1.50 (3 H, triplet, J = 7 cps), 2.35 (3 H, singlet), 2.70 (3 H, singlet), 7.10 (1 H, broad singlet), and 7.49 (1 H, singlet).

2,7-Dimethyl-3-carbethoxy-5-hydroxyindole (**15**).—Repeated recrystallization of the straw-colored solid B from ethanol gave 232 mg of pure product: mp 201–202° (lit.[13] mp 200–202°); ν_{max}^{Nujol} 3400, 3200 (broad), 1650, and 1600 cm^{-1}; nmr (methanol) δ 1.50 (3 H, triplet, J = 7 cps), 2.48 (3 H, broad singlet), 2.73 (3 H, singlet), 6.56 (1 H, broad multiplet), and 7.35 (1 H, doublet, J = 3 cps).

Ethyl 3-Amino-2-(2,5-dihydroxy-4-methylphenyl)crotonate (**17**).—Repeated trituration of the red gum C with diethyl ether gave a tan solid. Several crystallizations from acetone–methanol furnished 223 mg of pure product: mp 192–195° (lit.[8] mp 186–188°); ν_{max}^{Nujol} 3475, 3350 (broad), 1635, and 1590 cm^{-1}; nmr (methanol) δ 1.22 (3 H, triplet, J = 8 cps), 1.83 (3 H, singlet), 2.25 (3 H, singlet), 6.51 (1 H, singlet), and 6.67 (1 H, slightly broadened singlet).

Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.24; H, 6.79; N, 5.51.

Tlc analysis of the combined residue, 900 mg, from the three purifications above revealed equal amounts of **14**, **15**, and **17**. No further separation was undertaken.

Ethyl 3-Amino-2-(2,5-dihydroxy-3-methylphenyl)crotonate (**18**).—Repeated diethyl ether trituration of the red oil obtained by evaporation of the initial dichloroethane mother liquors (D) of the reaction furnished 45 mg of an amorphous solid which was homogeneous by tlc: ν_{max}^{Nujol} 3460, 3350, 1650, and 1615 cm^{-1}; nmr (methanol) δ 1.20 (3 H, triplet, J = 8 cps), 1.80 (3 H, singlet), 2.23 (3 H, singlet), 6.38 (1 H, doublet, J = 3 cps), and 6.61 (1 H, doublet, J = 3 cps).

Attempted Cyclization of 4 to 3.—Repeated crystallization of **4** from acetonitrile or acetone resulted in some decomposition (red-brown mother liquors) but no apparent formation of **3** (tlc). A sample of **4** was heated under reflux in dichloroethane for 4 hr. and worked up in the normal manner. Thin layer chromatography revealed two transformation products, one with the same R_f value as **10**, in addition to starting material **4**; no **3** appeared to be formed.

Nmr Spectra.—**Ethyl 3-aminocrotonate** (**2**) showed (neat) δ 1.18 (3 H, triplet, J = 7 cps), 1.87 (3 H, singlet), 4.07 (2 H, quartet, J = 7 cps), and 4.45 (1 H, singlet).

3-Acetylindole[16] showed (methanol) δ 2.57 (3 H, singlet), 7.35 (3–4 H, broad multiplet), 8.14 (1 H, singlet), and 8.33 (1 H, multiplet).

Indole showed δ 6.80 (C-2 H).[17]

6-Methoxytetrahydrocarbazole showed δ 6.91 (C-4 H).[5]

2-Methylindole showed δ 2.20 (C-2 CH_3).[17]

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[16] J. E. Saxton, *J. Chem. Soc.*, 3592 (1952).

[17] L. A. Cohen, J. W. Daly, H. Kny, and B. Witkop, *J. Am. Chem. Soc.*, **82**, 2184 (1960).

