factors based on a reference mixture; these values of r were 1.84 and 1.80.

B. Dimethyl Sulfoxide.—In a typical run, a 25-ml solution, 0.1052 and 0.2052 M in 2,6- and 3,5-dibromophenoxides, respectively, prepared from the phenols and dimethylsodium solution under nitrogen, and contained in a 100-ml volumetric flask (containing a magnetic stirring bar) sealed with a serum cap, was placed in the constant-temperature bath at 25.6 ± 0.3°. After temperature equilibration a solution of dimethyl sulfate (an insufficient amount to methylate completely either of the phenoxides) in *ca.* 1 ml of DMSO was added slowly to the stirred solution as before during *ca.* 7 min. After stirring for 1 hr the reaction was quenched with 1 ml of acetic acid. Internal standard 2,3,4-trichloroanisole was added, and the concentrations of the anisole products were determined as before by glpc (2-ft LAC-446 column at 165°, then at 220° to remove the unchanged phenols). The glpc reference solution was made up to approximate the reaction solutions. The values of r for two runs in DMSO were 3.57 and 3.60.

Acknowledgment.—Sincere appreciation is extended to Dr. J. W. Crump of Albion College for valuable discussions of the work and for suggesting some of the experiments. Appreciation is also extended to Mr. D. V. Wysong for technical assistance.

Some New Sulfonyl- and Trifluoromethylthio-p-benzoquinones. Their Reactions, Polarographic Reduction Potentials, and π Acid Strengths

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Several new p-benzoquinones substituted with one to four electron-withdrawing groups were prepared, including 2,3-dicyano-5-phenylsulfonyl-p-benzoquinone (**3**), 2,3-dicyano-5-chloro-6-phenylsulfonyl-p-benzoquinone (**6**), trifluoromethylsulfonyl-p-benzoquinone (**8**), 2,6-bis(trifluoromethylthio)-p-benzoquinone (**10**), and tetrakis(trifluoromethylthio)-p-benzoquinone (**15**). Polarographic reduction potentials of the new quinones were measured in anhydrous acetonitrile, and quinones **3** and **15** were found to have half-wave reduction potentials ($E_{1/2}$) close to those of the well-known oxidizing reagents, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) and chloranil, respectively. Addition and substitution reactions of several of the new quinones were examined, and dehydrogenations of steroid 4-en-3-ones by quinones **3** and **15** were compared to dehydrogenations by DDQ and chloranil. From quinone polarographic reduction data, substituent constants ($\Delta E_{1/2}$) were calculated which correspond to the additive effects of each of the substituents Cl, CF_3S, $C_6H_5SO_2$, C≡N, and CF_3SO_2 on polarographic (first wave) reduction potentials. The constants $\Delta E_{1/2}$ were shown to correlate approximately with the corresponding Hammett substituent parameters, σ_{meta}. The absorption spectra of π complexes formed between these quinones and pyrene in methylene chloride were also analyzed and the wave numbers of the absorption peaks associated with these π complexes were found to fall in the same order as the polarographic $E_{1/2}$ values observed for the corresponding quinones. The novel 1,4-dimethoxytetrakis(trifluoromethylsulfonyl)benzene (**17**) was prepared and found to have a marked affinity for electrons; it undergoes polarographic reduction more readily than chloranil, it is reduced by iodide ion in benzene to form a paramagnetic species formulated as an anion free radical (**26**), and, though it can be crystallized unchanged from boiling concentrated nitric acid, it undergoes rapid nucleophilic substitution by water in acetone at room temperature.

Substitution of p-benzoquinone with electron-withdrawing groups enhances its oxidation potential,[1] its strength as a π acid,[2] and its reactivity in reactions involving the transfer of hydride ions[3] or addition of free radicals.[4] For example, 2,3-dichloro-5,6-dicyano-p-benzoquinone has a relatively high oxidation–reduction potential and finds widespread use as a dehydrogenating agent in organic synthesis.[5] Tetracyano-p-benzoquinone is a strong oxidizing agent and an exceptionally strong π acid.[6]

Hammett σ parameters indicate that sulfonyl groups (*e.g.*, CH_3SO_2) are more strongly electron withdrawing than cyano groups.[7a] In fact, among the uncharged groups, the trifluoromethylsulfonyl group (CF_3SO_2)[7] is exceeded in strength as an electron-withdrawing substituent only by the tricyanomethyl group.[7c] Since very few sulfonyl quinones[8] and no trifluoromethylsulfonyl quinones have been reported, the following study of their synthesis and chemical properties was undertaken.

