

**2-Azido-1,4-naphthoquinone.**—An aqueous solution of 2.2 g. of sodium azide was added to a suspension of 5 g. of 2-chloro-1,4-naphthoquinone in 65 cc. of boiling alcohol. The chloro compound soon dissolved and after two minutes the solution was cooled and the orange crystals which separated were collected and washed with alcohol and then with water (90% yield). Crystallized from alcohol, the substance formed yellow prisms melting at 118° with the evolution of gas. Analysis was not attempted.

Nitrogen was evolved when the quinone was treated under various conditions with alkaline hydrosulfite solution, with zinc dust and acetic acid, or with 1,4-naphthohydroquinone, indicating that the azido group is attacked prior to, or along with, the reduction of the quinone group. 2-Amino-1,4-naphthoquinone usually was found as an end-product after air-oxidation, but the reductions were not smooth.

**The Reaction of Hydrazoic Acid with other Quinones.**—Azidohydroquinone corresponding to the description of Oliveri-Mandalà<sup>3</sup> was obtained in 40% yield by adding an aqueous solution of sodium azide (110% excess) to a solution of quinone in acetic acid (instead of from anhydrous hydrazoic acid in benzene). With only a 15% excess of sodium azide a quinhydrone (black needles) of explosive character was obtained. Treated in the same way with a 57% excess of sodium azide, toluquinone was converted

partly into toluquinhydrone, m. p. 96–98°, and partly into an azido-toluhydroquinone. This formed colorless needles from ether-petroleum ether, it turned pink in the sunlight, and exploded when heated. From *ar*-tetrahydro- $\alpha$ -naphthoquinone there was obtained a substance crystallizing as purple-black needles and having the character of a quinhydrone. The substance exploded on being heated, and when shaken with dilute alkali it evolved nitrogen and gave a blue solution.

### Summary

Korczynski's account of the reaction of hydrazoic acid with  $\alpha$ - and  $\beta$ -naphthoquinone is in error, for the reaction products, obtainable in excellent yields, are 2-amino-1,4-naphthoquinone and 4-amino-1,2-naphthoquinone. It is believed that hydrazoic acid adds to the conjugated system of the quinones and that the azidonaphthohydroquinones at once suffer intramolecular oxidation-reduction with the liberation of nitrogen and formation of the aminoquinones.

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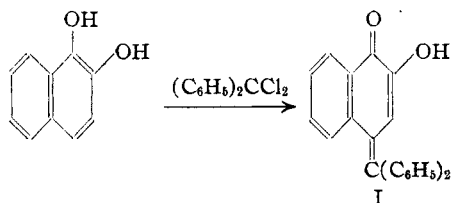
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## The Tautomerism between Diphenylmethyl- $\beta$ -naphthoquinone and Hydroxy- $\alpha$ -naphthofuchsone

BY LOUIS F. FIESER AND JONATHAN L. HARTWELL

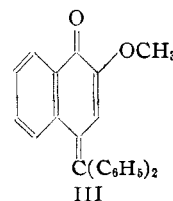
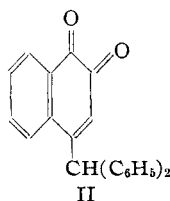
On treating 1,2-dihydroxynaphthalene with benzophenone dichloride in the expectation of obtaining a colorless, inert diphenylmethyle ether, there was produced instead an orange-red, alkali-soluble compound,  $C_{28}H_{16}O_2$ . In view of the ease with which monohydric phenols and naphthols are converted into fuchsones and naphthofuchsones by the same reagent, the reaction can be formulated as follows



The color, acidity and composition of the compound all correspond well with its formulation as 2-hydroxy-1,4-naphthofuchsone-1 (I). Such a substance is unknown in the benzene series, for catechol reacts with benzophenone dichloride to

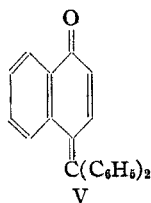
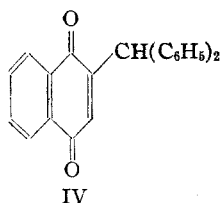
give the diphenylmethyle ether.<sup>1</sup> The greater reactivity of the  $\alpha$ -position of naphthalene probably is responsible for the nuclear substitution observed in the present case.

