TABLE I

Phenol (mmoles)	DDQ, mmoles	CH_3OH, ml.	Time	Product (% yield)	M.p., °C.	DDH, % yield
4-Hydroxydiphenylmethane (2)	4	5	16 hr	XXV (91)	133–134	94
2,6-Di-*t*-butyl-α-methoxy-*p*-cresol (2)	2	8	16 hr.	XXVI (94)	188–189	93
Ionol[a] (1)	2	50	40 min.	XXVI (86)	188–189	90
2,6-Di-*t*-butyl-4-methoxyphenol[b] (2)	2	15	12 hr.	XV (81)	66–68	90
4-Bromotetramethylphenol (2)	2	4	24 hr.	XXI (91)	109	91

[a] Ionol was added to the solution of DDQ in methanol. [b] Acetic acid could also be used as solvent.

butyl-α-methoxy-*p*-cresol, m.p. 98–99°. Its infrared spectrum was identical with that of authentic material.

Bis(1-bromo-3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadien-yl-1) (XVII).—DDQ (227 mg., 1 mmole) was added to a solution of 570 mg. (2 mmoles) of 4-bromo-2,6-di-*t*-butylphenol in 5 ml. of absolute methanol, agitated by a stream of nitrogen. The reaction mixture turned deep brown, then after a few seconds very bright yellow as a light yellow crystalline substance precipitated. After 5 min., the reaction mixture was filtered and the residue was washed with little methanol, yielding 450 mg. (79%) of XVII as light yellow crystals. The yield can be increased to 85% if the reaction mixture is kept in the refrigerator for several hours before filtration. The substance turned red at about 90° (*cf.* ref. 25), losing bromine upon heating, thus forming 3,3′,5,5′-tetra-*t*-butyldiphenoquinone, m.p. 242–244°.

Anal. Calcd. for $C_{28}H_{40}Br_2O_2$ (568.43): C, 59.16; H, 7.09; Br, 28.1. Found: C, 59.13; H, 7.08; Br, 27.4.

Oxidation of 2,4,6-Trimethylphenol (Mesitol).—DDQ (908 mg., 4 mmoles) was added to a solution of 272 mg. (2 mmoles) of mesitol in 10 ml. of methanol, agitated by a stream of nitrogen. The solution turned deep blue with evolution of heat, then brown after 1 min., and finally yellow. The reaction mixture was kept standing under nitrogen for 12 hr. and then evaporated *in vacuo* yielding a solid, light yellow residue. Treatment with 50 ml. of boiling benzene left 875 mg. (95%) of 2,3-dichloro-5,6-dicyanohydroquinone undissolved. Evaporation of the filtrate left a light yellow solid that was washed with aqueous methanol and filtered, yielding 250 mg. of 3,5-dimethyl-4-hydroxybenzaldehyde (83%), m.p. 113–114°. Recrystallization from aqueous methanol raised the melting point to 114–115°.

Other oxidations involving a similar work-up as the oxidation of mesitol are summarized in Table I.

Oxidation of 2,6-Dimethoxyphenol.—DDQ (454 mg., 2 mmoles) was added to a solution of 308 mg. (2 mmoles) of 2,6-dimethoxyphenol in 3 ml. of absolute methanol. The solution turned warm and a dark violet-colored precipitate was formed. Filtration after 1 min. yielded 188 mg. (62%) of 3,3′,5,5′-tetramethoxydiphenoquinone. To the filtrate were added 2 drops of water, yielding a yellow crystalline precipitate. It was sublimed at 180° (10 mm.) yielding 43 mg. (13%) of 2,6-dimethoxy-1,4-benzoquinone, m.p. 255°.

Spectra.[34]—The infrared spectra were taken on a Perkin-Elmer grating infrared spectrophotometer, Model 521.

Ultraviolet spectra were obtained with a Cary recording spectrophotometer, Model 14. Figure 4 represents the spectrum obtained by dissolving 5.5 mg. of IX in 500 ml. of isooctane, corresponding to a 2.5 × 10^{-5} *M* solution. The spectrum of Figure 5 was obtained by dissolving an unweighed amount of IX in ether directly in the ultraviolet cell. The ε-scale given in Figure 5 is based on the ε-value calculated from the experiment given in Figure 4.

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[34] All spectra were taken with the technical assistance of Miss D. V. McClung of this laboratory.

Quinone Dehydrogenation. II. The Oxidative Dimerization of Enols and Enolizable Ketones

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2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) under mild conditions reacts smoothly with enols and enolizable ketones. Flavonol is readily oxidized by DDQ to give a C–O-coupled dehydro dimer. 2-Arylindane-1,3-diones are easily converted into 2,2′-diaryl-2,2′-biindane-1,1′,3,3′-tetrones. Treatment of 2-methylsulfonylindane-1,3-dione with DDQ gives the addition product, 2-(2,3-dichloro-5,6-dicyano-4-hydroxyphenoxy)-2-methylsulfonylindane-1,3-dione. A mechanism for the oxidation of enolizable ketones involving a one-electron transfer from the enolate ion to the quinone is discussed on the basis of an ultraviolet spectroscopic investigation.

In the preceding paper on quinone dehydrogenation it has been shown that 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (henceforth abbreviated DDQ) represents a powerful oxidizing agent for phenols.[1] The results obtained in the oxidation of phenols suggested the extension of the reaction to enols and ketones known to exist in a keto–enol equilibrium in solution.

