4-Phenyl-quinol and its Innermolecular Rearrangements.

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Although simple *p*-alkylated tertiary quinols (VIII) had been widely investigated by Bamberger and his collaborators, *p*-arylated ones are yet unknown. To examine the behaviours of these quinols, the present author has now prepared 4-phenyl-quinole or diphenyl-quinol (III), the simplest of this type, through a modified Bamberger's reaction from 4-diphenylhydroxylamine(1) (I).

The new quinol thus obtained showed many characteristic reactions as *p*-alkylated ones. For example, on heating with alkali it became red, which was so-called quinol reaction, and when reduced by zinc dust and ammonium chloride it gave *p*-hydroxydiphenyl (IV), furthermore by the action of phenylhydrazine 4-benzene-azodiphenyl(2) (V) was produced in place of phenylhydrazone. The absorption curve closely resembled those of dimethyl quinol(3).

However by a mild acetylation 4-phenyl-quinol gave a monoacetate (VI), when refluxed with acetic anhydride and sodium acetate it gave rise to a diacetate which melted at 92° (Diacetate A). It is evident that an innermolecular rearrangement took place under vigorous acetylation as in the case of dibromo-tetralin-quinol(4), on the contrary the 4-methylquinol gave its monoacetate under the same conditions. The course of the reaction is dependent upon the conditions, for using concentrated sulphuric acid in place of sodium acetate another diacetate which melted at 73° was formed (Diacetate B).

According to Bamberger(5) *p*-alkylated quinol can rearrange in two direcitons. When heated with mineral acid or alkali as well as by light, C_4-alkyl migrated to C_3 or C_5 and simultaneously the quinonoid ring recovered his true benzene form, resulting a hydroquinone derivative (IX) (1st type of rearrangement). Another rearrangement was accomplished by alcoholic sulphuric acid, in which quinol hydroxyl group rearranged to its *o*-position under etherification, so as to give a resorcinol derivative (VII) (2nd type of rearrangement).

From these known facts it was supposed that two diacetates obtained from 4-phenyl-quinol might be either 2-phenyl-hydroquinone-diacetate or 4-phenyl-resorcinol-diacetate.

Actually it was the case for 1st type; diacetate B was found to be 4-phenyl-hydroquinone-diacetate (XIII). On the other hand the diacetate

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(1) Gilman and Kirby, *J. Am. Chem. Soc.*, **48**(1926), 2192.

(2) Griess, *Ber.*, **9**(1876), 132.

(3) Ruzicka, Choen, Furter and van der Sluys-Veer, *Helv. Chim. Acta*, **21**(1938), 1737.

(4) Miki, *J. Pharm. Soc. Japan*, Japanese Text, **61**(1941), 272.

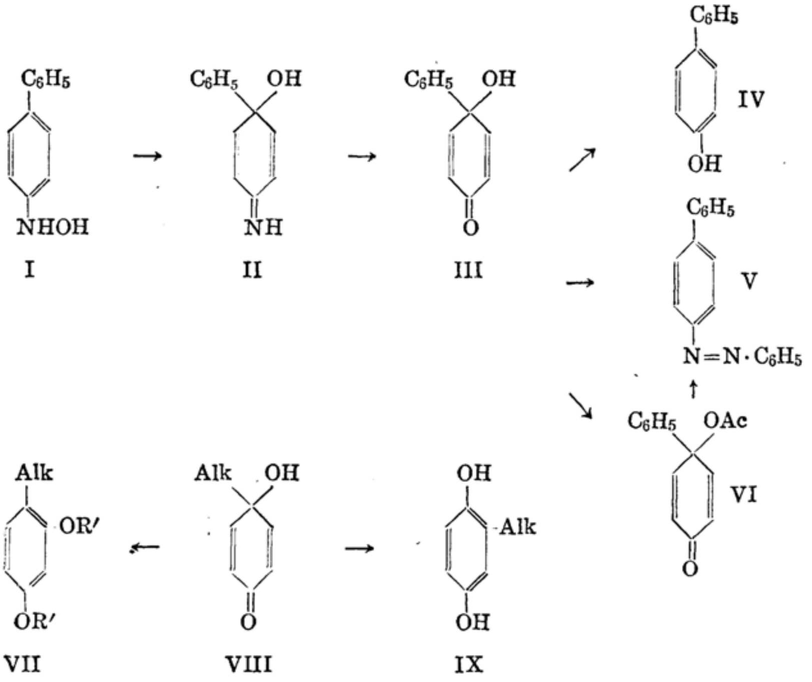
(5) Bamberger, *Ber.*, **33**(1900), 3618.