While there is no doubt about the nature of the reaction, it is a more subtle problem to determine whether the substance exists wholly or chiefly in the naphthofuchsone form I or in the tautomeric form of 4-diphenylmethyl-1,2-naphthoquinone, II. The solubility of the substance in alkali



speaks for the naphthofuchsone structure, and it has been found also that the compound forms an acetate and that it is converted into the methyl ether III by the action of diazomethane.

(1) Sachs and Thonet, *Ber.*, **37**, 3328 (1904).



The isomeric compound IV lacks all of these special properties,<sup>2</sup> and the substance obviously is incapable of existing as a hydroxy- $\beta$ -naphthofuchsone. In the case under discussion it is possible that the substance exists in solution as a mobile equilibrium mixture containing both the fuchsone I and the quinone II.

For the acceptance of such a view it would be necessary to discover in the compound properties specific for the quinone structure. Like a true quinone, the compound is easily reduced by such reagents as sodium hydrosulfite, but so is  $\alpha$ -naphthofuchsone, V. It is not the ease of reduction which distinguishes the quinones from many other classes of reducible substances, but the ability to form on partial reduction an electromotively active system. When tested in this way the condensation product behaved exactly like a true quinone, the titration of the reductant with tetrabromo-*o*-benzoquinone in 50% alcohol (0.1 *N* in HCl, 0.2 *N* in LiCl) at 25° giving a curve of the usual type. With  $\alpha$ -naphthofuchsone (V) and its methoxyl derivative (III), on the other hand, no indication of active oxidation-reduction systems could be found in titrations of both the oxidant and the reductant in various solvents, and it is concluded that the fuchsone structure does not share the property so characteristic of the quinones. Clearly the potential observed in the other case must be due to the presence in the equilibrium mixture of an appreciable quantity of 4-diphenylmethyl-1,2-naphthoquinone. An average value of 0.567 v. was found for the normal potential, and this is 0.134 v. higher than the normal potential of the diphenylmethyl derivative of  $\alpha$ -naphthoquinone, IV.<sup>3</sup> As far as can be judged, the relationship is a usual one, for 4-methyl-1,2-naphthoquinone is 0.124 v. higher in potential than 2-methyl-1,4-naphthoquinone.<sup>3</sup> The value of 0.567 v. is about what would be expected for a compound of the structure II, although the figure seems somewhat high on comparison with the potential of  $\beta$ -naphthoquinone ( $E_0 = 0.576$  v.). Since a correction for the re-

moval of oxidant through tautomerism to the electromotively inactive form I would give a still higher value for the true potential of II, it can be inferred that the quinone form II constitutes a large part (50% at least) of the equilibrium mixture.

According to this analysis the relationship with respect to tautomerism of the diphenylmethyl derivatives of  $\alpha$ - and  $\beta$ -naphthoquinone corresponds to the usual rule that the orthoquinone is more prone to undergo tautomeric change than the paraquinonoid isomer.<sup>4</sup> A particularly clear case is that of the aminonaphthoquinones.<sup>5</sup>

The possible resemblance of the naphthofuchsones to quinones in reactions other than reduction was studied with entirely negative results. We were unable to effect the 1,4-addition to the conjugated system of  $\alpha$ -naphthofuchsone (V) of such typical reagents for quinones as aniline, *p*-toluenesulfonic acid, hydrazoic acid, or sodiomalonic ester. Diazomethane, phenyl azide, methyl azide and 2,3-dimethylbutadiene failed to add to the ethylenic linkage of the quinonoid nucleus. The equilibrium mixture containing the hydroxynaphthofuchsone I resembles 2-hydroxy-1,4-naphthoquinone only in reactions involving an acidic hydroxyl group, for the material cannot be esterified by the Fischer method and fails to condense with aldehydes. The fuchsones are quinonoid in structure but not quinone-like in properties other than color.