Dehydrogenation of ketones by quinones has previously been applied in the preparation of $\Delta^{1,4}$ or $\Delta^{1,4,6}$ steroidal ketones from Δ^{4} or $\Delta^{4,6}$ steroidal ketones. The reaction requires elevated temperature.[2] At room temperature the α,β-unsaturated steroidal ketones are stable toward quinones. They can be prepared by oxidation of the corresponding allylic alcohols with DDQ.[3]

This paper is concerned with the quinone dehydrogenation of enols and enolizable ketones for which α–β unsaturation is structurally not possible. Such enols and enolizable ketones are found to undergo oxidative dimerization in excellent yields.

Results

A. Flavonol.—DDQ reacts with flavonol (I) in dioxane solution at room temperature to give 2,3-dichloro-5,6-dicyanohydroquinone (henceforth abbreviated DDH) and a yellow crystalline compound (yield 64%) for which elemental analysis and molecular weight are in agreement with a flavonol dehydro dimer. The infrared spectrum of this dehydro dimer (in KBr; Figure 1) exhibits carbonyl peaks at 1740 and 1695

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[1] H.-D. Becker, *J. Org. Chem.*, **30**, 982 (1965).

[2] D. Burn, D. N. Kirk, and V. Petrow, *Proc. Chem. Soc.*, 14 (1960).

[3] D. Burn, V. Petrow, and G. O. Weston, *Tetrahedron Letters*, **No. 9** 14 (1960).

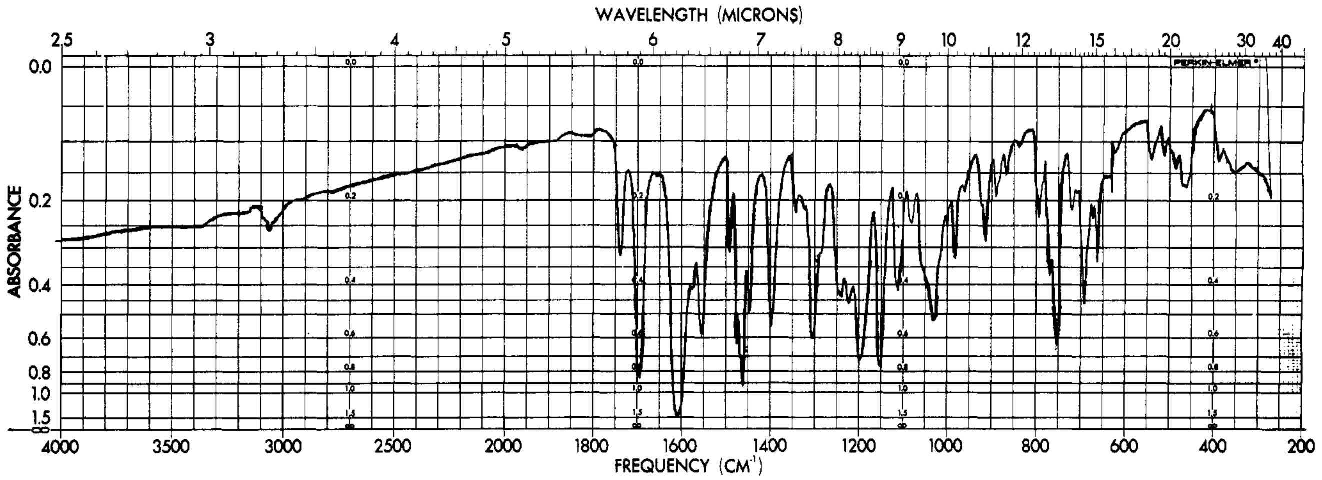
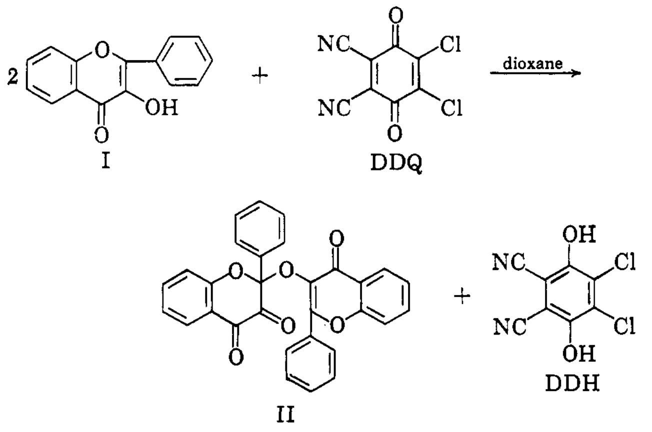
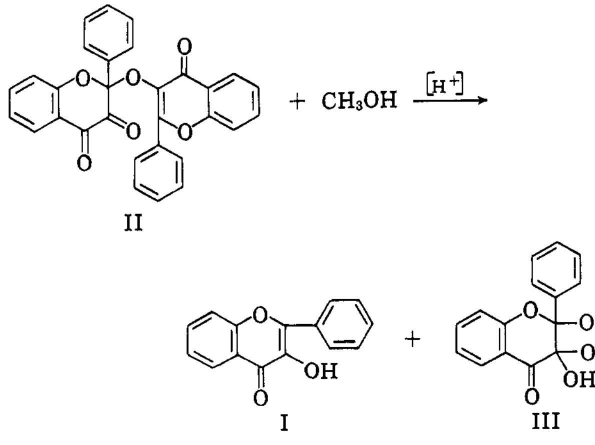