A was not 4-phenyl-resorcinol-diacetate, but was identified as 4-phenyl-catechol-diacetate (X), whose melting points reported by Norris et al.⁽⁶⁾ and by American patent⁽⁷⁾ were both incorrect.

Thus a new type of rearrangement proved that the quinol hydroxyl group migrate to its *m*-positions (C_2 or C_6).

Besides these two acetylating rearrangements 1st type of rearrangement reported by Bamberger is also possible for this quinol, but even in milder conditions than by *p*-alkylated ones. Namely in a dilute acid 4-phenyl-quinol rearranged so easily to 2-phenyl-hydroquinone⁽⁸⁾ (XV) already at room temperature, as it was unable to prepare pure quinol by the usual method, unless a continuous extraction method was applied. In the latter the quinol was separated from the acidic medium as quickly as it was produced by hydrolysis of 4-phenyl-iminoquinol in sulphuric acid or phosphoric acid. The alkaline rearrangement could occur when boiled with alcohol in the presence of weak alkali such as sodium-carbonate or acetate, and Borsche's quinhydrone⁽⁸⁾ (XVI) was obtained, which was autoxidized product of 2-phenyl-hydroquinone (XV).

The following diagram shows how the present experiments proceeded:—



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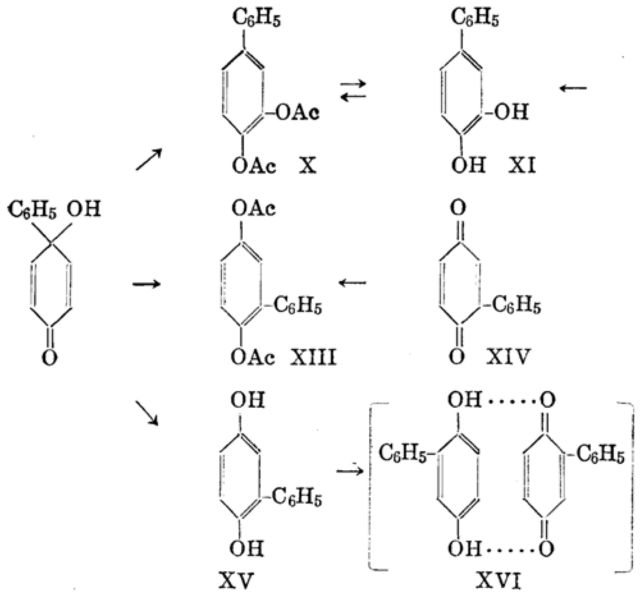
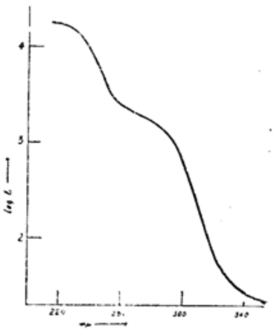
(6) Norris, Macintire and Corse, *Am. Chem. J.*, **29** (1903), 125.

(7) Squibb and Sons, U. S. P. 1952755; *Chem. Zentr.*, **1934**, II, 1846.

(8) Borsche, *Ann.*, **312** (1900), 221.





The mechanism of these innermolecular rearrangements will be cleared in further investigation.

Experimental.