The Question of Sulfoquinone Intermediates

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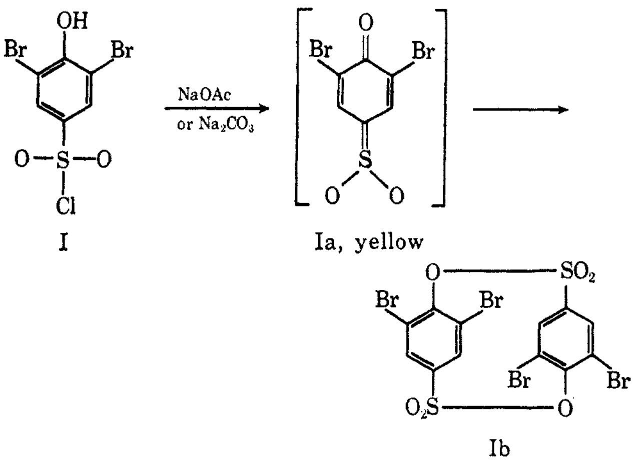
Zincke and Brune[1] reported in 1908 that treatment of 3,5-dibromo-4-hydroxybenzenesulfonyl chloride (I) with either sodium acetate or carbonate in aqueous acetone resulted in the formation of a yellow solution; they attributed the color to the presence of an intermediate "quinoid sulfene" or sulfoquinone (Ia). The color was said to have faded during the reaction and a colorless precipitate thought to have structure Ib was formed.

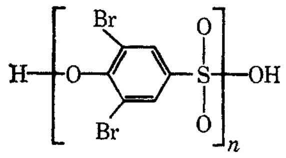


I

Ia, yellow

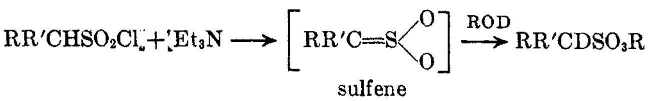
Ib

Oae and Kiritani[2] have recently re-examined this reaction and were unable to give further evidence for the intermediacy of the colored species Ia, but showed that the yellow solution had a clear maximum at 310 mμ. They also examined the colorless product of this reaction and suggested that it was the linear oligomer Ic.



Ic

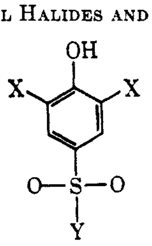
Evidence for the intermediacy of sulfenes has been reported recently in the reaction of sulfonyl chlorides with deuterated alcohols in the presence of triethylamine. The formation of monodeuterated sulfonate esters was rationalized by King and Durst[3] and Truce, *et al.*,[4] in terms of the following reaction scheme.



$$RR'CHSO_2Cl + Et_3N \longrightarrow \underset{\text{sulfene}}{\left[RR'C{=}S\begin{smallmatrix}O\\ \\O\end{smallmatrix}\right]} \xrightarrow{ROD} RR'CDSO_3R$$

The latter findings prompted us to reinvestigate the work of Zincke and Brune[1] with the intention of trapping the sulfoquinone, Ia, and establishing its intermediacy in the reaction of phenolic sulfonyl chlorides with bases. For the purpose of doing this sulfonyl halides and esters were prepared and characterized (Table I).

TABLE I
SULFONYL HALIDES AND ESTERS



Substituent	I	II	III	IV	V	VI
X	Br	Cl	CH_3	Cl	CH_3	CH_3
Y	Cl	Cl	Cl	F	F	OCH_3

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[1] (a) T. Zincke and R. Brune, *Ber.*, **41**, 902 (1908); (b) T. Zincke and W. Glahn, *ibid.*, **40**, 3039 (1907).

[2] S. Oae and R. Kiritani, *Bull. Chem. Soc. Japan*, **38**, 1543 (1965).

[3] J. F. King and T. Durst, *J. Am. Chem. Soc.*, **86**, 287 (1964).

[4] W. E. Truce, R. W. Campbell, and J. R. Morell, *ibid.*, **86**, 288 (1964).

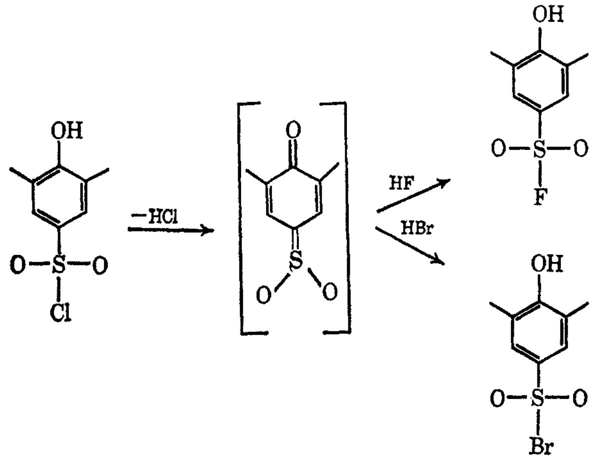
When a concentrated solution of I, II, or III was treated with bases such as triethylamine, triethylenediamine, or *n*-butyllithium, a yellow color developed which faded quickly. When the reactions were carried out in a ultraviolet cell with dilute ethereal solutions, the absorption band of the phenol decreased in intensity as the base was added and a new absorption band appeared at longer wavelengths. The absorption band of the compounds formed tailed into the visible spectral region and were apparently the cause of the yellow color in concentrated solutions. (See Table II and Figure 1.)

