

VII.—*On Benzyl-phenol and its Derivatives.*

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BENZYL-PHENOL was first prepared a few years ago by Paternò (*Gazzetta*, **2**, 1), and further investigated by Paternò and Fileti (*ibid.*, **3**, 121—251). These chemists state that by treatment with nitric acid, a nitro-compound may be obtained, and by treatment with bromine dissolved in carbon disulphide, a solid bromo-compound is produced; but these substances do not appear to have been very thoroughly examined. By the action of excess of sulphuric acid for about an hour at 100°, they obtained an uncrystallisable disulphonic acid, which yielded only uncrystallisable salts.

The following experiments were undertaken with the view of obtaining, if possible, more definite information regarding the deriva-

tives of this body. The benzyl-phenol used in the operations to be described, was prepared by the method given by Paternò, viz., by the action of benzyl chloride on phenol in presence of zinc. It was found advantageous to cool the mixture, otherwise the reaction becomes very violent, some of the liquid being often projected from the mouth of the flask. The crude product obtained by distillation was well pressed and crystallised from alcohol, and then melted at 84° , the melting point given by Paternò.

When concentrated pure sulphuric acid, slightly in excess of the quantity required theoretically for the formation of a monosulphonic acid, is added to some benzyl-phenol, and the mixture warmed on the water-bath for a few minutes, the whole dissolves to a clear liquid, which on cooling and standing for a short time solidifies to a crystalline mass. On dissolving this in water, adding ammonia, shaking up with ether to remove any unattacked phenol (which is moderately soluble in water), and then concentrating, an ammonium salt crystallises out in fine needles as the liquid cools. After recrystallisation it yielded, on analysis, the following numbers:—

0.5536 gram of the air-dried salt lost at 100° 0.0336 gram = 6.07 p.c.

Theory for $C_7H_7.C_6H_5(OH)SO_3.NH_4 + H_2O = 6.02$ per cent.

0.2423 gram burnt with oxide of copper by Dumas' method, gave 10.409 c.c. of nitrogen at 0° and 760 mm., equal to 0.0130115 gram = 5.37 per cent. Theory = 5.00 per cent. If potassium carbonate be used instead of the ammonium salt, proceeding otherwise as above, a potassium salt separates in groups of feathery crystals. On analysis it proved to be anhydrous, and gave the following results:—

0.6203 gram gave 0.1813 gram $K_2SO_4 = 0.08127$ gram K = 13.10 p.c.

Theory for $C_7H_7.C_6H_5(OH)SO_3K = 12.91$ per cent.

On adding barium chloride to a solution of either of the above salts, a barium salt separates out, which, after filtering off, may be dissolved in boiling water. On slow cooling it separates out in moss-like crystals. After drying in air they yielded, on analysis, the following results:—

0.501 gram lost at 100° 0.0132 gram = 2.63 per cent.

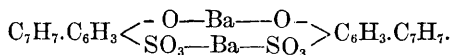
Theory for $[C_7H_7.C_6H_5(OH)SO_3]_2Ba + H_2O = 2.64$ per cent.

0.5454 gram gave 0.189 gram $BaSO_4 = 0.1107$ gram Ba = 20.41 p.c.

Theory 20.66 per cent.

If this barium salt be dissolved in hot water and barium hydrate, or barium chloride and ammonia be added, an almost insoluble basic salt separates in minute glistening crystals. A single analysis gave

36.5 per cent. of barium instead of 34.4 per cent. required for a basic salt of the composition—



The great difficulty of preventing the formation of barium carbonate in preparing this salt, will easily account for the high percentage of barium obtained on analysis.

All the salts of the acid, which have been examined, are but sparingly soluble in water, the mono-barium salt being much less soluble than the alkaline salts, and the di-barium salt almost insoluble. In order to isolate the acid, some of the pure potassium salt was dissolved in water, and acetate of lead added. A very insoluble lead salt was thereby precipitated, which was well washed, suspended in pure water, and decomposed by sulphuretted hydrogen. The clear filtrate was evaporated to a small bulk in a platinum dish, and then placed over sulphuric acid. In a few hours it solidified to a crystalline mass. The quantity hitherto obtained, however, is insufficient for a detailed examination. A further description will follow in a subsequent paper.

The acid and its salts give a splendid violet coloration with ferric chloride.

Potassium Nitro-benzyl-phenol-sulphonate.

If potassium benzyl-phenol-sulphonate be added in fine powder to dilute nitric acid (equal volumes of ordinary concentrated acid and water), keeping the liquid constantly stirred, a sparingly soluble crystalline yellow salt separates out. After recrystallisation and drying at 100°, it gave on analysis the following numbers:—

0.283 gram gave 0.0704 gram $\text{K}_2\text{SO}_4 = 0.03156$ gram $\text{K} = 11.15$ p.c.

Theory for $\text{C}_7\text{H}_7.\text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)\text{SO}_3\text{K} = 11.24$ per cent.

0.224 gram by Dumas' method gave 7.36 c.c. of nitrogen at 0° and 760 mm. = 0.0092 gram = 4.10 per cent.

Theory 4.03 per cent.

This salt is therefore a mononitro-benzyl-phenol-sulphonate. On boiling with potassium carbonate it yields an orange-coloured dipotassium salt.

Potassium Bromo-benzyl-phenol-sulphonate.

When one molecular proportion of bromine is added drop by drop to a solution of potassium benzyl-phenol-sulphonate, keeping the liquid in constant agitation, a white salt separates out, which on recrystal-

lisation from hot water separates in beautiful glistening scales. On analysing the anhydrous salt the following numbers were obtained:—

0·224 gram gave 0·05 gram $K_2SO_4 = 0·0224$ gram $K = 10·00$ p.c.

