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XCV.—A New Method of Preparing β -Dinaphthylene Oxide, C₂₀H₁₂O, and the Constitution of its Tetrasulphonic Acid.

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THIS substance has already been prepared in a variety of ways: by heating naphthol with lead oxide (Graebe, Knecht, and Unzeitig, *Annalen*, **209**, 138), by long boiling of naphthol in contact with air (Merz and Weith, *Ber.*, **14**, 200), by heating naphthol with phosphoric anhydride, and by the dry distillation of calcium naphthylate (*Ber.*, **15**, 1122).

Our new method of formation is to heat the sodium salt of Schaeffer's β -naphtholmonosulphonic acid in a metal retort, platinum or copper, to low redness. The distillate condenses almost immediately to a vellowish solid. The total yield from the dry sodium salt is considerable, but was not determined quantitatively; the main portion of this distillate was found to consist of I, β -naphthol; II, β -dinaphthyl ether; and III, dinaphthylene oxide. To separate these three compounds, the distillate was first treated with dilute sodium hydrate solution, in which about 50 per cent. dissolved, and on acidifying the alkaline solution, a very pure β -naphthol, melting at 122°, was Little else appeared to have been dissolved. precipitated. The portion insoluble in soda was then boiled with glacial acetic acid, in which it dissolved completely, and, on slightly cooling, a yellow, fluorescent substance crystallised out, which, on recrystallisation from acetic acid, formed very fine, rhombic plates melting at 153°.

Analysis :---

0.1850 gram substance gave 0.6080 gram CO₂, and 0.0755 gram H_2O .

	Found.		Theory.	
C_{20}	89.62 p	er cent.	89.55 per	cent.
H_{12}	4.23	,,	4.48	,,
0		,,	5.97	,,

With pieric acid in alcoholic solution, a compound is formed which melts at 134°. It forms groups of dark-red needles.

The acetic acid solution evaporated to some extent, on cooling, gave colourless crystals of a substance of low melting point, which, on recrystallisation from dilute alcohol, was obtained in bright, silky plates melting at 105°.

The analysis of this substance and its physical properties show it to be dinaphthyl ether. 0.2010 gram substance gave 0.8536 gram CO_2 and 0.0350 gram H_2O .

	Found. 88.67 per cent.		Theory. 88.88 per cent.	
C_{20}				
\mathbf{H}_{14}	5.25	"	5.18	,,
0		,,	5.94	"

The yield of dinaphthylether thus obtained is between 4 and 5 per cent., and that of dinaphthylene oxide about 25 per cent. of the total crude distillate.

The dinaphthylene oxide agrees in all its properties with the compound described by Knecht and Unzeitig (*Ber.*, **13**, 1724, and (*Annalen*, **209**, 138). It melts at 153°, and boils without any decomposition at a temperature close upon, if not above, 500° .

This method of formation of dinaphthylene oxide from Schaeffer's β -naphtholmonosulphonic acid points quite clearly to its constitution.

Schaeffer's acid has the constitution



The sodium salt of this acid when heated gives sodium sulphite. The two residues unite to form dinaphthol and dinaphthylene oxide respectively.

As a matter of fact, dinaphthol does exist amongst the products of the distillation, but only in very small quantity, for, as might be expected, the high temperature at which the reaction takes place causes the elimination of water and formation of dinaphthylene oxide.



Dinaphthylene oxide is easily sulphonated, either by warming with ordinary strong sulphuric acid, or by dissolving in chloroform and treating with sulphuric acid mixed with 80 per cent. of the anhydride; or by the action of sulphonic monochloride, SO_3HCl . As the sulphonation proceeds, the colour changes from blue to brown, and the solution of the acid in water is also brown. The same stage of sulphonation is obtained by all the above mentioned methods, namely, a tetrasulphonic acid.

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The barium salt of this acid is very soluble in water when first made, and the solution when filtered through animal charcoal is not fluorescent. After evaporating to dryness, the salt is not quite so soluble in water. When slowly crystallised from the original solution, it contains 10 mols. H_2O , which can be driven off at 120° . The less soluble salt contains but 2 mols. H_2O .

 $C_{20}H_8(SO_3)_4Ba_2,10H_2O$ requires 17.6 per cent. water and 26.8 barium.

The ammonium and other salts of this acid have been made, but no particular interest attaches to them.

This sulphonic acid is of interest, because it can be obtained directly from β -naphthol. When β -naphthol is heated with sulphuric acid to a high temperature (120—150°), there is always produced along with the β -naphtholsulphonic acid a certain quantity of sulphonic acid, which does not react with diazo-compounds, and contains therefore no hydroxyl group. The amount of this acid depends on the extent of heating with the sulphuric acid. That these sulphonic acids are derivatives of dinaphthylene oxide can be shown in the following manner:—

The mixture of naphtholsulphonic acids obtained by sulphonating naphthol at a high temperature is made into an alkaline salt, and after the removal of the excess of sulphuric acid with barium carbonate, treated with a diazo-compound. For this purpose diazobenzidine is very convenient, as it forms coloured compounds with all the isomeric naphtholsulphonic acids. These compounds can be precipitated by the addition of salt to their aqueous solutions. The filtrate, which should give no colour reaction on the addition of a little more of the diazo-compound, is somewhat concentrated by evaporation, mixed with an equal bulk of dilute sulphuric acid, and heated in a sealed tube or other closed vessel at a moderately high temperature, 150° or thereabout. By this means all the sulphonic groups are eliminated, and the dinaphthylene oxide separated in a crystalline form. After one or two crystallisations from acetic acid, it is obtained quite pure of m. p. 153°, and is otherwise also identical with the product from Schaeffer's acid above mentioned.

