on hydroquinone may be rationalized from the known facts. Michaelis and co-workers[7] have observed that strongly alkaline solutions of duroquinone and durohydroquinone exhibit paramagnetism consistent with the presence of a large proportion of the intermediate oxidation state, or semiquinone free radical. Formation of such free radicals may be expected to proceed rapidly from duroquinone and doubly charged durohydroquinone anions and is a logical path for the exchange reaction. In the relatively acid solutions employed in this study, the concentration of doubly-charged anion would be extremely low, and its rate of formation may be assumed to be rate-controlling. The reactions may be represented as

$$H_2Q^* \rightleftharpoons HQ^{*-} + H^+ \qquad (3)$$

$$HQ^{*-} \rightleftharpoons Q^{*=} + H^+ \qquad (4)$$

$$Q^{*=} + Q \rightleftharpoons Q^{*\cdot -} + Q^{\cdot -} \rightleftharpoons Q^* + Q^= \qquad (5)$$

where H_2Q^* represents radioactive durohydroquinone, Q represents inactive duroquinone, $Q^{\cdot -}$ represents a semiquinone radical, etc.

This formulation implies that the rate of reaction (4) is slow. This seems rather unusual, but possible factors suppressing the rate are the low initial concentration of singly-charged hydroquinone anions in the solution, and the low second ionization constant for hydroquinones. A study of the effect of hydrogen-ion concentration on the rate of reaction is indicated.

Acknowledgments.—I wish to express my appreciation to Professor R. W. Dodson, to Dr. J. Silverman and to Dr. A. P. Wolf for helpful discussions, and to Miss Yvette Delabarre for the performance of a large number of analyses and isotopic assays.

UPTON, LONG ISLAND, NEW YORK

(7) L. Michaelis, M. P. Schubert, R. K. Reber, J. A. Kuck and S. Granick, THIS JOURNAL, **60**, 1678 (1938); L. Michaelis, *ibid.*, **63**, 2446 (1941).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND THE RICE INSTITUTE AND THE RESEARCH LABORATORY OF THE PAINT DIVISION OF THE PITTSBURGH PLATE GLASS COMPANY]

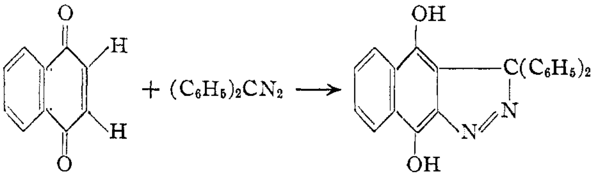
Pyrolysis of the Addition Product of Diphenyldiazomethane and 1,4-Naphthoquinone

BY ALFRED R. BADER AND MARTIN G. ETTLINGER

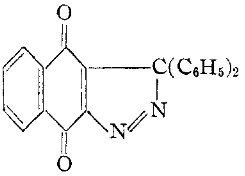
RECEIVED JULY 7, 1952

The pyrolysis product of 2,3-(3′,3′-diphenylisopyrazolo)-1,4-naphthohydroquinone previously formulated as a derivative of methylenecyclopropane consists of 4-hydroxy-1-phenyl-2,3-benzofluorenone, the major component, and 4-hydroxy-9-phenyl-2,3-benzo-1-isofluorenone.

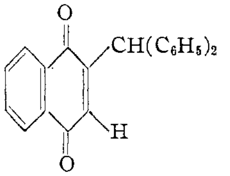
During the study of the addition of diazo compounds to quinones, Fieser and Peters[1] pyrolyzed the azo compound I, the adduct of diphenyldiazomethane and 1,4-naphthoquinone, and isolated besides II and III a small portion of nitrogen-free fiery red needles, m.p. 274°. To the red substance, which dissolved in aqueous carbonate, formed a monoacetate, m.p. 245°, and was believed to be reducible to 2-benzhydryl-1,4-naphthohydroquinone, characterized as its diacetate and the quinone III, the unusual structure IV was tentatively assigned. The present investigation began with the idea that structure V, analogous to the known enols of 1,2-naphthoquinones,[2,3] might fit the properties of the red substance. The molecule V would form in base the resonant anion VI, which would be obtained also by removal of a proton from III. However, it was found that although both the red pyrolysis product and III formed purple solutions in hot alcoholic alkali, the pyrolysis product was recovered on acidification, whereas III furnished an unknown mixture. Furthermore, III did not yield well-defined products on treatment with sulfuric acid or with acetic anhydride and catalysts and thus gave no indication of the existence of a stable enol V.[2]