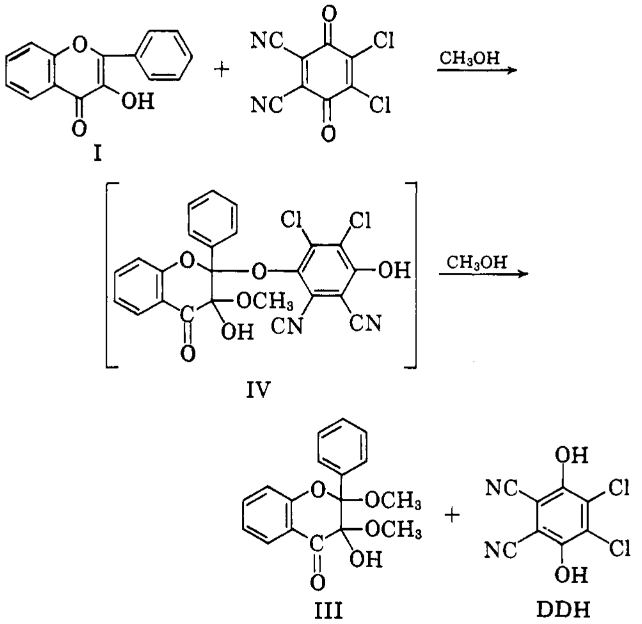
Figure 1.—The infrared spectrum of the flavanol dehydro dimer II, in potassium bromide.

cm.$^{-1}$, as well as a strong absorption at 1610 cm.$^{-1}$ indicating the presence of the flavone system, since this absorption is also found in flavonol. The structure II suggested by these data for the flavonol dehydro dimer is established by acid-catalyzed cleavage of the ketal II in methanol solution to give flavonol (isolated in 70% yield) and the methyl 3-hemiketal of 2-methoxy-3,4-flavandione (III) which was identified by vapor phase chromatographic comparison with authentic material.





Treatment of flavonol with DDQ in methanol solution leads to a product which could not be obtained in analytically pure form, but for which the infrared spectrum is suggestive of structure IV. Such a ketal structure is supported by the conversion of IV into DDH (90% yield) and the flavandione derivative III (60% yield), which has been prepared recently by Smith by oxidation of flavonol with periodate in methanol solution.[4]



B. 2-Substituted Indane-1,3-diones.—Addition of DDQ to an orange-colored suspension of 2-phenylindane-1,3-dione (Va) in alcohol leads to rapid color discharge and precipitation of 2,2′-diphenyl-2,2′-biindane-1,1′,3,3′-tetrone (VIa). This compound has been known for a long time and its structure as C–C-coupled dehydro dimer of 2-phenylindane-1,3-dione has recently been proved in a detailed investigation.[5,6]

In a similar fashion to Va, 2-(4-methoxyphenyl)indane-1,3-dione (Vb) and 2-(4-phenylsulfonylphenyl)-indane-1,3-dione (Vc) are rapidly converted in high yields into 2,2′-di-(4-methoxyphenyl)-2,2′-biindane-1,-1′,3,3′-tetrone (VIb) and 2,2′-di-(4-phenylsulfonyl-phenyl)-2,2′-biindane-1,1′,3,3′-tetrone (VIc), respectively.

2-(4-Phenylsulfonylphenyl)indane-1,3-dione (Vc) was synthesized by base-catalyzed condensation of phenyl

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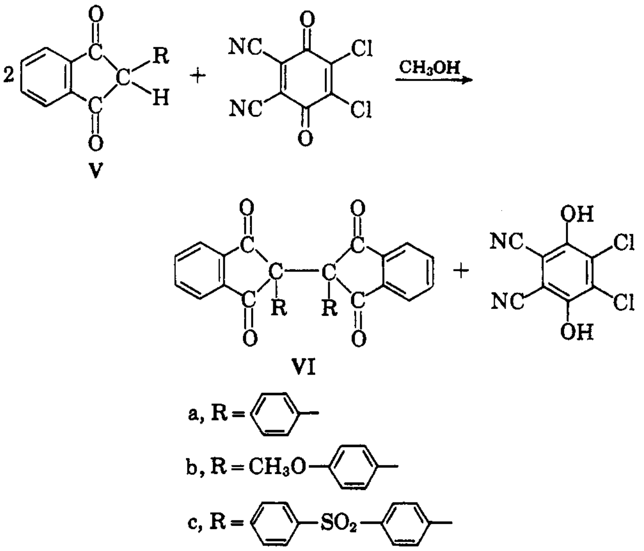
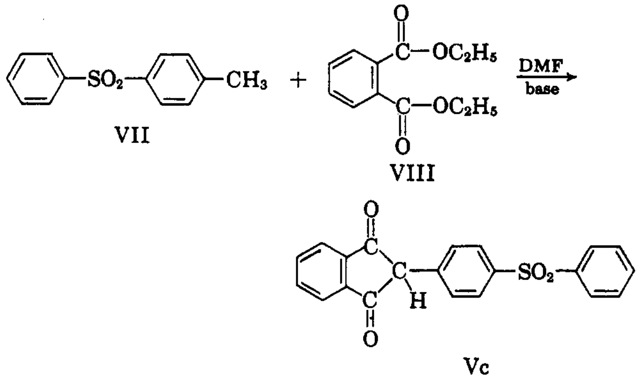
[4] M. A. Smith, R. A. Webb, and L. J. Cline, *J. Org. Chem.*, **30**, 995 (1965).

