above. The solid product obtained directly from the benzene solution (pale yellow, 4.90 g., 98% yield, m.p. 139–140°) was recrystallized from benzene to give 2-benzenesulfonylspiro(cyclopropane-1,9′-fluorene) (VIIa) as a white powder (m.p. 140–141°).

Anal. Calcd. for $C_{21}H_{16}O_2S$: C, 75.88; H, 4.85; S, 9.65. Found: C, 75.70; H, 4.99; S, 9.56.

The infrared spectrum showed absorption at 1025 cm.$^{-1}$, characteristic of the cyclopropane structure.

3. **With Phenyl β-Styryl Sulfone (VIc).**—A solution of VIc (2.24 g., 0.01 mole) and diazofluorene (1.80 g., 0.0094 mole) in benzene (50 ml.) was heated at the reflux temperature for 3 days. The benzene solution was allowed to stand for 7 days at 32° and the resulting red solid (2.72 g., 72%, m.p. 190–220°) was washed with ether and recrystallized from benzene. 2-Phenyl-3-benzenesulfonylspiro-(cyclopropane-1,9-fluorene) (VIIc) was obtained as a white solid, m.p. 238–240°. The benzene solution contained additional VIIc, but this was not processed.

Anal. Calcd. for $C_{27}H_{20}O_2S$: C, 80.97; H, 5.03; S, 7.85. Found: C, 81.23; H, 5.24; S, 7.70.

Dimerization of 3-Carboxybenzoquinone-1,2

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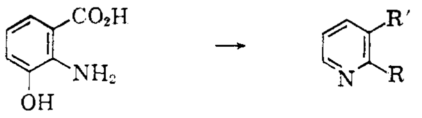
During the course of a program designed to study the chemistry of the intermediates in the enzymatic transformation of 3-hydroxyanthranilic acid (I) into quinolinic (II. R = R′ = CO_2H), nicotinic (II. R = H, R′ = CO_2H), and picolinic acids (II. R = CO_2H, R′ = H),[1] the possibility of 3-carboxybenzoquinone-1,2 or a dimer being an intermediate was investigated. While neither 3-carboxybenzoquinone-1,2 nor a dimer have been previously reported, some have postulated them as products in the above degradations.[2]



I II

We now wish to report the successful oxidation of 2,3-dihydroxybenzoic acid leading to 3-carboxybenzoquinone-1,2 and the isolation of a dimer of the quinone.

Treatment of 2,3-dihydroxybenzoic acid with silver oxide in anhydrous methanol containing a trace of 98% formic acid afforded 3-carboxybenzoquinone-1,2, which dimerized to III upon refluxing in anhydrous ether for forty-eight hours.

An assignment of III as a Diels-Alder adduct formed by the addition of one molecule of quinone to another based upon infrared absorption from a Nujol mull at 2.84, 5.69, 5.75, 5.80, 5.93, and 6.12 μ is supported by ultraviolet absorption in chloroform λ_{max} 213 mμ (log ε 3.97); 255 mμ (log ε 3.87). Infrared absorption at 2.84 μ could represent the OH absorption of carboxyls while the four peaks, 5.69, 5.75, 5.80, and 5.93 μ are characteristic of carbonyls; the first three corresponding to unconjugated and the last to conjugated carbonyl groups.[3] In addition, the peak at 6.12 μ corresponds to the double bond of the system —COCH=CH— and the ultraviolet spectrum agrees, with a maximum at 255 mμ,[4] a wave length too low for a benzenoid system while the absorption at 213 mμ compares favorably with that for α,β-unsaturated acids.[5]

Heating an ethanolic (10% hydrochloric acid) solution of the dimer causes rapid conversion to a more stable phenolic material, IV (R = H), which gives an intense ferric chloride reaction indicating a phenol nucleus. The infrared spectrum shows new peaks at 2.81 (hydroxyl), 5.57 (γ-lactone), 6.23 and 6.67 μ (benzene ring) and there is a shift in the ultraviolet absorption, $\lambda_{max}^{C_2H_5OH}$ 270 mμ (log ε 4.01).[6]

Treatment of IV (R = H) with acetic anhydride and pyridine gives a monoacetate, IV (R = Ac), and with o-phenylenediamine a phenazine. Refluxing IV (R = H) with 10% sodium hydroxide in methanol results in V (R = H), which when refluxed with acetic anhydride and pyridine gives a diacetate, V (R = Ac). The diacetate has a strong infrared absorption at 8.04 μ (—O·CO—), 6.03 μ (—CH:CH—), and 5.80 μ (—CO·CO—).

Pyrolysis at 200–210° causes III to undergo a smooth reverse Diels-Alder reaction with reduction to two molecules of 2,3-dihydroxybenzoic acid. Under similar conditions V (R = H) is converted to VI. Oxidation of VI with silver oxide in anhydrous methanol gave a good yield of 3,8-dicarboxynaphthoquinone-1,2 (VII). With o-phenylenediamine in acetic acid VII gave a yellow phenazine. the absorption spectrum of which was similar to those reported for benzo[*a*]phenazines.[7]

In accordance with the stereochemical factors

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[1] A. H. Mehler, *Proc. Intern. Congr. Biochem. 4th, Vienna*, **13**, 164 (1958).