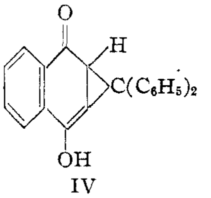
I



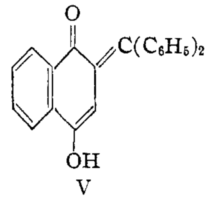
II



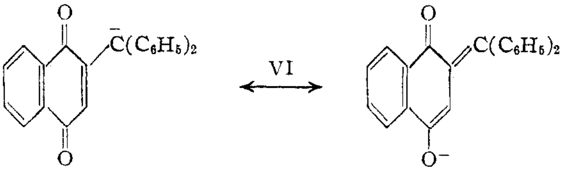
III



IV



V



VI

The red pyrolysate, m.p. 274°, was eventually found to be a mixture of two compounds which could not be separated by crystallization. The previously described acetate, m.p. 245°, was difficultly purifiable and furnished on hydrolysis an

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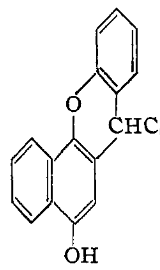
(1) L. F. Fieser and M. A. Peters, THIS JOURNAL, **53**, 4080 (1931).

(2) L. F. Fieser and J. L. Hartwell, *ibid.*, **57**, 1484 (1935).

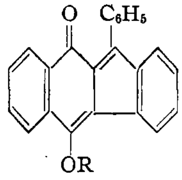
(3) L. F. Fieser and M. Fieser, *ibid.*, **61**, 596 (1939); *cf.* F. Sachs and L. Oholm, *Ber.*, **47**, 955 (1914).

orange compound, m.p. 297°. The pyrolysis product could be resolved directly by chromatography on alumina into the orange substance, which constituted some two thirds of the mixture, and a *deep* red substance, m.p. 227°. The orange compound, which could be reconverted to the monoacetate, m.p. 245°, and methylated to a yellow monoether, m.p. 180°, formed in alkali a purple solution unaltered by cold dithionite but decolorized by hot hydrogen peroxide. The red substance, m.p. 227°, gave a monoacetate, m.p. 223°, and a methyl ether, m.p. 153°, and dissolved in alkali to a dark blue solution. Analyses of the two pyrolysis products and derivatives failed to provide clear distinction between the parent molecular formulas $C_{23}H_{14}O_2$ and $C_{23}H_{16}O_2$. Determination of structures proved that the parent substances each contained fourteen hydrogen atoms, two less than formula IV. Neither pure pyrolysis product could be reduced by zinc in acetic acid and acetic anhydride to 2-benzhydryl-1,4-naphthohydroquinone diacetate. The previous contrary report stemmed perhaps from misapprehension of the reduction product or contamination of the benzene-insoluble pyrolysate with the quinone III.

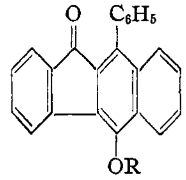
The types of structures containing an acidic hydroxyl group that could be formed from I by loss of nitrogen and potential rearrangement of the residue by 1,2-migrations were VII, VIII (R = H), IX (R = H), X and XI. Of these formulas, VII did not imply intense color[4] and was discarded. The choice for the orange compound was delimited by the infrared absorption spectra of the substance (Fig. 1) and its methyl ether, which exhibited carbonyl maxima at 5.85–5.92 μ. A carbonyl group conjugated, as in VIII–XI, to unsaturation on both sides would absorb in a strainless system at 5.97 μ or more,[5] but inclusion of the carbonyl in a five-membered ring decreases the peak wave length.[6] The model substance fluorenone was found to absorb in chloroform solution at 5.83 μ,[7,8] 0.17 μ less than benzophenone. Hence the orange substance might be IX (R = H) or X. Oxidation by alkaline peroxide furnished *o*-benzoylbenzoic acid, which could arise only from IX. Furthermore, the ultraviolet absorption spectra (Table I) of the acetate of the orange substance and the known 1,4-diacetoxy-2,3-benzofluorenone[9] (XII, R = R' = $COCH_3$) were remarkably similar. As 1-substituents on the 2,3-benzofluorenone nucleus both the phenyl group, which is non-coplanar,[10] and acetoxyl[11] would be expected to be weakly bathochromic and spectrally nearly equivalent. Hence the orange product, m.p. 297°, of pyrolysis of I was IX (R = H), 4-hydroxy-1-phenyl-2,3-benzofluorenone.