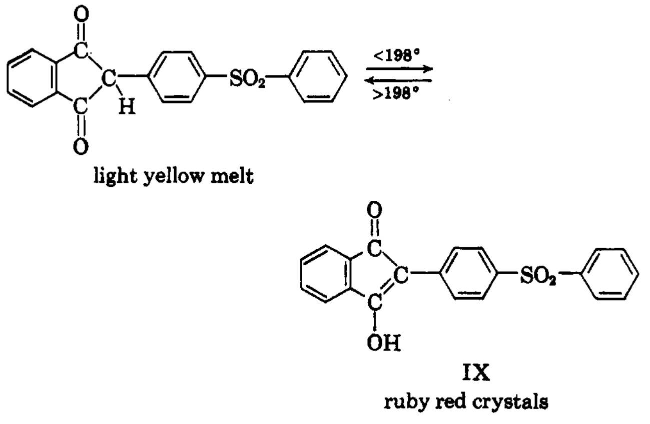
[5] F. Nathanson, *Ber.*, **26**, 2576 (1893).

[6] F. M. Beringer, S. A. Galton, and S. J. Huang, *Tetrahedron*, **19**, 809 (1963).



p-tolyl sulfone (VII) with diethyl phthalate (VIII) in dimethylformamide solution. Compound Vc forms deep red crystals and the infrared spectrum (in KBr) indicates that Vc in the solid state exists as the enol, 3-hydroxy-2(4-phenylsulfonylphenyl)-inden-1-one (IX). Above its melting point, or in chloroform solution, IX rearranges into the light yellow tautomer Vc (Figure 2).





When the reaction of DDQ with cyclic β-diketones is extended to 2-methylsulfonylindane-1,3-dione (X; for an improved synthesis of X, see Experimental), no dehydro dimerization is observed, but the quinone readily adds to X to give 2-(2,3-dichloro-5,6-dicyano-4-hydroxyphenoxy)-2-methylsulfonylindane-1,3-dione (XI) in high yield.

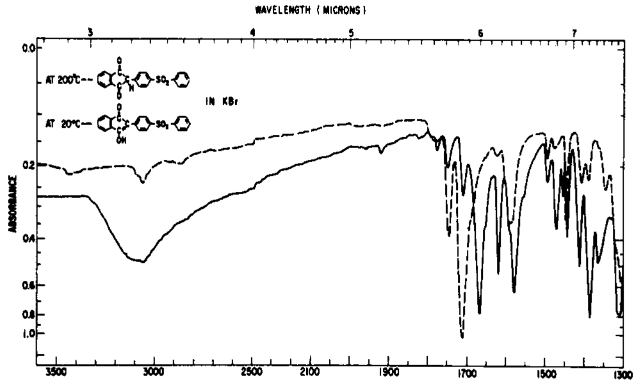
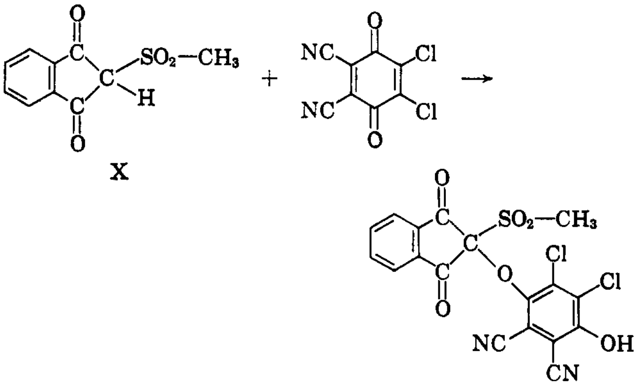


Figure 2.

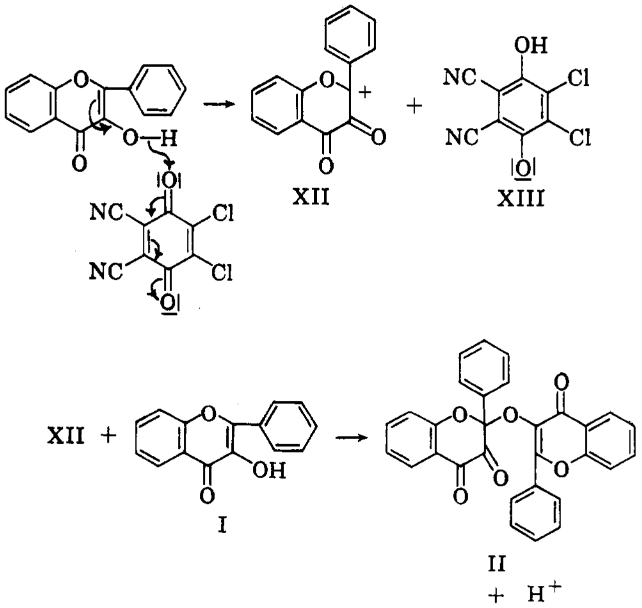


XI

Discussion

Flavonol has been found earlier by Smith to undergo oxidation upon treatment with periodate in both aqueous and methanol solutions.[4,7] The ionic mechanism for the periodate oxidation has been substantiated by an O^{18} tracer study by Adler, Falkehag, and Smith.[8] An ionic mechanism for the dehydro dimerization of flavonol (Scheme I) involving a hydride ion abstraction

Scheme I



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[7] M. A. Smith, *J. Org. Chem.*, **28**, 933 (1963).

[8] E. Adler, I. Falkehag, and B. Smith, *Acta Chem. Scand.*, **16**, 529 (1962).