Synthesis and Reactions

Sulfonyl Quinones.—The first synthetic route to new sulfonyl quinones studied was based on the reaction of sulfinic acids with p-benzoquinones. Addition of 2,3-dicyanobenzoquinone to excess benzenesulfinic acid in acetonitrile gave 2,3-dicyano-5-phenylsulfonylhydroquinone (**1**) conveniently and in good yield (62%). A second product, 2,3-dicyano-5,6-bis(phenylsulfonyl)-

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[1] See, for example, D. J. Cram and G. S. Hammond, "Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, 1964, p 551.

[2] (a) P. R. Hammond, *J. Chem. Soc.*, 471 (1964); (b) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

[3] See, for example, D. H. Reid, M. Fraser, B. B. Molloy, H. A. S. Payne, and R. G. Sutherland, *Tetrahedron Letters*, 530 (1961).

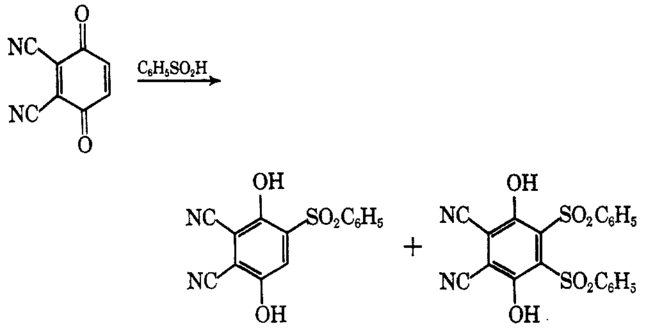
[4] F. J. Lopez Aparicio and W. A. Waters, *J. Chem. Soc.*, 4666 (1952).

[5] (a) D. Walker and T. D. Waugh, *J. Org. Chem.*, **30**, 3240 (1965); (b) P. J. Neustaedter, "Steroid Reactions," C. Djerassi, Ed., Holden-Day, Inc., San Francisco, Calif., 1963, p 129.

[6] (a) K. Wallenfels and G. Bachmann, *Angew. Chem.*, **73**, 142 (1961); (b) K. Wallenfels, D. Hofmann, and R. Kern, *Tetrahedron*, **21**, 2231 (1965); (c) K. Wallenfels, G. Bachman, D. Hoffman, and R. Kern, *ibid.*, **21**, 2239 (1965).

[7] (a) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958); L. M. Yagupolskii and L. M. Yagupolskaya, *Proc. Acad. Sci. USSR* (Eng. Transl.), **134**, 1207 (1960); (b) W. A. Sheppard, *J. Am. Chem. Soc.*, **85**, 1314 (1963); (c) J. K. Williams, E. L. Martin, and W. A. Sheppard, *J. Org. Chem.*, **31**, 919 (1966).

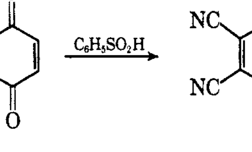
[8] O. Hinsberg, *Ber.*, **27**, 3259 (1894); *ibid.*, **28**, 1315 (1895); W. H. Hunter and D. E. Kvalnes, *J. Am. Chem. Soc.*, **54**, 2869 (1932); D. Libermann and A. Rouaix, French Patent 1,022,812 (1953). N. Dost [*Rec. Trav. Chim.*, **71**, 856 (1952)] claimed to have prepared 2,5-bis(ethylsulfonyl)-3,6-bis(ethylsulfinyl)-p-benzoquinone (mp 221–222°) by oxidation of tetrakis-(ethylthio)-p-benzoquinone. The product (mp 218–219°) that we obtained from this reaction is instead the corresponding *hydroquinone*. See the Experimental Section for details.



1 **2**

hydroquinone (**2**),[9] was isolated in 6% yield from the reaction mixture as a sparingly soluble sodium salt. Both quinols are soluble in aqueous sodium bicarbonate, the anion of **1** exhibiting blue-green fluorescence in water. Action of nitrogen tetroxide[10] on a solution of quinol **1** in methylene chloride gave 2,3-dicyano-5-phenylsulfonyl-*p*-benzoquinone (**3**) in 87% yield. However, reaction of nitrogen tetroxide with a suspension of the sodium salt of quinol **2** in chloroform gave only the conjugate acid (**2**) in good yield.