This process can even be watched, as the β -naphtholtrisulphonic acid is gradually converted into dinaphthylene oxide tetrasulphonic acid :—

1. By analysis at different stages of heating, when it is observed

that both the sulphur and the barium (in the barium salt) diminish in amount.

2. By the difference in the colour of the fluorescence of the acid solution, the green fluorescence of the trisulphonic acids passing into blue as the dinaphthylene oxide acids are formed.

3. In a more definite manner by heating naphthol with five times its weight of slightly fuming sulphuric acid quickly to 120—130°, and keeping it at that temperature for one hour. It is then converted completely into the trisulphonic acid. Small weighed quantities of this are taken, rendered alkaline, and titrated with a solution of diazobenzidine of known strength, as long as the colouring matter is formed. From the amount of diazobenzidine solution used, the quantity of the trisulphonic acid can be calculated. If the heating be continued past this stage, sulphur dioxide is formed, and the amount of trisulphonic acid regularly diminishes. This can also be watched by taking analyses at different stages.

- An analysis of the barium salt of a portion immediately after the stage of formation of the trisulphonic acid gave Ba 34.85 per cent. and S 16.15 per cent.
- Barium β -naphtholtrisulphonate requires Ba 35.04 per cent. and S 16.37 per cent.
- After several hours continued heating at 140—150°, an analysis of a barium salt gave considerably less barium : Ba 32.6 per cent. and S 14.8 per cent.
- Barium dinaphthylene oxide tetrasulphonate, $C_{20}H_8(SO_3)_4Ba_2$, dried at 120°, requires Ba 32.54 per cent. and S 15.2 per cent.

It would appear, therefore, that in this action, as in the distillation of the sodium salt first mentioned, the SO_3 groups in the para-position relatively to the hydroxyl are successively removed with simultaneous joining up of the two naphthol rings.

The constitution of this tetrasulphonic acid is also clear from the fact that all the isomeric mono- or di-sulphonic acids of β -naphthol give one and the same trisulphonic acid on further, somewhat drastic, treatment with sulphuric acid; (Limpach, Ber., 16, 726); see also Nietzki (Chem. Zeit., 15, 296; also Jour. Chem. Ind., 10, 6, 536).

As this acid must have the constitution



the only possible constitution for dinaphthylene oxide tetrasulphonic acid is

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1100 METHOD OF PREPARING β -DINAPHTHYLENE OXIDE.



Dinaphthylene oxide is brominated tolerably easily either in acetic or chloroform solution; with a large excess of bromine, a product was obtained crystallising in very slender needles, and almost colourless; it melts at 231°.

On analysis, 0.2578 gram substance gave 0.3353 gram AgBr, or 55.35 per cent. of bromine.

The formula $C_{10}H_8Br_4O$ requires 55.17 Br. It is therefore a tetrabromo-derivative. When less bromine is employed, evidently some lower brominated derivatives are formed; these have lower melting points than the one mentioned, but were not examined further. Chlorine in large excess acting on dinaphthylene oxide in chloroform solution gives a chlorine derivative of similar appearance to the bromine one. It melts at 220°.

Dinaphthylene oxide dissolves in glacial acetic acid very easily, and on adding strong nitric acid to this solution without heating, a nitro-derivative is precipitated in fine, red needles, melting at 185°.

0.2658 gram substance gave 10.3 c.c. N at 763 mm. and $17.4^{\circ} = 4.47$ per cent. N; $C_{20}H_{11}NO_3$ requires 4.47 per cent. of nitrogen.

Attempts to reduce this substance have not as yet been successful. On boiling with strong nitric acid for a little time the nitro-derivative dissolved, and on cooling separated in crystals not very distinct in shape. It was washed with hot acetic acid, dried, and analysed.

0.1264 gram substance gave 13.9 c.c. N at 755.2 mm. and 18° , or 12.5 per cent. nitrogen.

0.1036 gram substance gave 11.4 c.c. N at 754 mm. and 17°, or 12.66 per cent. nitrogen.

C₂₀H₈N₄O₉ requires 12.5 per cent. nitrogen.

It is therefore a tetranitro-derivative. This compound begins to melt at about 250°, but decomposes at the same time.

The mononitro-derivative, when treated with excess of bromine, gives a yellow bromonitro-derivative forming rhombic prisms, somewhat resembling nailhead spar in appearance. It melts at 295°.