Theory for $C_7H_7.C_6H_5.(OH)Br.SO_3K = 10·23$ per cent.

0·2108 gram gave 0·1036 gram $AgBr = 0·44085$ gram $Br = 20·91$ p.c.

Theory 20·99 per cent.

The salt is therefore a monobromo-benzyl-phenol-sulphonate.

Trinitrobenzyl-phenol.

If potassium or ammonium benzyl-phenyl-sulphonate in fine powder be added with constant agitation to an excess of ordinary concentrated nitric acid the salt dissolves easily, with scarcely any evolution of red fumes, forming a deep red liquid. If this liquid be exposed to the air in a shallow dish for several hours it becomes semi-solid from separation of a yellow crystalline substance. On diluting more of the yellow substance is precipitated. When well washed with water and recrystallised two or three times from boiling alcohol, the body separates in fine silky needles of a pale yellow colour. It is very sparingly soluble in cold alcohol, and only moderately soluble in the boiling liquid. A specimen crystallised three times melted at 148° , and after a fourth crystallisation the melting point was the same.

The following are the results of analysis:—

0·052 burnt in a vacuum with copper oxide gave 0·0067088 gram nitrogen, 12·90 per cent. N.

(The details of a combustion have been lost, the results only by some oversight having been entered in the note-book.)

	Found.		Theory for $C_{13}H_8(NO_2)_3OH$.
	I.	II.	
C	48·86	—	48·90
H	3·73	—	2·82
N	—	12·90	13·16

These numbers point clearly to a *tri-nitro*-derivative. The percentage of hydrogen is very high, but this was found to be due to the condensation of nitrous fumes in the drying tube. It was found extremely difficult to prevent their formation.

In order to confirm the above numbers some of the substance was boiled up with a dilute solution of pure potassic carbonate. It dissolved to a deep red liquid, which on cooling deposited small orange-

red needles of the potassium-derivative. The dry substance explodes when heated. On analysis it yielded the following numbers:—

- I. 0.069 gram gave 0.0164 gram K_2SO_4 = 0.00735 gram K.
 II. 0.1066 „ „ 0.0258 „ „ K_2SO_4 = 0.011565 „ „

These correspond to the following percentages:—

I.	II.	Required for dinitro-derivative.	* Required for tri-derivative.
10.65	10.85	12.50	10.92

Constitution of the foregoing Bodies.

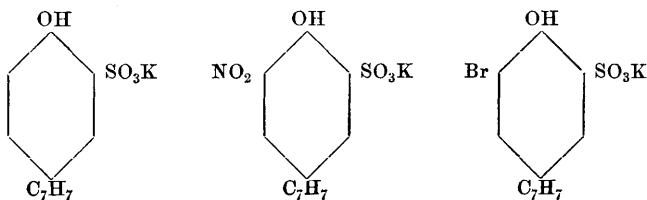
From the mode of formation of benzyl-phenol, from its properties, and from what is known of laws of substitution in phenol, there can be little doubt that it is a para-derivative. No direct proof of this has, however, been given. With the view of solving, if possible, this question, the methyl ether was prepared by digesting the phenol with the theoretical quantity of potassium hydrate, and a slight excess of methyl iodide mixed with some methyl alcohol in a flask attached to a reversed condenser. The action was complete in an hour or two. On distilling the product after thorough washing, the greater part came over from 305—315°. On redistilling this product, the greater part came over between 304° and 308°. The boiling point of this substance, as given by Paternò, who prepared it by the action of benzyl chloride on anisol in presence of zinc, is about 305°, and the product obtained as above agrees in all particulars with that previously described. On oxidation with chromic liquor, the ether yielded only benzoic acid (melting at 121°), but no anisic acid. This result evidently throws no light on its constitution. On oxidation with alkaline potassic permanganate, neither benzoic nor anisic acid is obtained, but a white crystalline substance easily soluble in alcohol and ether, and crystallising from the latter in fine prisms. This body is probably formed by the oxidation of the methylene (CH_2) group, and is in all likelihood a ketone, having the formula $C_6H_5.CO.C_6H_4.O.CH_3$. It is undergoing further investigation.

Oxidation with fused potash remains to be tried, but for want of material I have been compelled to leave it for the present. Should it fail to yield anisic acid, I hope to establish the constitution of benzyl-phenol by another method.

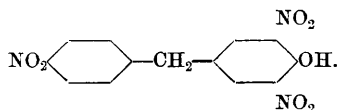
The great resemblance which benzyl-phenol shows to paracresol on treatment first with sulphuric acid and then with nitric acid and bromine, affords strong evidence in favour of the view that it is really a para-derivative.

Armstrong and Field have shown that when paracresol is treated

with sulphuric acid, an ortho-sulphonic acid is produced, and that when the salts of this acid are treated with dilute nitric acid or bromine, the other ortho-position (with regard to the OH group) is taken by the nitro-group or the bromine. The following formulæ therefore represent in all probability the constitution of the potassium salts above described:—



When potassium paracresol-sulphonate is treated with concentrated nitric acid, a diorthonitroparacresol is formed, whereas the corresponding potassium benzyl-phenol-sulphonate yields a *trinitro*-derivative. This is easily explained when it is remembered how easily the benzyl-group is nitrated. This trinitro-body very probably has the constitution:—



Should this be so, it would probably yield paranitrobenzoic acid on oxidation.

Experiments to decide this point, if possible, are in progress, and I hope soon to be in a position to lay before the Society the results of a further investigation of the whole subject.