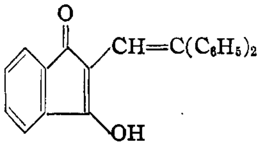
VII



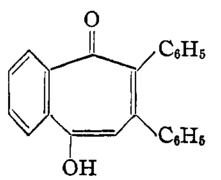
VIII



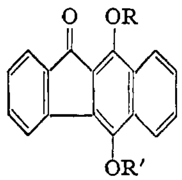
IX



X



XI



XII

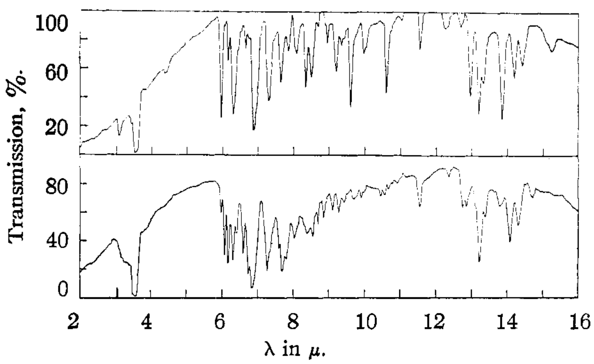


Fig. 1.—Infrared absorption spectra of the orange pyrolysis product (upper), 4-hydroxy-1-phenyl-2,3-benzofluorenone (IX, R = H), and the red pyrolysis product (lower), 4-hydroxy-9-phenyl-2,3-benzo-1-isofluorenone (VIII, R = H), as crystalline mulls in mineral oil.

TABLE I

ULTRAVIOLET AND VISIBLE SPECTRA

Compound	Absorption maxima: wave lengths in mμ (log ε)
IX (R = H)[b]	260(4.67), 293(4.55), 320(4.14), 350[a](3.66), 455(3.45)
IX (R = CH_3)[c]	260(4.57), 289(4.75), 315(4.07), 335[a](3.65), 425(3.28)
IX (R = $COCH_3$)[c]	263(4.56), 288(4.81), 312(4.05), 330[a](3.65), 412(3.20)
XII (R = R' = $COCH_3$)[c]	255(4.53), 285(4.86), 310(4.00), 330[a](3.62), 413(3.24)

[a] Inflection. [b] Solvent, 0.1% acetic acid in ethanol. [c] In ethanol.

The spectra of substituted 2,3-benzofluorenones reported in Table I resemble those of the parent

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[4] *Cf.* E. Mayer-Pitsch, *Z. Elektrochem.*, **49**, 368 (1943).

[5] H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 640 (1945); M. St. C. Flett, *ibid.*, 1441 (1948); R. N. Jones, *et al.*, THIS JOURNAL, **72**, 956 (1950).

[6] J. Lecomte, *J. phys. radium*, **6**, 257 (1945); R. N. Jones, *et al.*, THIS JOURNAL, **70**, 2024 (1948); C. D. Gutsche, *ibid.*, **73**, 786 (1951).

[7] *Cf.* E. D. Bergmann, *et al.*, *Bull. soc. chim.*, [5] **18**, 661, 669 (1951).

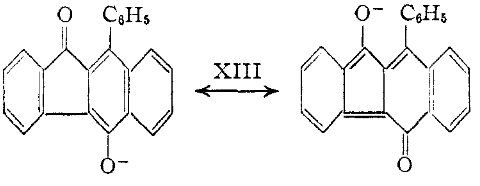
[8] The cyclic carbonyl group of fluorenone-1-carboxylic acid, reported to absorb at 6.00μ (M. L. Josien and N. Fuson, THIS JOURNAL, **73**, 478 (1951)), may be bonded internally to the acidic hydrogen atom. 1,4-Dihydroxy-2,3-benzofluorenone (XII, R = R' = H) absorbs in an oil mull at 6.01μ.

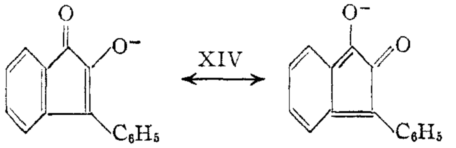
[9] C. F. Koelsch, *ibid.*, **67**, 159 (1945).

[10] R. N. Jones, *ibid.*, **67**, 2127 (1945).

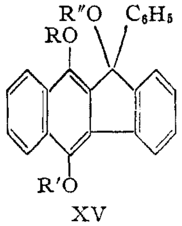
[11] J. W. H. Lugg, A. K. Macbeth and F. L. Winzor, *J. Chem. Soc.*, 1597 (1937).

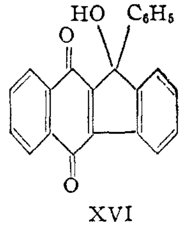
compound and an alkyl derivative.[12,13] The phenol IX (R = H) absorbs at longest wave length and shares the notable color of previously known 4-hydroxyfluorenones[9,14] and the vinylogous 2-hydroxy derivatives.[15] The hypsochromic effects of methylation or acetylation of the hydroxyl group may be electric[16] and steric[10] in origin. In the deeply colored anion (XIII) of IX (R = H) the negative charge presumably is distributed between the two oxygen atoms through the benzene ring. The anion (XIV) of 2-hydroxy-3-phenylindone[17] contains a similar chromophore.