4-Phenyl-quinol. An ethereal solution of *p*-diphenyl-hydroxylamine(1), newly prepared from *p*-nitrodiphenyl (20 g.), was added to 10% sulphuric acid (900 c.c.) with stirring, and from the obtained *p*-diphenyl-hydroxylamine sulphate suspension ether layer was removed. No change took place at room temperature, but when warmed, a part of the white sulphate dissolved in solution and the other changed into yellow insoluble substance, while all of ether contained in acid was distilled off. After being kept for 20 minutes at 40°, cooled, and the acidic solution, removed from the residue, was extracted continuously with ether at 35° as long as 40 hours. The ether extract was washed with water, dried, and evaporated. Recrystallization of the residue from benzene gave colourless prisms (1.67 g.), m.p. 104°. When phosphoric acid was used in place of sulphuric acid yield was 0.61 g. This compound has sweet taste, and reduced Fehling's solution not in cold, but on heating. The alkaline solution gave red colour by heating. The crystals gradually changed to blue black on long exposure in light. Found: C 77.52; H 5.47. Calculated for $C_{12}H_{10}O_2$: C 77.39; H 5.42%. Absorption spectrum: max. at 220 mμ (log ε=4.23), inflexion at 280 mμ (log ε=3.20).

Monoacetate. Prepared through heating the foregoing quinol (0.25 g.) with acetic anhydride (1.5 c.c.) and anhydrous sodium acetate (0.125 g.) on a water-bath for an hour. Colourless prism, m.p. 109° from ligroin. It became pink by exposure to light. Found: C 73.66; H 5.10. Calculated for $C_{14}H_{12}O_3$: C 73.65; H 5.30%.

The Mild Reduction. The 4-phenyl-quinol (80 mg.) was refluxed with zinc powder (0.3 g.) in a mixture of ammonium chloride (0.06 g.), alcohol (5 g.) and water (3 c.c.) for 20 minutes. On treating the reaction products, colourless crystals, m.p. 163.5° were obtained. No depression was observed in the mixed melting point test with authentic sample of *p*-hydroxydiphenyl.

The Action of Phenylhydrazine. When phenylhydrazine acetate was added to an alcoholic solution of 4-phenyl-quinole, yellow precipitates were separated instantly, which soon changed to orange red. After boiling for half an hour, cooled, and filtered. The precipitates were recrystallized from alcohol in orange leaflets, m.p. 154°. Found: C 83.50; H 5.69; N 10.89. Calculated for $C_{18}H_{14}N_2$: C 83.68; H 5.47; N 10.85%. This was obtained from 4-phenyl-quinol monoacetate in the same procedure.

Acetylating Rearrangements. *Formation of Diacetate A.* 4-Phenyl-quinol (0.5 g.) was acetylated by boiling with anhydrous sodium acetate (0.5 g.) in acetic anhydride (3 c.c.) for 3 hours. The reaction mixture was treated as usual and colourless prisms (494 mg.) were formed from benzene-ligroin, m.p. 92°. Found: C 71.30; H 5.20. Calculated for $C_{16}H_{14}O_4$: C 71.08; H 5.22%.

Formation of Diacetate B. 4-Phenyl-quinol (0.1 g.) was suspended in acetic anhydride (1 c.c.) and to which a drop of conc. sulphuric acid was added. After heating on a boiling water-bath for an hour, colourless parallelpiped crystals, m.p. 73° were obtained from ligroin by the usual method.

Diol A (Saponification of Diacetate A). The foregoing diacetate A (0.15 g.) was saponified through boiling with methyl alcoholic potassium carbonate for 4 hours. M.p. 141° from benzene. This crystals gave bluish green colouration with calcium chlorate. The compound also showed a light green colour with ferric chloride, which changed to a reddish-brown on standing, and which was changed to a deep violet on the addition of sodium carbonate. Found: C 77.56; H 5.26. Calculated for $C_{12}H_{10}O_2$: C 77.39; H 5.42%.