### Experimental Part

**Starting Materials.**—1,2-Dihydroxynaphthalene (Compound No. 1) was conveniently prepared by the reduction of  $\beta$ -naphthoquinone in hot aqueous solution with sulfur dioxide, the reaction product separating on cooling as colorless needles, m. p. 56–60°. Analysis (see table) showed that the material contained one molecule of water of crystallization. This is held very tenaciously, for the melting point rose to 101–102° only after repeated crystallization from benzene. The value of 60° given in the early literature<sup>6</sup> is probably for the hydrated product. 6-Bromo-1,2-dihydroxynaphthalene (No. 2), prepared in the same way, formed pale yellow, flat needles melting (and remelting) at 88–88.5° from benzene. According to the analysis, water of crystallization in this case survives recrystallization from benzene. The diacetate (No. 3) forms prisms from alcohol, m. p. 117–118°.

Benzophenone dichloride was prepared most conveniently by the method of Gattermann and Schulze.<sup>7</sup>  $\alpha$ -Naphthofuchsone was obtained in 57% yield by the

(2) Fieser and Hartwell, *THIS JOURNAL*, **57**, 1479 (1935).

(3) Fieser and Fieser, *ibid.*, **57**, 491 (1935).

(4) Fieser, *ibid.*, **50**, 439 (1928).

(5) Fieser and Fieser, *ibid.*, **56**, 1565 (1934).

(6) Liebermann and Jacobson, *Ann.*, **211**, 58 (1882).

(7) Gattermann and Schulze, *Ber.*, **29**, 2944 (1896).

standard method<sup>8</sup> and reduced with zinc dust and acetic acid to 4-diphenylmethyl-1-naphthol,<sup>8</sup> m. p. 170–171.5° (acetate, No. 4, m. p. 140–141°).

**The Fuchson Condensation.** 4-Diphenylmethyl-1,2-naphthoquinone (2-Hydroxyfuchson-1) was prepared by warming a mixture of 8.1 g. of 1,2-dihydroxynaphthalene (m. p. 60°) and 12 g. of benzophenone dichloride on the steam-bath for a short time, the mixture soon setting to a red solid. On crystallization from glacial acetic acid, in which the substance is moderately soluble, orange needles, m. p. 202–202.5° (No. 5) were obtained (14 g.). The compound is soluble in 10% alkali with a deep red color. The 6-bromo derivative (No. 6) was obtained in the same manner in 83% yield from 6-bromo-1,2-dihydroxynaphthalene. It forms bright red needles, m. p. 223–224°, soluble in alcoholic alkali but not in 10% aqueous alkali.

**Derivatives of 2-Hydroxy-1,4-naphthofuchson-1.** The acetate (No. 7), prepared with the use of acetic anhydride and fused sodium acetate, crystallizes from benzene-ligroin as yellow prisms, m. p. 158–159°, dec. The methyl ether (No. 8) was obtained with ethereal diazomethane in a benzene solution of the starting material (yield, 71%); yellow needles from acetic acid, m. p. 177–178°. The azine (No. 9) was prepared with *o*-phenylenediamine in glacial acetic acid solution and crystallized from the same solvent; feathery, yellow needles, m. p. 263–264°.

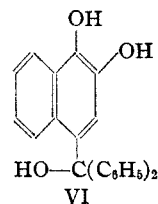
**1,2-Dihydroxy-4-diphenylmethylnaphthalene and Derivatives.**—This reduction product was required for use as reductant in the electrometric titrations and also for a study of its oxidation under other conditions. A suspension of 13.2 g. of the quinone (fuchson) in 75 cc. of glacial acetic acid was warmed with zinc dust until decolorized and the hot solution was filtered into water. The gummy mass which separated was dissolved in dilute acetic acid and treated with sulfur dioxide; on chilling gray crystals separated. After further crystallization the substance was obtained in 68% yield as white needles which rapidly turned gray (No. 10), m. p. 161–161.5°.

The diacetate (No. 11) was obtained by the reductive acetylation of the oxidant and crystallized from glacial acetic acid. The material, m. p. 159–161°, contained acetic acid of crystallization which was lost after vacuum drying at 140° and the sample then melted at 163–164°. The diphenylmethylene ether (No. 12) was obtained from the dihydroxy compound and benzophenone dichloride. It crystallized from benzene-ligroin as colorless needles, m. p. 174–175°.