XIII


XIV

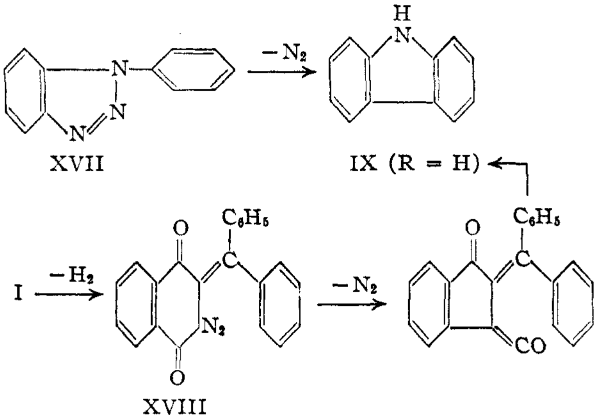
The red pyrolysis product, m.p. 227°, absorbed in the infrared (Fig. 1) at 5.99 (weakly) and 6.07 μ, consistently with structures VIII (R = H) or XI. Oxidation with alkaline peroxide gave much neutral material and no identifiable fragment save phthalic acid. An unambiguous synthesis of VIII (R = H) was eventually accomplished by reaction of phenyllithium and 1,4-dihydroxy-2,3-benzofluorenone[9] (XII, R = R′ = H). The phenolic ketone initially formed only a salt,[18] but prolonged treatment with excess phenyllithium in boiling ether effected addition to the carbonyl group to furnish in good yield 1,4,9-trihydroxy-9-phenyl-2,3-benzofluorene (XV, R, R′, R″ = H). The diacetoxybenzofluorenone XII (R = R′ = COCH$_3$) was phenylated much more rapidly than the dihydroxy compound, evidently because reaction at the 9-position preceded cleavage of the ester groups, but the final yield was less. The intermediate XV (R, R′, R″ = H), which was never purified but was characterized by conversion to the 1,4-diacetate XV (R = R′ = COCH$_3$, R″ = H) and the quinone XVI, was smoothly dehydrated by hot acetic acid to the *o*-fuchsone VIII (R = H).[19] The resultant authentic 4-hydroxy-9-phenyl-2,3-benzo-1-isofluorenone, judged by melting points and comparisons of the spectra and monoacetates, proved to be identical with the deep red compound, m.p. 227°, from I.


XV


XVI

In parallel experiments, 1-acetoxy-4-methoxy-2,3-benzofluorenone[9] (XII, R = COCH$_3$, R′ = CH$_3$) reacted with phenyllithium to afford 1,9-dihydroxy-4-methoxy-9-phenyl-2,3-benzofluorene (XV, R = R″ = H, R′ = CH$_3$), isolated in pure crystalline condition. The carbinol was dehydrated to 4-methoxy-9-phenyl-2,3-benzo-1-isofluorenone (VIII, R = CH$_3$) by fusion or treatment with acids, and notably also by hot aqueous base, which precipitated the neutral product. The methoxyisofluorenone was also obtained from VIII (R = H) and diazomethane. A reverse transformation from the isofluorenone to the fluorene series was achieved by reaction of VIII (R = H) with acetic anhydride and sulfuric acid in a Thiele-type addition to produce 1,4,9-triacetoxy-9-phenyl-2,3-benzofluorene (XV, R, R′, R″ = COCH$_3$). The two acetates XV (R = R′ = COCH$_3$, R″ = H or COCH$_3$) resembled 2,3-benzofluorene[13] in ultraviolet absorption, with a small bathochromic shift of the 260-mμ maxima and marked diminution of the 340-mμ fine structure.

The structural change on pyrolysis of I to VIII (R = H) involves, apart from dehydrogenation, attack at an *o*-position of a phenyl group and closely resembles the decomposition of 1-phenylbenzotriazole (XVII) and derivatives at 300–380° to carbazoles.[20] The formation of IX (R = H) from I may be represented conveniently to proceed through the diazo ketone XVIII, an isomer of II, which undergoes a Wolff rearrangement similar to that of azibenzil to diphenylketene[21]



XVII

IX (R = H)

XVIII

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(12) L. F. Fieser and M. D. Gates, Jr., This Journal, **62**, 2335 (1940).