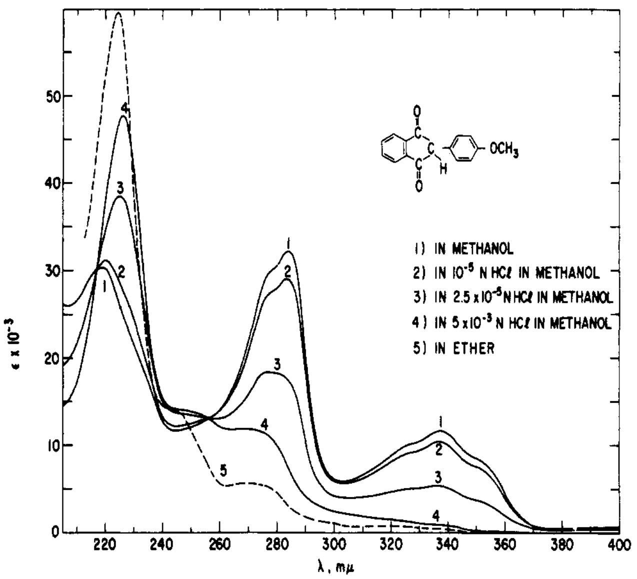
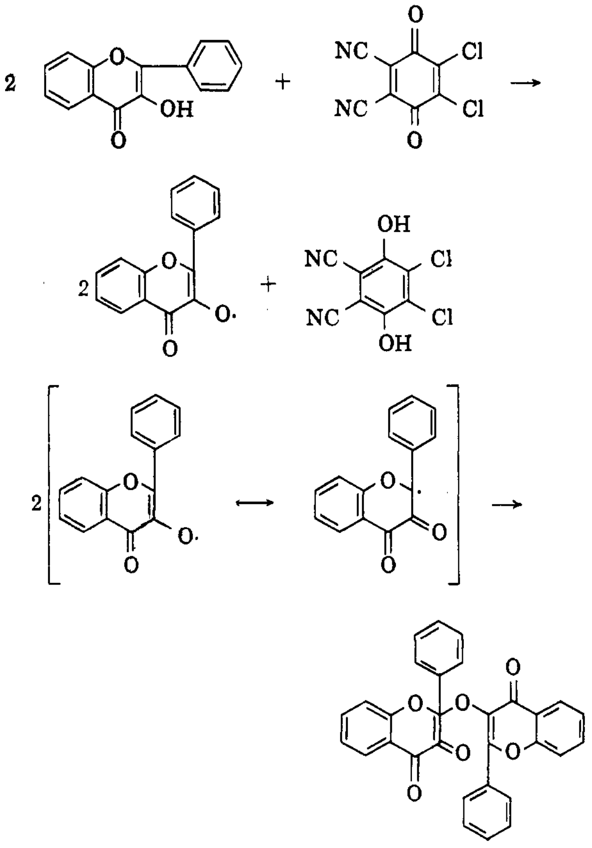


Figure 3.

by the quinone seems unlikely since one would expect nucleophile XIII to react with carbonium ion XII. Thus, a one-electron transfer reaction as substantiated for the oxidative dimerization of phenols by DDQ[1] might also be occurring in the dehydro dimerization of flavonol (Scheme II). The oxidation of flavonol by DDQ in methanol would then involve the combination of the semiquinone radical with the flavonoxy radical to give a 2-aryloxy-substituted 3,4-flavandione in which the 3-keto group undergoes methanol addition to yield intermediate IV (*cf.* ref. 4) and in which in a subsequent reaction, the aryloxy moiety is exchanged by an alkoxy moiety (*cf.* ref. 1) to give III.

SCHEME II

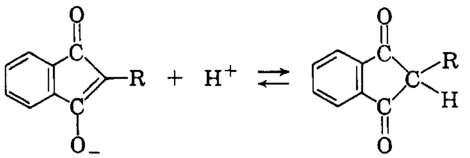


The discussion about the dehydro dimerization of 2-aryl-substituted indane-1,3-diones has to start with the question: in which tautomeric form is the cyclic β-diketone attacked by the quinone? To solve this problem a detailed ultraviolet spectroscopic investigation of 2-substituted indane-1,3-diones became necessary.

The spectroscopic behavior of 2-substituted indane-1,3-diones was studied some 50 years ago by Hantzsch.[9] The observation that indane-1,3-diones form colorless solutions in ether or chloroform, but deep-colored solutions in alcohol or alkali was interpreted in terms of keto–enol tautomerism. Later, certain 2-substituted indane-1,3-diones have been isolated in both the colorless diketone and in the colored enol form.[10,11]

The ultraviolet spectra of the 2-substituted indane-1,3-diones Vb, Vc, and X have been measured in methanol and in all three cases the spectra obtained in methanol do not change upon the addition of sodium methoxide to the indane-1,3-dione solution. Therefore, it can be assumed that the 2-substituted indane-1,3-diones investigated are completely ionized in methanol solution. The same is true for 2-phenylindane-1,3-dione since its ultraviolet spectrum in methanol has been found to be identical with that in sodium hydroxide solution.[12]

Addition of hydrochloric acid to the methanol solutions of Vb, Vc, and X changes the spectra significantly (Figures 3, 4, and 5). If no further spectral change is observed upon addition of hydrochloric acid, then the spectra are essentially identical with the spectra of VIIa, VIIb, and X taken in ether solution. Therefore, and because of the exhibition of isosbestic points in the spectra, it can be assumed that the addition of hydrochloric acid to a methanol solution of the 2-substituted indane-1,3-diones shifts the position of the equilibrium from the enolate side to the side of the β-diketone. It has been pointed out earlier that for



this type of equilibrium the existence of the free enol form *in solution* has not been established.[13] If it can be assumed that the addition of DDQ to a methanol solution of the 2-substituted indane-1,3-dione does not effect the position of this equilibrium, then the spectroscopic results described suggest that the reactive species undergoing oxidation by DDQ in alcohol solution is the enolate ion rather than the enol or cyclic β-diketone. This is supported by the finding that 2-methylsulfonylindane-1,3-dione (X) in dioxane solution at room temperature does not react with DDQ. The ultraviolet spectrum of X in dioxane is that of the diketone. Compound Vc was found to react with DDQ

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[9] A. Hantzsch, *Ann. Chem.*, **392**, 286 (1912).