**2-Methoxy-4-diphenylmethyl-1-naphthol** (No. 13) was prepared by reduction of methoxynaphthofuchson with zinc dust and acetic acid (96% yield) and it crystallized from ether-petroleum ether as long, white needles, m. p. 136–137.5°. The acetate (No. 14) formed white prisms, m. p. 166–167°, from benzene-ligroin.

**Oxidation of the Naphthofuchsons.**—It was of interest to learn if the reduced naphthofuchsons would yield the original materials on oxidation or whether, being triarylmethanes, they would yield carbinols. The only satisfactory method of oxidation found, other than that employed in the electrometric titrations, was with lead dioxide in boiling acetic acid. When treated in this way, 4-diphenyl-

methyl-1,2-dihydroxynaphthalene soon passed into solution and on filtering into water a curdy yellow product was precipitated. The substance formed small, orange-yellow crystals from alcohol-benzene melting with decomposition at 175–176°. Analysis (No. 15) indicated that the substance is a mixture of the carbinol, VI, and the hydroxynaphthofuchson, I, in the ratio 72:28. The two compounds may be formed by independent mechanisms, or I may come from the dehydration of VI. Oxidized in the same way, dihydronaphthofuchson gave an amorphous yellow powder melting at about 80° which could not be crystallized without dehydration to naphthofuchson. The substance had the same character as a sample of the carbinol prepared by the method of Gomberg and Sullivan.<sup>8</sup> We are of the opinion that lead dioxide attacks the methane carbon atom, but that in the titrations in dilute alcoholic solution with tetrabromo-*o*-benzoquinone the hydroxyl hydrogen atoms are directly eliminated, in other words, that either hydroxylation or dehydrogenation may occur according to the conditions of the experiment.



#### ANALYSES

Compound	Formula	Calcd.		Found	
		% C	% H	% C	% H
1	C <sub>10</sub> H <sub>8</sub> O <sub>2</sub> ·H <sub>2</sub> O	67.4	5.66	67.6	5.21
2	C <sub>10</sub> H <sub>7</sub> O <sub>2</sub> Br·H <sub>2</sub> O	46.8	3.53	46.8	3.91
3	C <sub>14</sub> H <sub>11</sub> O <sub>4</sub> Br	52.0	3.43	51.8	3.48
4	C <sub>26</sub> H <sub>20</sub> O <sub>2</sub>	85.2	5.72	85.0	5.97
5	C <sub>23</sub> H <sub>16</sub> O <sub>2</sub>	85.2	4.98	85.2	5.17
6	C <sub>23</sub> H <sub>16</sub> O <sub>2</sub> Br	68.5	3.73	68.2	4.05
7	C <sub>28</sub> H <sub>18</sub> O <sub>3</sub>	81.9	4.75	81.7	4.98
8	C <sub>24</sub> H <sub>18</sub> O <sub>2</sub>	85.2	5.36	85.4	5.58
9	C <sub>29</sub> H <sub>20</sub> N <sub>2</sub>	87.9	5.09	87.7	5.65
10	C <sub>23</sub> H <sub>18</sub> O <sub>2</sub>	84.6	5.57	84.4	5.83
11	C <sub>27</sub> H <sub>22</sub> O <sub>4</sub> ·CH <sub>3</sub> COOH	74.1	5.58	74.0	5.72
12	C <sub>36</sub> H <sub>26</sub> O <sub>2</sub>	87.8	5.48	87.6	5.81
13	C <sub>24</sub> H <sub>20</sub> O <sub>2</sub>	84.7	5.93	84.5	6.13
14	C <sub>26</sub> H <sub>22</sub> O <sub>3</sub>	81.7	5.80	81.5	5.98
15	Mixture	84.0	5.07	83.9	5.12

#### Summary

The product of the condensation of 1,2-dihydroxynaphthalene and benzophenone dichloride exists in solution as a mobile equilibrium mixture of the tautomers diphenylmethyl- $\beta$ -naphthoquinone and hydroxy- $\alpha$ -naphthofuchson. The presence of the latter is recognized by the acidic properties of the substance, while the presence of the quinone form is indicated by the establishment of an electromotively active oxido-reduction system. The fuchsons do not display the properties characteristic of the true quinones with respect to oxido-reduction 1,4-addition and 3,4-addition.

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(8) Gomberg and Sullivan, *THIS JOURNAL*, **42**, 1864 (1920).