(13) M. Orchin and R. A. Friedel, *ibid.*, **71**, 3002 (1949); R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, spectra 427–429.

(14) C. Graebe and P. Schestakow, *Ann.*, **284**, 306 (1895); H. Richtzenhain and P. Nippus, *Ber.*, **77**, 566 (1944).

(15) O. Diels, *ibid.*, **34**, 1758 (1901); E. R. Wasserman, Ph.D. Thesis, Radcliffe College, 1948; W. Borsche, *Ann.*, **526**, 1 (1936).

(16) M. G. Ettlinger, This Journal, **72**, 3085 (1950).

(17) C. F. Koelsch, *ibid.*, **58**, 1321 (1936).

(18) Compare C. F. Koelsch and E. J. Prill, *ibid.*, **67**, 1299 (1945). Analogs with acyclic carbonyl groups add organometallic reagents more readily.

(19) *Cf.* H. Kauffmann and M. Egner, *Ber.*, **46**, 3779 (1913); F. Preissecker, *Monatsh.*, **35**, 889 (1914); M. Gomberg and W. J. McGill, This Journal, **47**, 2392 (1925).

(20) C. Graebe and F. Ullmann, *Ann.*, **291**, 16 (1896); F. Ullmann, *ibid.*, **332**, 82 (1904); F. Ullmann and E. Illgen, *Ber.*, **47**, 380 (1914); H. Lindemann and F. Werther, *ibid.*, **57**, 1316 (1924); R. W. G. Preston, S. H. Tucker and J. M. L. Cameron, *J. Chem. Soc.*, 500 (1942).

(21) G. Schroeter, *Ber.*, **42**, 2336 (1909).

or 2-diazo-1-naphthone to 1-indylketene dimer,[22] followed by cyclization.[23]

The authors thank Dr. L. F. Fieser for kind interest.

Experimental

2,3-(3′,3′-Diphenylisopyrazolo)-1,4-naphthohydroquinone (I) was prepared and pyrolyzed at 210° as previously described.[1] The combined products of eight pyrolyses of 1-g. portions were extracted several times with warm benzene to remove the bulk of the major constituents, 2,3-(3′,3′-diphenylisopyrazolo)-1,4-naphthoquinone and 2-benzhydryl-1,4-naphthoquinone, and chromatographed on alumina (Fisher, 80–200 mesh). The hexane–benzene eluate contained a little quinonoid material. The orange benzene–ether and ether–methanol eluates furnished 0.50 g. of 4-hydroxy-1-phenyl-2,3-benzofluorenone, pure after one crystallization. The red methanol–water eluate (from acid-washed adsorbent) afforded 0.29 g. of 4-hydroxy-9-phenyl-2,3-benzo-1-isofluorenone. Chromatography of 150 mg. of the previously reported red material,[1] m.p. 273°, obtained by crystallization of the pyrolysate, gave 100 mg. of the fluorenone and 38 mg. of the isofluorenone. Since the mixtures were only sparingly soluble in hexane and benzene, it was advantageous to acylate with acetic anhydride and sodium acetate and chromatograph the more soluble acetates on ordinary alumina containing free alkali. The esters were hydrolyzed by the adsorbent and the fluorenone was obtained as before. The isofluorenone was eluted by aqueous methanol as the blue salt and precipitated by acetic acid.

4-Hydroxy-1-phenyl-2,3-benzofluorenone crystallized from ethanol as orange needles, m.p. 296.5–298°, giving a purple solution in alkali and in concentrated sulfuric acid an olive coloration.

Anal. Calcd. for $C_{23}H_{14}O_2$: C, 85.69; H, 4.38; mol. wt., 322.3. Found: C, 85.51; H, 4.45; mol. wt. (Rast), 323.

The ultraviolet and visible absorption spectrum (Table I) was measured with a Beckman spectrophotometer, model DU and the infrared spectrum (Fig. 1) with a Baird recording spectrophotometer, model B.

4-Acetoxy-1-phenyl-2,3-benzofluorenone was identical with the previously described[1] "2,3-diphenylmethylene-1-acetoxy-4-keto-3,4-dihydronaphthalene," m.p. 245°. The analysis was repeated.

Anal. Calcd. for $C_{25}H_{16}O_3$: C, 82.40; H, 4.43; mol. wt., 364.4. Found: C, 82.11; H, 4.44; mol. wt., 352.

4-Methoxy-1-phenyl-2,3-benzofluorenone, prepared from the hydroxy compound with diazomethane, formed lemon-yellow needles from ethanol, m.p. 180°. The ether was not hydrolyzed by hot 1% aqueous alcoholic sodium hydroxide.

Anal. Calcd. for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79. Found: C, 85.73; H, 4.95.