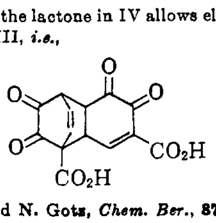
[2] A. Miyake, A. H. Bokman, and B. S. Schweigert, *J. Biol. Chem.*, **211**, 391 (1954).

[3] These peaks are practically identical to those found in substituted and unsubstituted o-benzoquinone dimers [*cf.*, J. Harley-Mason and A. H. Laird, *J. Chem. Soc.*, 1718 (1958) and E. Adler, R. Magnusson, B. Berggren, and H. Thomelius, *Acta Chem. Scand.*, **14**, 515 (1960)].

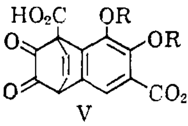
[4] This value agrees favorably with a value of 252 (log ε 3.95) for the anologous dimer of 4,5-dimethyl-o-quinone [*cf.*, L. Horner and K. Sturm, *Ann.*, **597**, 1 (1955)] and a value 254 mμ (log ε 3.87) for the dimer of o-benzoquinone [*cf.*, A. A. Patchett and B. Witkop, *J. Org. Chem.*, **22**, 1477 (1957)].

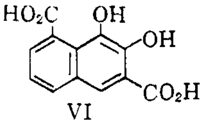
[5] H. E. Ungnade and I. Ortega, *J. Am. Chem. Soc.*, **73**, 1564 (1951).

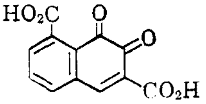
[6] The presence of the lactone in IV allows elimination of the other possible structure for III, *i.e.*,



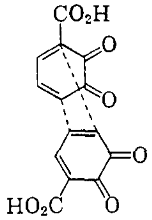
[7] H. J. Teuber and N. Gotz, *Chem. Ber.*, **87**, 1236 (1954).

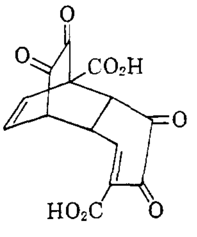

V


VI


VII

attendant upon the Diels-Alder reaction,[8] the dimeric product (III) is assumed to occur through a complex (VIII) rendering the *endo* product (IX). *It is interesting to note that only one isomer could be isolated.*


VIII


IX

Experimental[9]

3-Carboxybenzoquinone-1,2.—2,3-Dihydroxybenzoic acid (3 g.) was dissolved in 100 ml. of anhydrous methanol containing 1 ml. of 98% formic acid and added at 0° to a mixture of anhydrous sodium sulfate (10 g.) and freshly prepared dry silver oxide (7 g.). The mixture was vigorously shaken for 15 min. and filtered. The red solution was allowed to stand at −10° for 2 hr. and the red needles of *3-carboxybenzoquinone-1,2* that formed collected and dried, 1.5 g. (49%), m.p. 195–197° dec.; $\lambda_{max}^{C_2H_5OH}$ 420 mμ (log ε 3.10).

Anal. Calcd. for $C_7H_4O_4$: C, 55.27; H, 2.65; O, 42.07. Found: C, 55.20; H, 2.41; O, 41.89.

Refluxing the quinone (700 mg.) in 150 ml. of methanol with a solution *o*-phenylenediamine dihydrochloride (900 mg.) and sodium acetate (1.3 g.) in 5 ml. of water for 30 min. afforded 900 mg. of 1-carboxyphenazine (recrystallized from ethanol as yellow needles), m.p. and mixture m.p. 242–244°.

***o*-Quinone Dimer (III).**—3-Carboxybenzoquinone-1,2 (3.0 g.) was refluxed in 1 l. of dry ether with anhydrous magnesium sulfate for 8 hr. The magnesium sulfate and the precipitated material were filtered off and extracted with about 500 ml. of hot benzene. The extract was concentrated until turbid, cooled to 0°, and the flocculent precipitate recrystallized from petroleum ether (b.p. 65–70°) and benzene as yellow microcrystals of the dimer III 0.13 g. (4.3 %), m.p. 216–218° dec., $\lambda_{max}^{CHCl_3}$ 213 mμ (log ε 3.97), 255 mμ (log ε 3.87), λ_{max}^{Nujol} 2.84, 5.69, 5.75, 5.80, 5.93, and 6.12 μ.

Anal. Calcd. for $C_{14}H_8O_8$: C, 55.27; H, 2.64; O, 42.07; mol. wt., 304. Found: C, 55.12; H, 2.51; O, 42.37; mol. wt., 302.[10]

Pyrolysis of III.—In a small distillation apparatus, 3 g. of III was heated for 30 min. at 200–220°. The dark residue after cooling to room temperature was recrystallized from ethanol affording colorless crystals of 2,3-dihydroxybenzoic acid, m.p. and mixture m.p. 201–202°, 2.1 g. (68%).