Table II

Sulfonyl Chlorides

Compd	Phenol		Yellow species		$\Delta\lambda_{max}$, mμ
	λ_{max}, mμ	ε	λ_{max}, mμ	ε	
I	265	8,400	313	12,000	48
II	264	9,000	319	15,000	55
III	272	9,500	328	...	56

If the reaction of a base with these phenols followed the course suggested by Zincke and Brune,[1] one would expect the formation of sulfonyl fluorides or bromides upon the addition of HF or HBr to the sulfoquinone.



However, experiments designed to trap the yellow species, thought to be the sulfoquinone, were not successful. Neutralization of the basic solutions of I, II, or III with ethereal HF or HBr in the ultraviolet cell resulted in the regeneration of the starting phenol as evidenced by the reappearance of the ultraviolet absorption bands previously recorded for these phenols. With II the two absorption maxima could be quantitatively interconverted by acid–base titrations as shown in Figure 1. The existence of an isosbestic point indicated that only two species were involved in this titration.

To rule out the possibility that the species formed upon HF titration was a sulfonyl fluoride, IV, this latter compound was prepared and its ultraviolet spectra recorded. The phenolic sulfonyl chloride and fluoride had different λ_{max} at 264 and 248 mμ, respectively.

The fact that only the starting phenol was produced indicated that the reaction was simply an acid–base interconversion and that *the yellow species was the phenolate anion.*

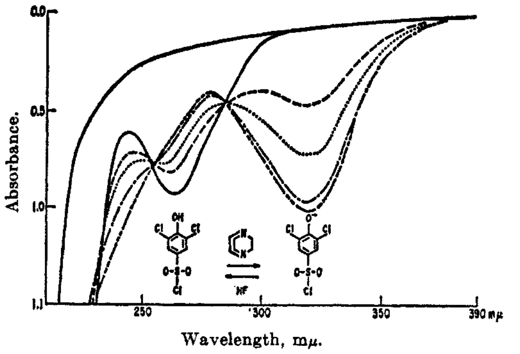
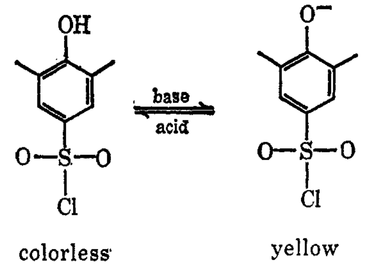


Figure 1.—Ultraviolet spectra of sulfonyl chloride (II) at various stages in the acid-base titration (——, acidic solution; – – –, basic solution).



The magnitude of the bathochromic shifts for the sulfonyl fluorides and methyl sulfonate as shown on Table III were of the same magnitude (30–40 mμ) as those previously found for sulfoxides and sulfones.[5]

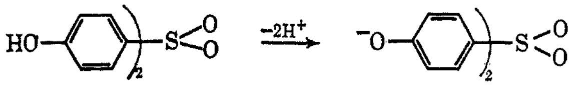
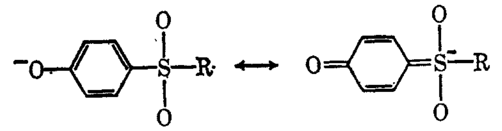


Table III

Sulfonyl Fluorides and Sulfonate Ester

Compd	Phenol, λ_{max}, mμ	Phenolate λ_{max}, mμ	Phenolate $\Delta\lambda_{max}$, mμ
IV	248	293	35
V	246	284	38
VI	238	269	31

Price[6] has recently discussed the contribution of the following quinoidal resonance structure for sulfones.



The sulfonyl chlorides, where R above is chlorine, are associated with larger bathochromic shifts in the phenol to phenolate anion interconversion than those found for sulfones and sulfoxides.[7] The enhanced shifts found for the sulfonyl chlorides are indicative of a larger contribution of the quinoidal structure. An indication that the bathochromic shifts were not due simply to electronegativity effects is shown by a comparison of the maxima shifts for the chloride, III, the fluoride, V, and the methyl ester, VI. In these cases it was found that the $\Delta\lambda_{max}$ correlated better

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(5) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962.