4-Hydroxy-9-phenyl-2,3-benzo-1-isofluorenone crystallized from ethanol or acetic acid as deep red blades with a black reflex, m.p. 225–229° (dec.), giving in alkali a dark blue solution and in sulfuric acid a reddish-orange.

Anal. Calcd. for $C_{23}H_{14}O_2$: C, 85.69; H, 4.38; mol. wt., 322.3. Found: C, 85.26; H, 4.42; mol. wt., 332.

4-Acetoxy-9-phenyl-2,3-benzo-1-isofluorenone, prepared with acetic anhydride and sodium acetate, formed small orange prisms from benzene–ligroin, m.p. 222.5–224°.

Anal. Calcd. for $C_{25}H_{16}O_3$: C, 82.40; H, 4.43. Found: C, 82.18; H, 4.69.

4-Methoxy-9-phenyl-2,3-benzo-1-isofluorenone, prepared with diazomethane, formed bright orange prisms from ligroin or fluffy needles from alcohol, m.p. 152.5–153.5°, gave a red solution in sulfuric acid and was decolorized by hot concentrated alcoholic potassium hydroxide. The "carbonyl" infrared absorption band in chloroform solution lay at 6.1 μ.

Anal. Calcd. for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79. Found: C, 85.32; H, 4.90.

Reduction of 4-Hydroxy-1-phenyl-2,3-benzofluorenone.—A mixture of 30 mg. of 4-hydroxy-1-phenyl-2,3-benzofluorenone, 0.5 g. of zinc dust, 10 mg. of sodium acetate and 5 cc. of acetic anhydride was boiled two minutes, filtered from the zinc and the colorless solution diluted with hot water. The resultant solid (21 mg., m.p. 98–110°) on two crystallizations from aqueous ethanol afforded some 5 mg. of white crystals, m.p. 209–210°. A mixture with authentic 2-benzhydryl-1,4-diacetoxynaphthalene (m.p. 215°) melted at 180–205°.

Oxidation of 4-Hydroxy-1-phenyl-2,3-benzofluorenone.—A solution of 100 mg. of the fluorenone and one pellet of potassium hydroxide in 15 cc. of methanol and 5 cc. of water was heated under reflux and treated dropwise with 12 cc. of 17% hydrogen peroxide. The mixture was boiled until colorless, cooled, washed with ether and acidified. Overnight the solution deposited 11 mg. of impure hydrated *o*-benzoylbenzoic acid. The filtrate was extracted with ether, the ether distilled and the residue crystallized from aqueous acetone by gradual evaporation. There formed first 11 mg. of stout needles of *o*-benzoylbenzoic acid, which after prolonged desiccation in high vacuum melted at 118–126°, undepressed by mixture with the authentic substance (m.p. 124.5–127.5°). The identity of the keto acid was confirmed by examination of the infrared spectrum and by cyclization in hot sulfuric acid to anthraquinone, crystallized and characterized by a pink vat. Further crops of oxidation products were 11 mg. of mixed crystals and finally 61 mg. of small hemispheres of impure phthalic acid, m.p. 185–190°, identified as phthalic anhydride, m.p. 129°.

Preparation of Benzofluorenones.—Benzalphthalide[24] was isomerized to 2-phenyl-1,3-indanedione by the theoretical quantity of a hot 2% solution of sodium in methanol and the dissolved sodium salt alkylated by methyl bromoacetate to methyl 2-phenyl-1,3-indanedione-2-acetate[25] in 88% yield. The vigorous isomerization of the ester by a 10% solution of sodium in methanol furnished in 83% yield **2-carbomethoxy-3-phenyl-1,4-naphthohydroquinone**, which formed pale yellow prisms from methanol, m.p. 121.5–122.5°.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80. Found: C, 73.58; H, 5.14.

Cyclization with hot sulfuric acid produced 1,4-dihydroxy-2,3-benzofluorenone as orange-bronze blades from acetic acid, m.p. 264–266°. The purple alkaline solution faded irreversibly in air. From the dihydroxy compound were prepared the diacetate and 1-acetoxy-4-methoxy-2,3-benzofluorenone, m.p. 187–189°.[26] The ether acetate in hot alcoholic alkali formed a bright yellow solution with green fluorescence.

