5.16%. The composition of the substance is also shown by the analysis of the barium salt of the sulphonic acid derivative.

**2-Methyl-5-Propyl-2'-Nitro Phenyl Ether Sulphonic Acid** ( $\text{NO}_2$ ,  $\text{C}_6\text{H}_4\text{OC}_6\text{H}_2$ ,  $\text{CH}_3$ ,  $\text{C}_3\text{H}_7$ ,  $\text{SOH}$ ) was prepared in precisely the same manner as in the preceding case. It crystallized in tufted plates of short, flat prisms. It is soluble in dilute sulphuric acid, rather soluble in cold water, but more so in hot water. It melts with decomposition at 223°-237°C. When dried at 120° it lost in weight corresponding to two molecules of water of crystallization. It seems likely that the sulphonic acid group enters the nucleus containing the alkyl groups for the reasons stated above. The ease with which the sulphuric acid reacts with the ether is noteworthy.

The Barium Salt ( $(\text{CH}_3, \text{C}_3\text{H}_7, \text{C}_{12}\text{H}_7\text{O}, \text{SO}_3) 2 \text{ Ba } 3 \text{ H}_2\text{O}$ ) was prepared by neutralizing the sulphuric acid solution of the sulphonic acid with barium carbonate and evaporating the filtrate to crystallization. It crystallizes from a hot water solution on cooling in radiating clusters of long white needles. It is somewhat soluble in cold water so that it was found necessary to evaporate and obtain a second crop of crystals. At 100°C it lost in weight corresponding to three molecules of water of crystallization. The salt decomposes at about 150°C. Analysis gave the following results:

Calculated for ( $\text{C}_{16}\text{H}_{16}\text{NO}_6\text{S}$ ) $2 \text{ Ba}_3, \text{H}_2\text{O}$	Found	
	I	II
Barium .....	15.40%	15.27%
Water .....	6.05%	6.16%    6.23%

The calcium salt was prepared in an analogous manner with the barium salt. It crystallizes from hot water, in

which it is sparingly soluble, in thin shining plates. The salt has a yellowish tinge and on heating to 100°C lost in weight corresponding to six molecules of water of crystallization.

The Lead Salt is very soluble in hot water and can be easily and quickly purified. It crystallizes in large clusters of radiating needles which on drying in an air bath lose in weight corresponding to eight molecules of water of crystallization.