XLI.—A *Third Naphthaquinone*.

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OF the four naphthaquinones indicated by theory, viz.:—

I.

II.

III.

IV.

only the first and second are at present known, these being the familiar compounds α - and β -naphthaquinone respectively (Groves, this Journal, 1873, 209; and Stenhouse and Groves, *ibid.*, 1877, ii, 52). In 1885, Ekstrand made the important observation that heteronuclear di-derivatives of naphthalene of the form $\alpha'_1 \alpha_1$ behaved in the same manner as ortho-derivatives (*Ber.*, 1885, 2881), a discovery which was confirmed and extended by Bamberger and Philip, in their interesting researches in connection with the constitution of acenaphthene and pyrene (*Ber.*, 1887, 237). This observation rendered possible theoretically the existence of a third ortho- (peri-) naphthaquinone, a compound which has not hitherto been prepared. By the action of nitric acid (sp. gr. 1.1) on acenaphthene, Quincke obtained

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two years ago a nitro-naphthaquinone, which is no doubt the nitro-derivative of the periquinone (*Ber.*, 1888, 1460).

In a paper recently communicated to the Society (*Trans.*, 1890, 393), we stated that by the action of fuming nitric acid on dibrom- α -naphthol we obtained, in addition to the monobromindone described in our paper, a small quantity of an insoluble bye-product, which was separated during the crystallisation of the crude indone from alcohol. This compound is formed only in very small quantity, but is invariably present in the crude product. We have in the course of our experiments accumulated just enough to enable us to confirm the statement that this insoluble residue consists of the missing peri-(γ -) naphthaquinone.

The insoluble residue obtained in the manner described was washed repeatedly with hot alcohol till free from all soluble matter. The product was then dried, and two specimens prepared for analysis, one by crystallisation from glacial acetic acid, in which it is but slightly soluble, and the other by crystallisation from nitrobenzene, in which it is more readily soluble. Both specimens were finally washed with alcohol and dried:—

I. 0.1294 gram gave 0.3577 gram CO_2 and 0.0450 gram H_2O .
 II. 0.1468 „ „ 0.4072 „ „ 0.0574 „ „

	Calculated for $\text{C}_{16}\text{H}_6\text{O}_2$	Found.	
		I.	II.
C	75.95	75.39	75.65
H	3.79	3.89	4.36

The quinone forms slender, pale-yellow needles, remarkably insoluble in most solvents, and having no definite melting point. Above 220° , it blackens and decomposes. The compound is not reduced by standing in aqueous sulphurous acid. Reduction was effected by heating the substance with glacial acetic acid and zinc-dust, and filtering the solution into water. The quinone dissolves very slowly on prolonged boiling with dilute caustic soda, the solution being reddish, and giving a yellowish, flocculent precipitate on the addition of hydrochloric acid. On adding phenylhydrazine to the solution of the quinone in glacial acetic acid, a red colour is at once developed, and reddish needles with a metallic lustre separate. This substance, which is probably an azo-compound, dissolves in aqueous alkalis with a reddish-brown colour, and is reprecipitated by acids.

Dihydroxynaphthalene.—The product of reduction of the quinone obtained in the manner described separates from the acetic acid solution on dilution with water, in the form of minute, whitish needles, which become slate-coloured by oxidation on exposure to the air. A,

specimen prepared for analysis by being collected, washed with water, and dried, gave the following result:—

0.1159 gram gave 0.3194 gram CO_2 and 0.0484 gram H_2O .

	Calculated for $\text{C}_{10}\text{H}_6(\text{OH})_2$.	Found.
O.....	75.0	75.16
H.....	5.0	4.64

This dihydroxynaphthalene is distinguished by the following properties:—It is insoluble in hot water, and but slightly soluble in cold alcohol. Its solutions become violet on exposure to the air. A piece of white filter-paper wetted with the solution and exposed to the air gradually acquires an indigo-blue colour. The substance dissolves readily in cold aqueous caustic soda, or in dilute ammonia, the solution rapidly becoming reddish-violet by oxidation, and finally acquiring an indigo-blue colour. A solution of a chromate added to the acetic acid solution of the substance causes a violet coloration, which soon disappears, and the quinone crystallises out. Nitric acid immediately reconverts the dihydroxy-derivative into the quinone. The substance has no definite melting point, but it blackens and shrinks about 205° . The diacetyl-derivative was obtained by heating the substance for a few minutes with acetic anhydride and dry sodium acetate. On dilution with water, the substance separates out in the form of small, whitish, flattened needles collected into stellate bundles. After crystallisation from glacial acetic acid, the melting point was $226\text{--}227^\circ$. This diacetyl-derivative is only very sparingly soluble in alcohol. An analysis gave the result:—

0.1434 gram gave 0.3626 gram CO_2 and 0.0620 gram H_2O .

	Calculated for $\text{C}_{10}\text{H}_6(\text{O}\cdot\text{C}_2\text{H}_3\text{O})_2$.	Found.
C.....	68.85	68.95
H.....	4.92	4.80

The constitution of the dihydroxynaphthalene was proved by its behaviour on oxidation by means of hot alkaline permanganate. After removal of the excess of permanganate by ferrous sulphate and filtration, the alkaline solution was concentrated to a small bulk, acidified by dilute sulphuric acid, and extracted with ether. After the latter solvent had evaporated, there remained a small quantity of a crystalline residue, only just sufficient for purification and the determination of a melting point. After being twice crystallised from water, the melting point was $194\text{--}197^\circ$. Phthalic acid melts at 184° . Of the two hydroxyphthalic acids—

the first melts when rapidly heated at $196-200^{\circ}$ (Jacobsen, *Ber.*, 1883, 1965), and the second at $180-183^{\circ}$ (Graebe, *Ber.*, 1885, 1130). Our acid, which gave the fluorescein reaction with resorcinol, agrees therefore most closely with formula No. I. This leads to the conclusion that the constitutions of the dihydroxynaphthalene and the quinone are:—

We thus have in this compound a type of a peroxide quinone as distinguished from a diketone.

We are at present unable to account for the formation of the quinone under the circumstances described. It is possible that during the bromination of α -naphthol a small trace of peri-monobrom- α -naphthol is produced, and that this, by the action of fuming nitric acid, furnishes the quinone. Experiments to test this suggestion, as well as to obtain the quinone by other methods, will be continued.

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