[10] C. F. Koelsch, *J. Am. Chem. Soc.*, **58**, 1328 (1936).

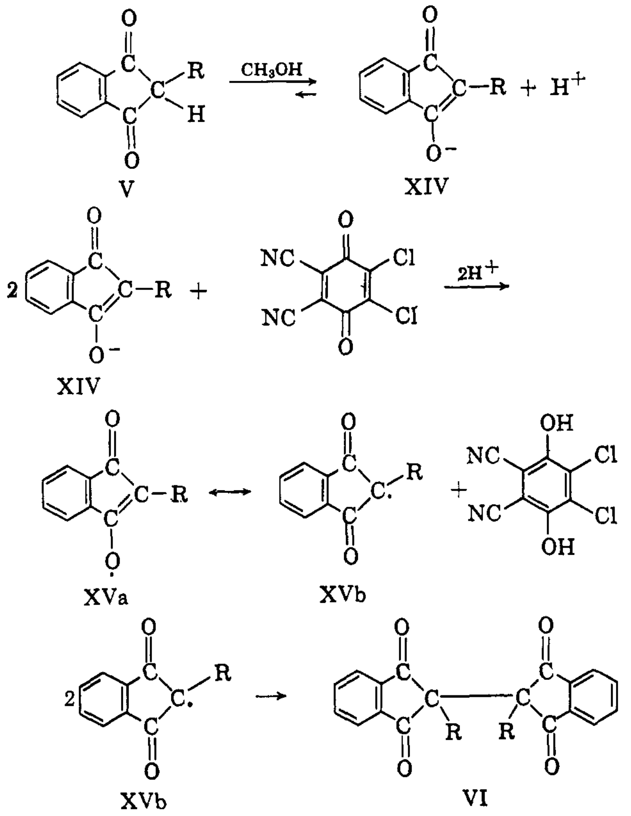
[11] A. Schönberg, A. Mustafa, and W. Asker, *Nature*, **171**, 222 (1953).

[12] M. Covello and E. Abignente, *Ann. chim.* (Rome), **52**, 923 (1962).

[13] O. Neiland in "Cyclic β-Diketones," G. Wanag, Ed. (in Russian), Riga, 1961 p. 41.

in dioxane solution; however, the reaction proceeds slowly and does not lead to a pure product.

Previously it has been suggested that the quinone dehydrogenation of steroidal ketones involves a hydride ion transfer from the enolized ketone to the quinone.[14] Such an ionic mechanism appears to be improbable in the case of the dehydrogenation of 2-arylindane-1,3-diones because the reaction products are C–C-coupled dehydro dimers, typical of a radical reaction. Thus, the mechanism for the oxidation of the cyclic β-diketones Va–c by DDQ in alcohol solution should be interpreted in terms of a one-electron transfer reaction from the enolate ion (XIV) to the quinone. The 2-arylindane-1,3-dione-2 radicals (XVa and b) thus formed then undergo dimerization to yield the products isolated. It can be assumed, however, that the same products are formed if not the enolate ion but the free enol undergoes oxidation.



The formation of 2-(2,3-dichloro-5,6-dicyano-4-hydroxyphenoxy)-2-methylsulfonylindane-1,3-dione (XI) can be explained by the combination of radical XVb with the semiquinone radical. It has been found earlier that 3,3′,5,5′-tetrachlorodiphenoquinone adds to ketones in an acid-catalyzed reaction to yield products of analogous structure.[15]

Experimental

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone was recrystallized from methylene chloride. Absolute methanol was commercial grade. Oxidation reactions were carried out in screw-cap bottles under nitrogen. All melting points were taken on a Fisher-Johns apparatus and are not corrected.

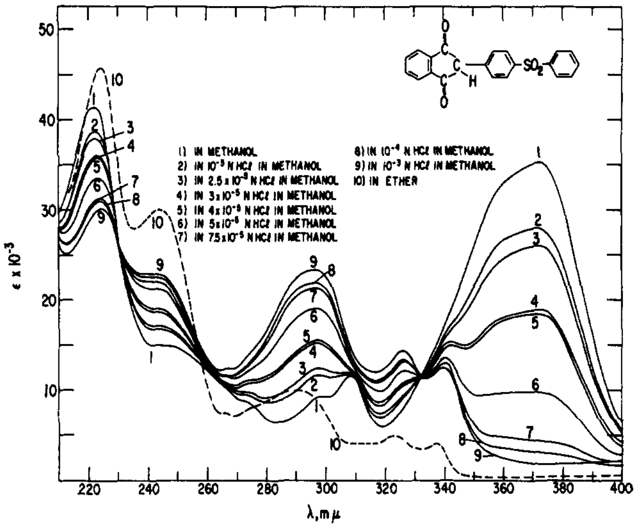


Figure 4.