Rearrangement of III with Acid.—When III was warmed with ethanolic hydrochloric acid (10%) for 15 min. on a steam bath, and taken to dryness *in vacuo*, the rearranged phenol, IV, could be isolated. Recrystallization from methylene chloride afforded colorless microcrystals of IV, m.p. 232–234°, $\lambda_{max}^{C_2H_5OH}$ 270 mμ (log ε 4.01), λ_{max}^{Nujol} 2.81, 2.87. 5.57, 5.80, 5.93, 6.03, 6.23, and 6.67 μ.

Anal. Calcd. for $C_{14}H_6O_7$: C, 58.75; H, 2.11. Found: C, 58.79; H, 2.01.

A phenazine derivative of IV was prepared by heating IV in glacial acetic acid with an equivalent amount of sodium acetate and *o*-phenylenediamine dihydrochloride on a steam bath for 30 min. Cooling afforded the crude phenazine, 0.021 g., which was crystallized from ethanol as brick red needles, m.p. 310–312° dec.

Anal. Calcd. for $C_{20}H_{10}N_2O_5$: C, 67.04; H, 2.81; N, 7.81. Found: C, 67.21; H, 2.61; N, 7.59.

Acetylation of IV (R = H).—The rearranged isomer, IV (R = H) (0.1 g.), was allowed to stand for 36 hr. with excess acetic anhydride and 6 drops of dry pyridine. The excess acetic anhydride and pyridine were removed *in vacuo* and the residue recrystallized from ethyl acetate–petroleum ether as yellow prisms of the monoacetate, IV (R = Ac), m.p. 149–151°, 0.08 g. (69.5%).

Anal. Calcd. for $C_{16}H_8O_8$: C, 58.54; H, 2.45. Found: C, 58.41; H, 2.57.

Hydrolysis of IV (R = H).—A solution of IV (0.3 g.) in 50 ml. of 10% methanolic sodium hydroxide was gently refluxed for 1.5 hr. Neutralization with 10% hydrochloric acid and extraction with ethyl acetate afforded a residue which recrystallized from ether–cyclohexane, as yellow microcrystals of V (R = H), m.p. 181–182°, 0.11 g. (31%).

Anal. Calcd. for $C_{14}H_8O_8$: C, 55.27; H, 2.64. Found: C, 55.32; H, 2.71.

Acetylation of V (R = H).—V (0.1 g.) was boiled with excess acetic anhydride and 7 drops of pyridine for 1 hr. The excess anhydride was removed *in vacuo* and the residue recrystallized from ethyl acetate–petroleum ether as yellow prisms of the diacetate, V (R = Ac), 0.087 g. (68.5%), m.p. 192–194°.

Anal. Calcd. for $C_{18}H_{12}O_{10}$: C, 55.67; H, 3.11. Found: C, 55.52; H, 3.23.

Pyrolysis of V (R = H).—In a small distillation apparatus 3 g. of V was heated for 30 min. at 195–200° and the resulting dark mass dissolved in benzene. Chromatography over silicic acid eluting with benzene afforded 1,2-dihydroxy-3,8-dicarboxy naphthalene (VI) as yellow microcrystals, m.p. 213–214°, 0.9 g. (34.5%).

Anal. Calcd. for $C_{12}H_8O_6$: C, 58.07; H, 3.24. Found: C, 58.31; H, 3.16.

Shaking VI with silver oxide and anhydrous sodium sulfate in methanol for 5 min. afforded 3,8-dicarboxynaphthoquinone-1,2 (VII), brick red needles, m.p. 273–275° dec., $\lambda_{max}^{C_2H_5OH}$ 267 mμ (log ε 4.31), 395 mμ (log ε 3.56).

Anal. Calcd. for $C_{12}H_6O_6$: C, 58.54; H, 2.45; O, 38.99. Found: C, 58.67; H, 2.31; O, 39.12.

The benzo[*a*]phenazine of VII was prepared by heating VII in acetic acid with an equivalent amount of *o*-phenylenediamine for 30 min. on a steam bath. Cooling to room temperature resulted in reddish microcrystals of 1,6-dicarboxybenzo[*a*]phenazine, m.p. 261–264°, $\lambda_{max}^{C_2H_5OH}$ 235 mμ (log ε 4.50); 247 mμ (log ε 4.56); 285 mμ (log ε 4.36); 430 mμ (log ε 4.02).

Anal. Calcd. for $C_{18}H_{10}O_4N_2$: C, 67.92; H, 3.16; N, 8.80. Found: C, 68.11; H, 3.09; N, 8.62.

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[8] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[9] Semimicro analyses by Alfred Bernhardt, Max Planck Institut Microanalytisches Laboratorium, Mulheim (Ruhr), Germany. Melting points are uncorrected. Ultraviolet absorption spectra were obtained on a Unicam S.P. 500 spectrophotometer. Infrared spectra were determined with a Baird Associates infrared spectrophotometer.

[10] Ebullioscopic determination in benzene by Huffman Microanalytical Laboratories, Wheatridge, Colorado.