(6) C. C. Price, *Chem. Eng. News*, **42**, No. 48, 58 (1964).

(7) The bathochromic shift associated with the phenol to phenolate conversion for bis(3,5-dimethyl-4-hydroxyphenyl) sulfone was found to be 39 mμ.

with σ constants for *p*-Cl, -F, and -OMe than for *m*-Cl, -F, and -OMe.

A plausible explanation for the large $\Delta\lambda_{max}$ found for the sulfonyl chlorides is that chlorine and sulfur d orbitals interact to cause a greater charge delocalization.

It was found that when appropriate conditions were chosen both high molecular weight polymer and cyclic tetramer could be prepared from the sulfonyl chloride, III. The details of this work will be reported in a forthcoming publication.

Experimental Section

Sodium 3,5-Dimethyl-4-hydroxybenzenesulfonic Acid.—This salt was prepared from 2,6-xylenol by the method of Karrer and Leiser[8] using sulfuric acid monohydrate at 100–110°.

3,5-Dimethyl-4-hydroxybenzenesulfonyl Chloride (III).—A solution containing 22.4 g of sodium 3,5-dimethyl-4-hydroxybenzenesulfonate in 40 ml of dimethylformamide was cooled to 0° with an ice–salt bath. To this solution 33 g of thionyl chloride was added dropwise over a 10-min period. The cooling bath was removed and the temperature rose to 39°. After a reaction period of 52 min, the reaction mixture was added to 100 g of ice. The white solid formed was isolated and washed several times with ice–water. The crude product (19.8 g) was vacuum dried at room temperature and then dissolved in a minimum amount of toluene. An equal volume of *n*-hexane was added and the solution was cooled to 0°. The solids formed were isolated by filtration and vacuum dried. The white crystals (13.5 g) melted at 134°. The sulfonyl chloride had nmr absorption at δ 7.63 (2 H, singlet, aromatic C–H), 5.67 (1 H, singlet, -OH), and 2.32 (6 H, singlet, benzylic C–H).

Anal. Calcd. for $C_8H_9ClO_3S$: C, 43.5; H, 4.1; Cl, 16.1. Found: C, 43.7; H, 4.1; Cl, 15.8.

Methyl 3,5-Dimethyl-4-hydroxybenzenesulfonate (VI).—3,5-Dimethyl-4-hydroxybenzenesulfonyl chloride (1.25 g) was added slowly to a 0° solution of 5 ml of diethyl ether, 10 ml of methanol and 0.25 ml of pyridine in a vaccine bottle. The bottle was capped and maintained at 5° for 15 hr. The solvent was then removed under vacuum and the solid remaining was washed several times with dilute HCl followed by a water wash. Recrystallization from a petroleum ether (bp 80–100°)–toluene mixture yielded 0.93 g of a crystalline solid melting at 128°. The sulfonate ester had nmr absorption at δ 7.40 (2 H, singlet, aromatic C–H), 5.67 (1 H, singlet, OH), 3.59 (3 H, singlet, methyl C–H), and 2.19 (6 H, singlet, benzylic C–H). The molecular weight was 217 using the Mechrolab technique compared with the calculated value of 216.3.

Anal. Calcd for $C_9H_{12}O_4S$: C, 50.0; H, 5.6; S, 14.8. Found: C, 50.2; H, 5.3; S, 15.1.

3,5-Dimethyl-4-hydroxybenzenesulfonyl Fluoride (V).—A suspension of 6 g of sodium 3,5-dimethyl-4-hydroxybenzenesulfonate in 20 ml of carbon disulfide was cooled to 0° under a nitrogen atmosphere. To this solution 17 g of fluorosulfonic acid was added dropwise over a 10-min period. The cooling bath was then removed and the temperature rose to ~17°. Ice was then added to quench the reaction and the solids formed were isolated and washed several times with ice–water. After vacuum drying the product was recrystallized from petroleum ether–toluene. The crystalline sulfonyl fluoride (3.1 g) melted at 127° and had nmr absorption at δ 7.64 (2 H, singlet, aromatic C–H), 5.61 (1 H, singlet, OH), and 2.33 (6 H, singlet, benzylic C–H).

Anal. Calcd for $C_8H_9FO_3S$: C, 47.1; H, 4.4; S, 15.7. Found: C, 47.2; H, 4.3; S, 15.8.