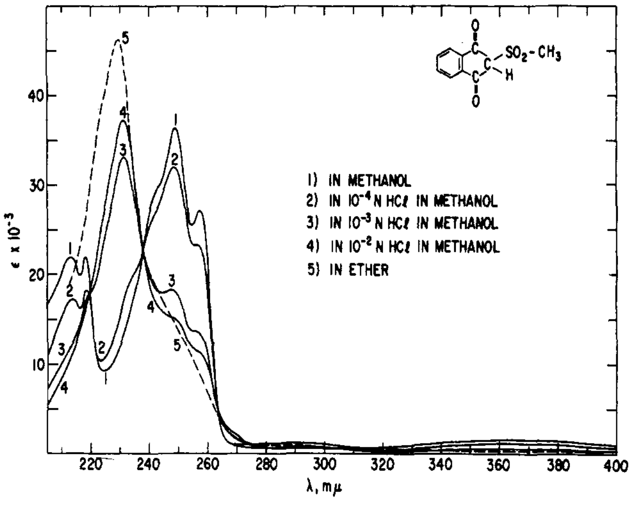


Figure 5.

Oxidation of Flavonol. A. In Dioxane.—DDQ (454 mg., 2 mmoles) was added to a solution of 952 mg. (4 mmoles) of flavonol in 15 ml. of dioxane. The dark-colored reaction mixture was kept under nitrogen for 12 days. By then the solution was light yellow and a heavy crystalline precipitate had formed. The reaction mixture was filtered, yielding a mixture of colorless needle-shaped crystals (DDH) and big cubic yellow crystals. This crystalline mixture was treated with 50 ml. of warm chloroform and filtered, giving 385 mg. of undissolved DDH. The chloroform filtrate was evaporated *in vacuo* yielding 770 mg. of yellow crystals, m.p. 210–215°. This material was washed with few milliliters of absolute ether and filtered, yielding 600 mg. of flavonol dehydro dimer II in the form of yellow crystals, m.p. 225–227°. Recrystallization by dissolving in chloroform and addition of ether did not raise the melting point. Evaporation of the original dioxane filtrate and treatment with chloroform and then ether gave an additional 10 mg. of DDH and 50 mg. of flavonol dehydro dimer: total yield of DDH, 87%; total yield of flavonol dehydro dimer II, 69%.

Anal. Calcd. for $C_{30}H_{18}O_6$ (474.44): C, 75.94; H, 3.82. Found: C, 75.98; H, 3.80; mol. wt., 476 (thermoelectric measurement in chloroform).

B. In Methanol.—DDQ (454 mg., 2 mmoles) was added slowly to a solution of 476 mg. (2 mmoles) of flavonol in 200 ml. of absolute methanol at 10°, agitated by a stream of nitrogen. The solution was kept under nitrogen at 0° for 1 hr. and at room temperature for 4 hr. Evaporation of the light yellow solution *in vacuo* and washing of the colorless residue with 5 ml. of ice-cold methanol gave 750 mg. of a colorless substance (IV) with an undefined melting point. The substance turned yellow-brown above 100°, softened about 140°, and melts with decomposition

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[14] E. J. Agnello and G. D. Laubach, *J. Am. Chem. Soc.*, **79**, 1257 (1957); H. J. Ringold and A. Turner, *Chem. Ind.* (London), 211 (1962); see also L. M. Jackman in "Advances in Organic Chemistry: Methods and Results," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, p. 329.

[15] H. B. Henbest and D. N. Jones, *Chem. Ind.* (London), 1113 (1960).

above 200°. The product was boiled in 25 ml. of methanol for 1 hr., giving a red solution. Evaporation at room temperature gave 325 mg. of III, m.p. 146°. (The compound lost methanol upon heating, turned yellow above 110°, and started to melt at about 120°, depending on the rate of heating.) An additional 35 mg. of III was isolated from the original methanol filtrate: total yield of III, 360 mg. (60%).

Anal. Calcd. for $C_{17}H_{16}O_5$ (300.30): C, 67.99; H, 5.37. Found: C, 67.94; H, 5.41; mol. wt., 296 (thermoelectric measurement in chloroform).

Addition of benzene to the above filtrate resulted in the crystallization of 290 mg. of DDH. From the original filtrate 120 mg. of DDH was isolated (total yield 90%).

Acid-Catalyzed Cleavage of Flavonol Dehydro Dimer (II) with Methanol.—Flavonol dehydro dimer (II; 100 mg.) was dissolved in 2 ml. of chloroform. Then 10 ml. of absolute methanol and 1 drop of concentrated hydrochloric acid were added, whereupon the yellow solution turned colorless. The solvent was evaporated at room temperature; the solid residue was treated with a little methanol and filtered, yielding 35 mg. (70%) of flavonol, m.p. 168–169°. Its infrared spectrum was identical with that of authentic material. The filtrate was subjected to v.p.c. analysis (2-ft. silicon rubber column). The only peak observed was that of III. It was identified by comparison with v.p.c. analysis of an authentic sample.

Oxidation of 2-Phenylindane-1,3-dione (Va).—DDQ (454 mg., 2 mmoles) was added to a suspension of 888 mg. (4 mmoles) of 2-phenylindane-1,3-dione in 25 ml. of absolute methanol under nitrogen. After about 1 min. a colorless substance precipitated from the clear solution. The reaction mixture was shaken for 15 hr. Filtration and washing of the light yellow residue with little boiling methanol gave 550 mg. (62%) of colorless VIa, m.p. 208–210° (lit. m.p. 208°.[5, 12] 213–214°[6]).

Anal. Calcd. for $C_{30}H_{18}O_4$ (442.44): C, 81.43; H, 4.10. Found: C, 81.33; H, 4.19; mol. wt., 449 (thermoelectric measurement in chloroform).

Oxidation of 2-(4-Methoxyphenyl)indane-1,3-dione (Vb).—DDQ (454 mg., 2 mmoles) was added under nitrogen to a suspension of 1.08 g. (4 mmoles) of 2-(4-methoxyphenyl)indane-1,3-dione in 75 ml. of absolute ethanol. The red color of the solution was discharged immediately and a colorless precipitate formed. The reaction mixture was shaken for 15 hr. Filtration and treatment of the colorless residue with boiling ethanol yielded 960 mg. (92%) of VIb, m.p. 246–247° (lit.[16] m.p. 247–248°).