Syntheses of Isofluorenones.—A mixture of 1.9 g. of lithium chips, 14.2 cc. of bromobenzene and 100 cc. of ether was boiled under reflux four hours, freed of unreacted metal (0.3 g.) and treated with 8.9 g. of solid 1,4-dihydroxy-2,3-benzofluorenone and 100 cc. of ether. The suspension was boiled six hours and decomposed cautiously with 100 cc. of 10% acetic acid and 100 cc. of ether. The dark aqueous layer was separated and filtered to give 1.65 g. of recovered dihydroxybenzofluorenone, m.p. 253–259°. The washed ether solution was run slowly into 350 cc. of acetic acid maintained at 90–102° and the acid was heated five minutes longer, cooled and filtered to furnish 5.5 g. (62% of unrecovered starting material) of shiny, dark red blades of 4-hydroxy-9-phenyl-2,3-benzo-1-isofluorenone, m.p. 230–240° (dec.). Experiments on phenylation in ether-benzene or ether-dioxane afforded no product.

When a solution of phenyllithium from 0.75 g. of lithium, 5.5 cc. of bromobenzene and 25 cc. of ether was treated with 2.5 g. of solid 1,4-diacetoxy-2,3-benzofluorenone and 25 cc. of ether, a vigorous reaction ensued. The mixture was boiled under reflux half an hour, decomposed and the ether phase added to 100 cc. of hot acetic acid. From the cold solution there crystallized 1 g. (43%) of dark red needles of 4-hydroxy-9-phenyl-2,3-benzo-1-isofluorenone, m.p. 222–230°.

A suspension of 0.35 g. of 1,4-dihydroxy-2,3-benzofluorenone with the phenyllithium from 0.08 g. of metal and 0.7 cc. of bromobenzene in 10 cc. of ether was boiled under

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[22] L. Horner, E. Spietschka and A. Gross, *Ann.*, **573**, 17 (1951).

[23] L. I. Smith and H. H. Hoehn, THIS JOURNAL, **63**, 1181 (1941).

[24] R. Weiss, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 61.

[25] D. Radulescu and G. Gheorgiu, *Ber.*, **60**, 186 (1927).

[26] Previously reported as 163–164°.[9] Dr. Koelsch has courteously informed us that according to a recent redetermination the original sample melted at 183–185°.

reflux six hours and decomposed with 10 cc. of 5% acetic acid, and the ether solution was washed with aqueous sodium bicarbonate, dried and evaporated in nitrogen. The dark residue was taken up in 5 cc. of boiling benzene, cooled and filtered to give 0.35 g. of crude 1,4,9-trihydroxy-9-phenyl-2,3-benzofluorene as a brown solid, m.p. 222–226° (dec.) (other specimens melted as low as 185°), soluble in alkali. The substance was converted to 4-hydroxy-9-phenyl-2,3-benzo-1-isofluorenone in ten minutes by acetic acid at 100°.

9-Hydroxy-9-phenyl-2,3-benzofluorene-1,4-quinone, obtained by oxidation of the hydroquinone in ether with silver oxide, formed bright orange-yellow prisms from ether, m.p. 193–194°. The compound gave a pink solution in alcoholic alkali, a greenish-yellow vat and a dark olive solution in sulfuric acid. The ultraviolet and visible absorption maxima in ethanol solution lay at 258 mμ (log ε 4.34), 308 (3.86) and 417 (3.41).

Anal. Calcd. for $C_{23}H_{14}O_3$: C, 81.64; H, 4.17. Found: C, 81.37; H, 4.45.

A solution of 0.03 g. of the quinone in 3 cc. of acetic acid mixed with a solution of 0.1 g. of stannous chloride dihydrate and 0.1 cc. of 6 *N* hydrochloric acid in 1 cc. of water and heated ten minutes at 100° deposited when cold 0.02 g. of dark red needles of 4-hydroxy-9-phenyl-2,3-benzo-1-isofluorenone, m.p. 223–227°.

1,4-Diacetoxy-9-hydroxy-9-phenyl-2,3-benzofluorene, obtained from the trihydroxy compound, acetic anhydride and sodium acetate or the quinone by reductive acetylation, formed white prisms from dilute acetic acid or ether–petroleum ether, m.p. 187.5–189°. The substance tended to separate as a gel from non-aqueous solvents. The ultraviolet absorption maxima in chloroform lay at 256 mμ (log ε 4.66), 265 (4.56) (inflection), 276 (4.50), 290 (4.18), 303 (4.28), 316 (4.34), 330 (3.09) (inflection) and 348 (2.68).

Anal. Calcd. for $C_{27}H_{20}O_5$: C, 76.40; H, 4.75. Found: C, 76.46; H, 5.44.