Ansell, *et al.*,[11] concluded from a study of the Diels–Alder reactions of unsymmetrically substituted *p*-benzoquinones that diene addition occurs preferentially at the more electron-deficient ethylenic linkage, provided there is no steric opposition to such a reaction. Hartzler and Benson[11] have shown that addition of 1,2-dimethylenecyclobutane to 2,3-dicyano-*p*-benzoquinone follows this rule, with the diene adding across the double bond bearing the two cyano groups. It was therefore of interest to note that addition of 2,3-dimethyl-1,3-butadiene to quinone **3** in benzene occurred in a sense opposite to that of a 2,3-dicyanobenzoquinone, affording an adduct which was identified by nmr analysis as a 2:3 mixture of epimeric adducts **4**. Thus, in quinone **3** the sulfonyl-substituted (polarized) double bond is a better dienophile than the dicyano-substituted double bond, even though the bulk of the phenylsulfonyl group might be expected to disfavor addition at that side of the molecule.



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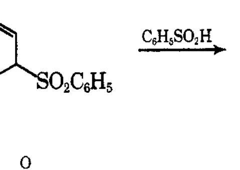
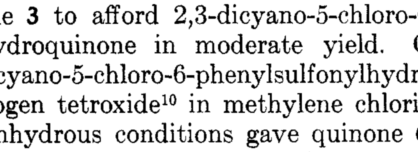


4

A crystalline 1:1 charge-transfer complex of quinone **3** with pyrene was prepared in 50% yield by slowly cooling a hot, concentrated solution of the reactants in acetonitrile. The black complex exhibited a weak epr signal and had a compaction resistivity of 1.5 × 10^{13} ohm cm.

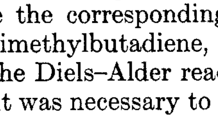
Benzyl alcohol was dehydrogenated rapidly and in high yield to benzaldehyde by quinone **3** in benzene at room temperature. The reaction probably involves abstraction of benzyl hydrogen as hydride ion and elimination of hydroxylic proton from the benzyl cation thus formed.

Hexamethylbenzene in benzene reacted quickly with quinone **3** to form a soluble, dark green, charge-transfer complex. Within several days at room temperature, however, the benzene solution turned dark brown and deposited a solid which, after repeated crystallization, was nearly colorless. Though this solid was too unstable to be isolated in a state sufficiently pure for good elemental analyses, its nmr spectrum indicated the presence of four benzyl hydrogens and four, dissimilar, aromatic methyl groups, suggesting for a tentative structure the diether **5**.[12]



5

Addition of benzenesulfinic acid in acetonitrile or ethanol to quinone **3** gave the bis(phenylsulfonyl)quinol **2**. Anhydrous hydrogen chloride in benzene added to quinone **3** to afford 2,3-dicyano-5-chloro-6-phenylsulfonylhydroquinone in moderate yield. Oxidation of 2,3-dicyano-5-chloro-6-phenylsulfonylhydroquinone with nitrogen tetroxide[10] in methylene chloride under strictly anhydrous conditions gave quinone **6**, a very strong oxidant and π acid (*vide infra*).



6

Quinone **6** reacted with 2,3-dimethylbutadiene in benzene to afford an adduct formulated as **7** on the basis of the similarity of its absorption spectra with those of adduct **4**. Unlike the corresponding reaction of quinone **3** with 2,3-dimethylbutadiene, which was markedly exothermic, the Diels–Alder reaction of quinone **6** was sluggish, and it was necessary to warm the reaction

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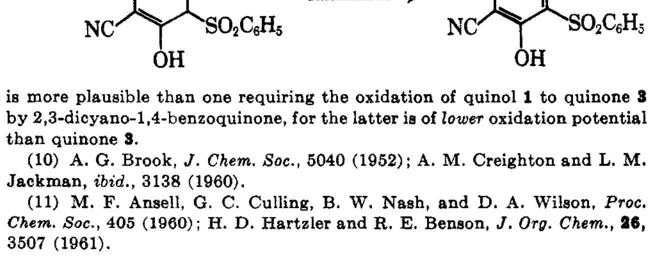
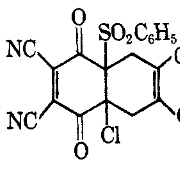
[9] By a mechanism analogous to one invoked by Wallenfels,[6b] the formation of quinol **2** can be rationalized by the following sequence. This sequence is more plausible than one requiring the oxidation of quinol **1** to quinone **3** by 2,3-dicyano-1,4-benzoquinone, for the latter is of *lower* oxidation potential than quinone **3**.