3,5-Dichloro-4-hydroxybenzenesulfonyl Chloride (II).—Chlorosulfonic acid (230 g) was added slowly to a solution of 50 g of 2,6-dichlorophenol in 100 ml of carbon disulfide which had been cooled to 0°. After the addition period of 1.5 hr, the solution was warmed to 20° where it was maintained for an additional hour. The reaction was quenched by addition to 1000 g of ice. The solid which separated was washed several times with ice–water and then vacuum dried. The crude sulfonyl chloride (75.5 g) was recrystallized several times from *sym*-tetrachloroethane. The white crystalline product melted at 126° and had nmr absorption at δ 8.06 (H singlet, aromatic C–H). The molecular weight as determined by the Mechrolab technique was 260 compared with the calculated value of 261.5.

Anal. Calcd for $C_6H_3Cl_3O_3S$: C, 27.6; H, 1.2; Cl, 40.7. Found: C, 27.8; H, 1.3; Cl, 40.7.

3,5-Dichloro-4-hydroxybenzenesulfonyl Fluroride (IV).—Fluorosulfonic acid (100 g) was added over a 0.5-hr period to a cold solution (0°) of 20 g of 2,6-dichlorophenol in 50 ml of carbon disulfide. The reaction temperature was raised to 20° where it was maintained for 2 hr. The reaction was quenched by the addition of 200 g of ice. The solids formed were isolated and washed several times with ice–water. After vacuum drying, the crude product (29 g) was extracted with 100 ml of chloroform. Upon stripping off the chloroform a solid residue was isolated. Recrystallization from petroleum ether yielded a white crystalline solid melting at 89°. The sulfonyl fluoride had nmr absorption at δ 7.93 (2 H singlet, aromatic C–H) and 6.76 (1 H singlet, -OH).

Anal. Calcd for $C_6H_3Cl_2FO_3S$: C, 29.4; Cl, 28.9. Found: C, 29.5; Cl, 29.1.

3,5-Dibromo-4-hydroxybenzenesulfonyl Chloride (I).—A solution of 5 g of 2,6-dibromophenol in 20 ml of carbon disulfide was added over a 5-min period to a cold (0°) solution of 18 g of chlorosulfonic acid in 30 ml of carbon disulfide. The solution was warmed to 20° over a 0.5-hr period and then quenched by adding 50 g of ice. The solid produced was washed several times with ice–water and vacuum dried. The white solid was recrystallized first from toluene and then from benzene. The crystalline product (3 g) melted at 127° compared with the reported value[2] of 128–129°. The sulfonyl chloride had nmr absorption at δ 8.13 (2 H singlet, aromatic C–H) and 6.10 (1 H singlet, -OH).

Anal. Calcd for $C_6H_3Br_2ClO_3S$: C, 20.6; H, 0.9; S, 9.2. Found: C, 20.9; H, 0.9; S, 9.4.

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[8] P. Karrer and P. Leiser, *Helv. Chim. Acta*, **27**, 678 (1944).

2-Phenyl-3-(1-methyl-2-indolyl)-4(1H)-quinolone

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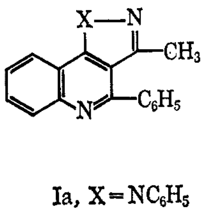
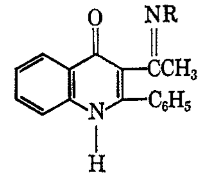
As previously indicated 2-phenyl-3-acetyl-4(1H)-quinolone condenses with phenylhydrazine in aqueous acetic acid solution to yield 3-methyl-1,4-diphenyl-1H-pyrazolo[4,3-*c*]quinoline (Ia).[1] Utilization of hydrazine hydrate in the reaction led to 3-methyl-4-phenyl-1H-pyrazolo[4,3-*c*]quinoline (Ib).

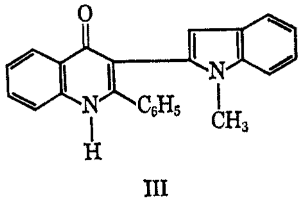
It is likely that base Ia, for example, is derived by cyclization of an intermediate hydrazone IIa produced initially during reaction. Thus, the product from *asym*-



Ia, X = NC_6H_5
b, X = NH
c, X = O



IIa, R = NHC_6H_5
b, R = $N(CH_3)C_6H_5$
c, R = OH



III

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[1] B. Staskun, *J. Org. Chem.*, **26**, 2791 (1961).