

1. Cutinelli, C., Ehrensward, G., Reio, L., Saluste, E. and Stjernholm, R. *Arkiv Kemi* **3** (1951) 315.
2. Hoare, D. S. *Biochem. J.* **87** (1963) 284.
3. Buchanan, B. B., Bachofen, R. and Arnon, D. J. *Proc. Natl. Acad. Sci. U. S.* **52** (1964) 239.
4. Ehrensward, G., Reio, L., Saluste, E. and Stjernholm, R. *J. Biol. Chem.* **189** (1951) 93.

Received October 12, 1965.

## Ozonolysis of Phenols

### IV. 2,3-Dihydroxynaphthalene

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In connection with our studies on the ozonolysis of phenols,<sup>1-3</sup> 2,3-dihydroxynaphthalene has been ozonised in ethyl acetate at 3–4°C. The ozonolysis of *o*-diphenols is of interest in view of the remarkable results of Woodward with the ozonolysis of a veratrol derivative as a step in his strychnine synthesis.<sup>4</sup> Catechol has been ozonized by one of the present authors,<sup>2</sup> but yielded small fragments only, resulting from a complete destruction of the aromatic ring.

Dihydroxynaphthalene readily absorbed ozone, at least five moles being taken up. This, however, leads to a far-reaching degradation of the naphthalene ring-system, and the present investigation is concerned with the reaction with two moles of ozone only.

The ozonation could be followed visually as a brownish-yellow colour developed in the reaction mixture. Maximum intensity of the coloration was obtained after the absorption of one mole of ozone. Thereafter it diminished until the solution was colourless after the absorption of two moles. At this point the ozonation mixture contained active oxygen in an amount roughly corresponding to half the absorbed ozone. After ozonation the solution was treated with water until the active oxygen

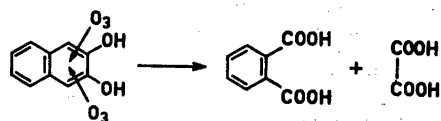
had disappeared. The quantitative determinations of reaction products are summarised in Table 1.

Table 1. Reaction products from ozonolysis of 2,3-dihydroxynaphthalene with 2 moles of ozone.

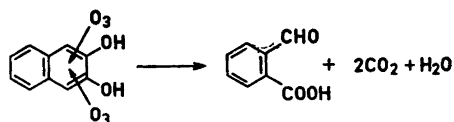
Reaction product	Moles	% recovered C
Carbon monoxide	0.03	0.3
Carbon dioxide	0.83	8.3
Formic acid	0.14	1.4
Oxalic acid	0.35	7.0
Phthalic acid	0.93	74.2

It will be seen that about 91 % of the initial carbon content has been recovered in the reaction products. The deficit is partly due to some intractable, dark tarry matter, which defied purification and identification.

Formation of phthalic acid can be caused by ozone-attack on the bonds adjacent to the hydroxyl groups with rearrangement of the intermediate zwitterion or peroxide:

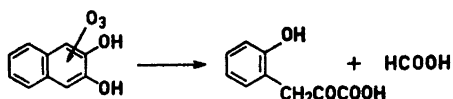


This reaction requires equimolecular amounts of phthalic and oxalic acids in the products, while the found ratio was 0.93:0.35. Obviously a major part of phthalic acid has been formed through a different reaction path. Evidence for this is found in the fact that, if hydrolysis of the ozonation mixture was omitted, phthalaldehydic acid was isolated in an amount of 0.49 mole per mole of starting material. The same mode of attack as before can be envisaged, but followed by a different rearrangement:



Further oxidation to phthalic acid is then effected by peroxidic substances, e.g. hydrogen peroxide during hydrolysis.

Assuming ozone attack on the hydroxylated ring exclusively, the formic acid must stem from carbon atoms 1 or 4. Rearrangement after attack by one molecule of ozone can give one molecule of formic acid and one molecule of a keto-acid:



The keto-acid has not been found in the reaction mixture, which is not surprising since it must be susceptible to ozone attack and may also contribute to the formation of tarry matter.

Combination of the three mentioned reaction paths can give approximately the reaction products in their proper proportions. Starting with the determination of oxalic acid as the most accurate one, 35 % participation of the first reaction gives the correct value for oxalic acid and 0.35 mole of phthalic acid. 49 % participation of the second reaction gives 0.98 mole of carbon dioxide, which is somewhat more than found, and 0.49 mole of phthalaldehydic acid. Quantitative oxidation of this gives together with the before-mentioned figure 0.84 mole of phthalic acid as compared to 0.93 mole found. 14 % participation of the third reaction gives the right amount of formic acid.

The encountered differences are partly due to inherent difficulties in the analytical procedures and partly due to the fact that the ozonolysis of 2,3-dihydroxynaphthalene is more complex than so far disclosed.

Carbon monoxide is found in very small amounts and are consequently of minor concern to the reaction schemes. It is probably formed by thermal decomposition of a formyl intermediate.

*Experimental. Ozonolysis.* The ozonation technique and the decomposition with water

are described previously.<sup>1</sup> Ozone absorption and active oxygen were also measured as usual.<sup>3</sup>

*Reaction products:* In all runs 10 g of dihydroxynaphthalene was used.

- a) Carbon monoxide was determined as before.<sup>5</sup> Found: 47 mg (mean).
- b) Carbon dioxide.<sup>1</sup> Found: 2.28 g (mean).
- c) Formic acid.<sup>1</sup> Found: 0.39 g (mean).
- d) Oxalic acid.<sup>1</sup> Found: 2.76 g (mean).
- e) Phthalic acid. After hydrolysis the aqueous phase and the ethyl acetate were separated. The former was extracted repeatedly with ether and the two organic solutions evaporated to dryness in a stream of warm and dry air. The residue consisted in both cases of a yellowish semisolid mass, which upon treatment with chloroform gave fairly pure phthalic acid. This was weighed, recrystallised from water and identified through its m.p., and mixed m.p. as well as through its infra-red spectrum. Found: 9.60 g (mean).
- f) Phthalaldehydic acid. The ozonised solution was concentrated to a small volume, warmed gently and petrol ether added until a slight turbidity prevailed. An oil which partly crystallised separated and when this was triturated with a small amount of chloroform, a white substance, m.p. 98–99°C, was obtained. This was weighed, recrystallised and identified as phthalaldehydic acid through its m.p. and mixed m.p., its 2,4-dinitrophenylhydrazone, semicarbazone and infra-red spectrum. Found: 4.62 g (mean).

1. Bernatek, E. and Frengen, C. *Acta Chem. Scand.* **15** (1961) 471.
2. Bernatek, E., Møskeland, J. and Valen, K. *Acta Chem. Scand.* **15** (1961) 1454.
3. Bernatek, E. and Frengen, C. *Acta Chem. Scand.* **16** (1962) 2421.
4. Woodward, R. B., Cava, M. P., Ollis, W. D., Hunger, A., Daeniker, H. U. and Schenker, K. *J. Am. Chem. Soc.* **76** (1954) 4749.
5. Bernatek, E. *Tetrahedron* **4** (1958) 213.

Received October 5, 1965.