[10] A. G. Brook, *J. Chem. Soc.*, 5040 (1952); A. M. Creighton and L. M. Jackman, *ibid.*, 3138 (1960).

[11] M. F. Ansell, G. C. Culling, B. W. Nash, and D. A. Wilson, *Proc. Chem. Soc.*, 405 (1960); H. D. Hartzler and R. E. Benson, *J. Org. Chem.*, **26**, 3507 (1961).

[12] Pentamethylbenzyl cation, a likely intermediate in the sequence of hydride ion abstractions which would lead to diether **5**, has recently been observed by nmr spectroscopy and noted to possess remarkable thermal stability: C. A. Cupas, M. B. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*, **88**, 361 (1966).



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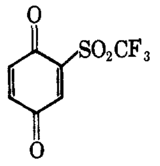

8

mixture to about 40° before the color change associated with reaction became apparent.

The first approach to the synthesis of trifluoromethylsulfonylquinones which we studied involved addition of trifluoromethylsulfinic acid to *p*-benzoquinones. Reduction of CF_3SO_2Cl with aqueous potassium sulfite[13] was found to give trifluoromethylsulfinic acid potassium salt, CF_3SO_2K, conveniently and in good yield (68%). Treatment of an acidified, aqueous, ethanol solution of this salt with *p*-benzoquinone gave 2-trifluoromethylsulfonylhydroquinone, which was oxidized by silver oxide to the corresponding quinone **8**. Quinone **8** is remarkably sensitive to moisture,[14] resinifying rapidly when exposed to solvent or atmosphere which has been scrupulously dried. This sensitivity and the concomitant problems associated with making moderately large quantities of quinone **8** made it unattractive as a key intermediate in the synthesis of more highly substituted trifluoromethylsulfonylquinones. For this reason we turned to a study of aryl trifluoromethyl sulfides which might serve as precursors to trifluoromethylthioquinones and, finally, to trifluoromethylsulfonylquinones.

Trifluoromethylthioquinones.—Introduction of gaseous CF_3SCl into phenol dissolved in chloroform in the presence of 1 molar equiv of pyridine has been reported by Andreades, *et al.*,[15] to afford 4-trifluoromethylthiophenol in 73% yield. No products resulting from substitution in the *ortho* position were isolated. Study of this type of reaction as a potential route to CF_3S-substituted quinones revealed that hydroquinone reacted with CF_3SCl by a process of aromatic chlorination. Thus, treatment of hydroquinone with CF_3SCl in pyridine–chloroform gave the pyridine salt of chlorohydroquinone.

When, however, the monomethyl ether of hydroquinone was employed in reaction with excess CF_3SCl in the presence of at least 3 molar equiv of pyridine,[16] *ortho* substitution took place twice, with the formation of 2,6-bis(trifluoromethylthio)-4-methoxyphenol (**9**) in excellent yield (Figure 1). For reasons not understood, methyl ether **9** was completely resistant toward cleavage by HBr or HI in refluxing acetic acid. However, oxidative cleavage of ether **9** was accomplished conveniently by using concentrated nitric acid under carefully controlled conditions, giving 2,6-bis(trifluoromethylthio)-1,4-benzoquinone (**10**) in 96% yield. The corresponding quinol (**11**) could then be prepared by reduction with aqueous sodium hydrosulfite. Quinol **11** could be converted back to quinone **10** by oxidation with nitrogen tetroxide.