Anal. Calcd. for $C_{32}H_{22}O_6$ (502.50): C, 76.48; H, 4.41. Found: C, 76.58; H, 4.52; mol. wt., 477 (thermoelectric measurement in chloroform).

Oxidation of 2-(*p*-Phenylsulfonylphenyl)indane-1,3-dione (Vc).—DDQ (454 mg., 2 mmoles) was added under nitrogen to a suspension of 1.448 g. (4 mmoles) of 2-(*p*-phenylsulfonylphenyl)-indane-1,3-dione in 75 ml. of absolute methanol. After 2 min. a clear solution was formed and then a colorless crystalline substance precipitated. The reaction mixture was shaken for 15 hr. Filtration and washing of the colorless residue with methanol gave 1.35 g. (94%) of VIc, m.p. 250°.

Anal. Calcd. for $C_{42}H_{26}O_8S_2$ (722.76): C, 69.79; H, 3.63; S, 8.87. Found: C, 69.58; H, 3.85; S, 8.76; mol. wt., 686 (thermoelectric measurement in chloroform).

The compound crystallized with 1 mole of solvent when recrystallized from chloroform.

Anal. Calcd. for $C_{42}H_{26}O_8S_2 \cdot CHCl_3$ (845.15): C, 61.32; H, 3.23; Cl, 12.63; S, 7.62. Found: C, 61.64; H, 3.19; Cl, 11.30; S, 7.99.

Reaction of DDQ with 2-Methylsulfonylindane-1,3-dione (X).—DDQ (908 mg., 4 mmoles) was added under nitrogen to a suspension of 896 mg. (4 mmoles) of 2-methylsulfonylindane-1,3-dione in 40 ml. of absolute methanol. The reaction mixture was shaken for 16 hr. The heavy, crystalline, colorless precipitate formed was then filtered, washed with a little methanol, and dried at 105° yielding 1.46 g. of XI (81%), m.p. 225–230° dec.

Anal. Calcd. for $C_{18}H_8Cl_2N_2O_6S$ (451.24): C, 47.91; H, 1.79; Cl, 15.71; N, 6.21; S, 7.11. Found: C, 47.94; H, 2.01; Cl, 15.85; N, 6.43; S, 7.04.

Preparation of 2-(*p*-Phenylsulfonylphenyl)indane-1,3-dione, Enol Form (IX).[17]—Diethyl phthalate (10 ml., 50 mmoles) was added dropwise to the deep red solution of 11.6 g. (50 mmoles) of phenyl *p*-tolyl sulfone and 12 g. (107 mmoles) of potassium *t*-butoxide in 200 ml. of dimethylformamide, agitated by a stream of nitrogen. The dark green reaction mixture was agitated with nitrogen for 1 hr. Then 500 ml. of ice–water was added and the mixture was extracted with 100 ml. of ether. The aqueous layer was acidified with a mixture of 40 ml. of concentrated hydrochloric acid and 60 ml. of water and shaken with 100 ml. of ether. The mixture containing the deep red solid enol suspended in the aqueous layer was filtered. The enol IX was recrystallized by dissolving in boiling chloroform and adding absolute methanol: 8.6 g. (47%), m.p. 197–198°.

Anal. Calcd. for $C_{21}H_{14}O_4S$ (362.32): C, 69.61; H, 3.89; S, 8.85. Found: C, 69.44; H, 3.83; S, 8.71.

Preparation of 2-Methylsulfonylindane-1,3-dione (X).[17]—Diethyl phthalate (20 ml., 0.1 mole) was added from a pipet to a solution of 18.8 g. (0.2 mole) of dimethyl sulfone and 10.8 g. (0.2 mole) of sodium methoxide in 150 ml. of dimethylformamide, agitated by a stream of nitrogen. Nitrogen was bubbled through the yellow reaction mixture for 68 hr. The reaction mixture was then acidified with cooling in an ice bath with a mixture of 100 ml. of concentrated hydrochloric acid and 250 ml. of water and was extracted with chloroform until the aqueous layer was colorless. The chloroform solution was evaporated *in vacuo* and the residue was subjected to vacuum distillation at about 1 mm. and a bath temperature of 65° in order to remove all solvent. Treatment of the residue with ethanol caused crystallization. The light yellowish substance was washed with boiling ethanol, thus removing the excess dimethyl sulfone, and the residue was recrystallized by dissolving in boiling chloroform and adding ethanol: yield 11.5 g. (51%), m.p. 153–154° (lit.[18] m.p. 150–151°). The yield obtained originally by base-catalyzed condensation of dimethyl sulfone with diethyl phthalate in the presence of potassium *t*-butoxide was only 13%.

Spectra.[19]—The infrared spectra were taken on a Perkin-Elmer grating infrared spectrophotometer, Model 521. Ultraviolet spectra were obtained with a Cary recording spectrophotometer, Model 14. The methanol solutions containing hydrochloric acid were obtained by diluting 12.5 ml. of aqueous 1 *N* hydrochloric acid with 87.5 ml. of methanol. All subsequent dilutions were made with methanol.

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[17] Larger quantities of this material were prepared by Mr. R. J. Marks of this laboratory.

[18] H.-D. Becker and G. A. Russell, *J. Org. Chem.*, **28**, 1896 (1963).

[19] All spectra were taken by Miss D. V. McClung of this laboratory.