2-Phenyl-hydroquinone Diacetate. To a mixture of stannous chloride (0.4 g.), conc. hydrochloric acid (1.6 c.c.), and water (4 c.c.) an alcoholic solution of phenylbenzoquinone(8) (0.276 g.) was added, heated on water-bath for an hour, cooled, and extracted with ether. On concentrating the ether extract there was obtained a yellow oil, which was immediately acetylated by the usual method. Colourless parallelepiped crystals, m.p. 73° were separated from ligroin. The compound showed no depression of melting point when admixed with the above diacetate B. Found: C 71.35; H 5.17. Calculated for $C_{16}H_{14}O_4$: C 71.08; H 5.22%.

4-Cyclohexylresorcinol-dimethyl Ether. 4-Cyclohexylresorcinol(9) (9.5 g.) was methylated with methyl iodide (42.6 g.) in the presence of anhydrous potassium carbonate (27.6 g.) in acetone (60 c.c.) at 57°. Light yellow viscous oil, b.p. 110–121° (0.2 mm.), yield 8.4 g. Found: C 76.11; H 9.06. Calculated for $C_{14}H_{20}O_2$: C 76.31; H 9.16%.

4-Phenyl-resorcinol-dimethyl Ether. The foregoing cyclohexylresorcinol dimethyl ether (5.06 g.) was dehydrogenated by heating with sulphur (2.2 g.) at 300° for 2 hours. Colourless oil, b.p. 135–136° (0.15 mm.). Yield 1.3 g. Found: C 77.90; H 6.26. Calculated for $C_{14}H_{14}O_2$: C 78.46; H 6.59%.

4-Phenyl-resorcinol. Prepared from the above dimethyl ether (1 g.) through refluxing with hydroiodic acid (6 c.c.) and acetic acid (3 c.c.) for 3 hours. The product was distilled in vacuum. Repeated crystallizations from tetrachlormethane, water and benzene gave colourless crystals, m.p. 145°(9). The compound gave violet colour with calcium chlorate, which changed to yellow. Found: C 77.27; H 5.38. Calculated for $C_{12}H_{10}O_2$: C 77.39; H 5.42%.

4-Phenyl-catechol. 3-Brom-4-hydroxydipdenyl(10) (7.8 g.) was dissolved in caustic soda (sodium hydroxide 5 g. in water 80 c.c.) and was heated with cuprous oxide (0.8 g.) in autoclave at 200–240° (20–40 kg./cm.^{2}) for 2 hours. After cooling, the

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(9) Suter and Smith, *J. Am. Chem. Soc.*, **61** (1939), 167.

(10) Bell and Robinson, *J. Chem. Soc.*, **1927**, 1132.

reaction mixture was made acidic with sulphuric acid, and extracted with ether. The ethereal extract was washed successively with water, 5% sodium bicarbonate, and again with water, dried, and evaporated. Oily residue was distilled in vacuo, and the distillate was recrystallized from benzene in colourless crystals, m.p. 141°. This compound showed the same colour reaction both with ferric chloride and calcium chlorate as above diol A, and no depression of the melting point was observed in admixture with the latter. Found: C 77.46; H 5.34. Calculated for $C_{12}H_{10}O_2$: C 77.39; H 5.42%.

Diacetate. Prepared from 4-phenyl-catechol and acetic anhydride in pyridine. Recrystallization from benzene-ligroin gave colourless prisms, m.p. 92°, alone and in admixture with the diacetate A.

Rearrangements in the Presence of Weak Alkali. 4-phenyl-quinol (0.1 g.) was boiled with sodium carbonate (0.4 g.), methyl alcohol (6 c.c.) and water (1.6 c.c.) for 3 hours. After cooling, diluted with water (30 c.c.) and extracted with ether. On concentrating the ether extract blue black crystals, m.p. 175° were formed. Upon recrystallization from acetic acid, the substance was identified as Borsche's quinhydrone(8), consisted of phenyl-benzoquinone and phenyl-hydroquinone by its failure in depressing the melting point of an authentic sample.

The same quinhydrone was obtained by a similar treatment after refluxing the 4-phenyl-quinol (0.1 g.) with anhydrous sodium acetate (0.1 g.) in absolute alcohol (3 c.c.) for 3 hours. Found: C 77.45; H 5.21. Calculated for $C_{24}H_{18}O_4$: C 77.82; H 4.90%.

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