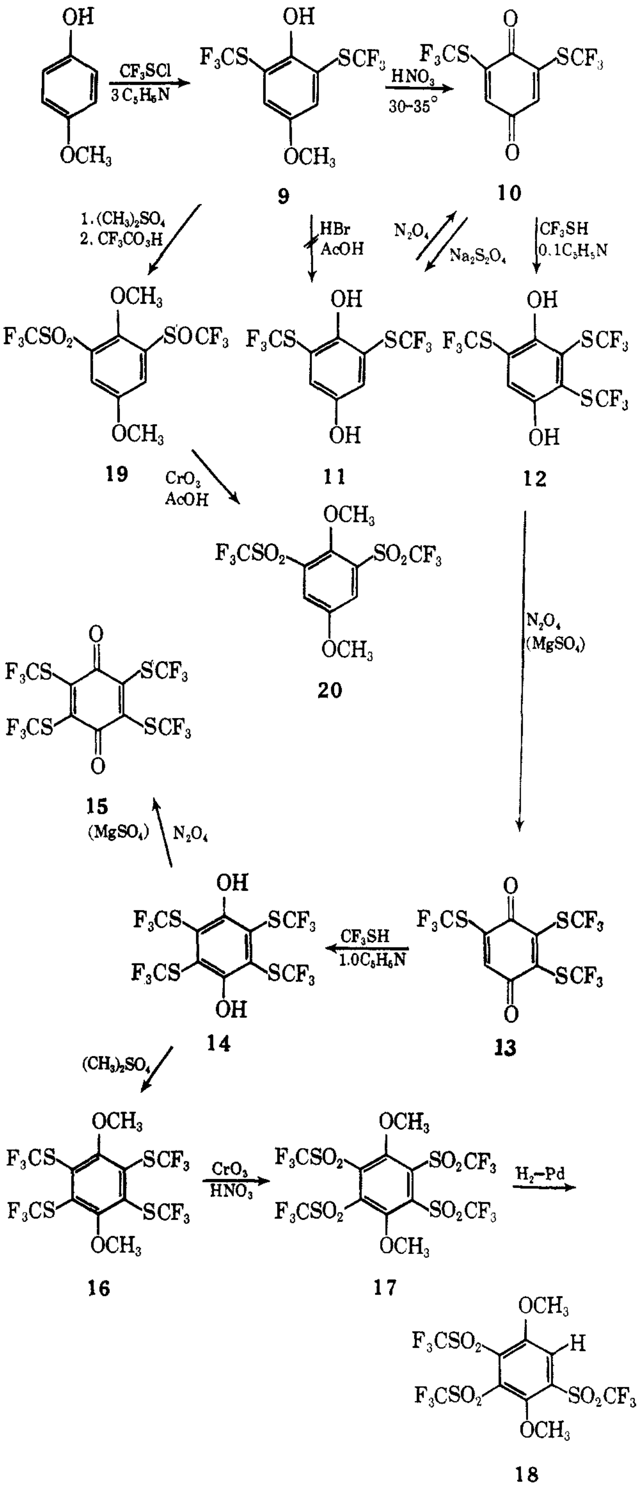

Figure 1.

The availability of trifluoromethanethiol[17] made attractive the possibility of using it for the next step in the preparation of quinones having a higher multiplicity of CF_3S groups. In contrast to the (apparently) uncatalyzed addition of hydrocarbon thiols to quinones,

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(13) R. N. Haszeldine and J. M. Kidd [*J. Chem. Soc.*, 2901 (1955)] described the synthesis of hygroscopic trifluoromethanesulfinic acid sodium salt by reduction of CF_3SO_2Cl with zinc in water. The present synthesis appears to be more convenient and affords the nonhygroscopic potassium salt in high purity.

(14) This is reminiscent of the extreme moisture sensitivity reported by Wallenfels for a related compound, cyano-*p*-benzoquinone.[6b]

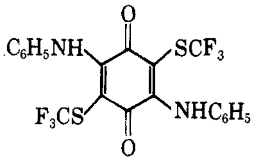
(15) (a) S. Andreades, J. F. Harris, Jr., and W. A. Sheppard, *J. Org. Chem.*, **29**, 898 (1964); (b) see also H. Richert, French Patent 1,339,764 (1963).

(16) When this reaction was carried out in the presence of less than 3 moles of pyridine for each mole of *p*-methoxyphenol, mixtures of **9** and 2-trifluoromethylthio-4-methoxyphenol were formed which could be separated only by gas chromatography.