A mixture of 0.1 g. of 4-hydroxy-9-phenyl-2,3-benzo-1-isofluorenone, 3 cc. of acetic anhydride and a drop of sulfuric acid was warmed five minutes at 60°, cooled and treated with 0.3 g. of sodium acetate, 1 cc. of acetic acid and 4 cc. of water, shaken vigorously to hydrolyze the anhydride and chilled. The product, 0.14 g. of yellow solid, m.p. 182–199° (dec.), afforded on recrystallization from ethyl acetate–ligroin pure **1,4,9-triacetoxy-9-phenyl-2,3-benzofluorene** as white prisms, m.p. 223–226° (dec., bath preheated to 210°). The decomposition point is sensitive to impurity: certain samples melted near 230°, whereas material precipitated from acetic acid by water sometimes melted below 160°. The ultraviolet absorption maxima in chloroform lay at 256 mμ (log ε 4.60), 265 (4.57), 275 (4.55), 291 (4.19), 303 (4.26) and 316 (4.32).

Anal. Calcd. for $C_{29}H_{22}O_6$: C, 74.67; H, 4.75. Found: C, 74.57; H, 5.05.

A solution of 0.4 g. of 1-acetoxy-4-methoxy-2,3-benzofluorenone in 10 cc. of benzene was added to a cold solution of phenyllithium from 0.8 cc. of bromobenzene and 0.1 g. of lithium in 5 cc. of ether, boiled half an hour under reflux and poured into 20 cc. of cold 10% sulfuric acid. The organic phase, washed, evaporated, taken up in 3 cc. of benzene and 3 cc. of petroleum ether and chilled, deposited 0.15 g. of **1,9-dihydroxy-4-methoxy-9-phenyl-2,3-benzofluorene**, which formed pale yellow prisms from benzene–ligroin, soluble without color in aqueous alcoholic alkali. The substance heated slowly turned orange at 140° and melted at 175–179° (dec.); the "instantaneous" decomposition point appeared to be near 193°.

Anal. Calcd. for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.17; H, 5.11.

4-Methoxy-9-phenyl-2,3-benzo-1-isofluorenone could be obtained from 1,9-dihydroxy-4-methoxy-9-phenyl-2,3-benzofluorene by fusion at 190° or by solution in acetic acid at 100° or sulfuric acid at room temperature. In addition, when 20 mg. of the phenol and 0.15 g. of potassium hydroxide were dissolved in 1 cc. of methanol and 3 cc. of water and boiled under reflux 20 minutes, the dark mixture on dilution with 10 cc. of water and filtration afforded 15 mg. of bright orange methoxyisofluorenone, m.p. 152–153.5°.

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[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY[1] AND THE RICE INSTITUTE]

Reaction between 2,6-Di-*t*-butyl-*p*-cresol and Bromine

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Bromine reacts with 2,6-di-*t*-butyl-*p*-cresol in methyl alcohol, *t*-butyl alcohol or acetic acid to form, respectively, 2,6-di-*t*-butyl-4-methyl-4-methoxy-2,5-cyclohexadienone, 3,5-di-*t*-butyl-4-hydroxybenzaldehyde and 3,5-di-*t*-butyl-4-hydroxybenzyl acetate. The reaction proceeds through formation of 2,6-di-*t*-butyl-4-bromo-4-methyl-2,5-cyclohexadienone. An explanation of subsequent reactions leading to the reported products is suggested.

In a recent publication[4] 3,5-di-*t*-butyl-4-hydroxybenzaldehyde (I) was reported as the principal product of the reaction between bromine and 2,5-di-*t*-butyl-4-methyl-4-*t*-butylperoxy-2,5-cyclohexadienone in acetic acid. Efforts to synthesize this aromatic aldehyde by the usual methods proved unsuccessful. However, a small yield was obtained by treatment of 2,6-di-*t*-butyl-*p*-cresol with bromine in acetic acid in the presence of sodium acetate. Some aspects of this unusual reaction are considered in this paper.

It was observed that when the reaction between bromine and 2,6-di-*t*-butyl-*p*-cresol (IIIc) was carried out in commercial *t*-butyl alcohol or in a mixture of *t*-butyl alcohol and water, the yield of the aldehyde was increased and the time of reaction greatly shortened. Bromination in acetic acid containing a little water permitted the isolation of the aldehyde in high yield also, the reaction being considerably slower than in *t*-butyl alcohol. If on the other hand the reaction was allowed to proceed in methyl alcohol or in a mixture of methyl alcohol and water, the only product obtained was a compound which possessed an ultraviolet spectrum characteristic of a substituted 2,5-cyclohexadienone,[4,5] exhibiting a maximum at 234 mμ, with an ε of 10,000 in 95% ethyl alcohol, 232 mμ in iso-

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[5] H. Dannenberg, *Abhand. preuss. Akad. Wiss.*, **21**, 3 (1939); L. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd Ed., Reinhold Publishing Co., New York, N. Y., 1941, p. 193.