(17) E. L. Muetterties [U.S. Patent 2,729,663 (1956)] described the reaction of carbon disulfide with mercuric fluoride at 250° to give bis(trifluoromethylmercapto)mercury. Treatment of the latter compound with HCl in dioxane gives CF_3SH (see the Experimental Section).

CF_3SH added to quinone **10** only in the presence of a basic catalyst.[18] When pyridine was added to a solution of quinone **10** and excess CF_3SH in chloroform, a fast reaction occurred to give 2,3,5-tris(trifluoromethylthio)hydroquinone (**12**) in 94% yield.[19] Oxidation of this trisubstituted quinol with nitrogen tetroxide in methylene chloride, in the presence of magnesium sulfate as a drying agent, gave the corresponding quinone **13**. Addition of CF_3SH to this quinone gave the tetrasubstituted quinol **14** in 82% yield. The latter addition required the presence of a molar amount of pyridine, perhaps because quinol **14** is a stronger acid than CF_3SH. Finally, oxidation of quinol **14** with nitrogen tetroxide in methylene chloride in the presence of magnesium sulfate gave tetrakis(trifluoromethylthio)-*p*-benzoquinone (**15**) in high yield. Quinone **15** is low melting (57–59°), easily sublimed, and bright orange.

Excess aniline in alcohol reacted readily with quinone **15** in a manner analogous to its reaction with chloranil,[20] giving orange-red 2,6-bis(trifluoromethylthio)-3,6-dianilinobenzoquinone (**21**) in good yield.



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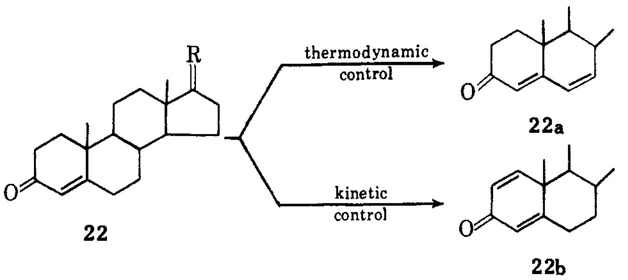
Dehydrogenation of steroid 4-en-3-ones (**22**) by chloranil in boiling *t*-butyl alcohol is known to afford the corresponding 4,6-dien-3-ones (**22a**),[21] whereas the higher potential 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in boiling benzene or dioxane gives instead 1,4-dien-3-one (**22b**) as the main reaction product together with small amounts of the 4,6-dien-3-one (**22a**) and 1,4,6-trien-3-one. The difference in these reactions has been explained by Ringold and Turner[22] as arising by abstraction of C-7 hydride ion by chloranil from a thermodynamically determined enol (a 3,5-dien-3-ol), whereas abstraction of a C-1 hydride ion is effected by DDQ from a kinetically determined enol (a 2,4-dien-3-ol). Essential to this hypothesis was the conclusion that chloranil lacked sufficient potential under these reaction conditions to introduce a 1,2-cross-conjugated double bond.



It was therefore of interest to see whether quinone **15**, having an oxidation potential (*vide infra*) close to that of chloranil, and quinone **3**, having an oxidation potential close to that of DDQ, would dehydrogenate steroid 4-en-3-ones in ways analogous to dehydrogenations by chloranil and DDQ, even though the steric requirements of quinones **15** and **3** must differ markedly from those of chloranil and DDQ.

Quinone **15** in boiling *t*-butyl alcohol, in the presence of *p*-toluenesulfonic acid, was found to dehydrogenate testosterone (**22**, $\mathrm{R} = {<}^{\mathrm{OH})}_{\mathrm{H}}$ to 4,6-androstadiene-17β-ol (partial formula **22a**). The absence of 1,4-androstadien-17β-ol was established by thin layer chromatography. Although in this reaction quinone **15** behaved in the same manner as chloranil, unlike chloranil quinone **15** in the absence of acid catalyst did not dehydrogenate testosterone to any detectable extent whatsoever, even after 7 hr in refluxing *t*-butyl alcohol. Quinone **3**, like DDQ, in refluxing benzene dehydrogenated 4-androstene-3,17-dione (**22**, R = O) mainly to the 1,4-dien-3-one (**22b**) with a smaller amount of the 4,6-dien-3-one (**22a**) being detected by thin layer chromatography. Even after 24 hr, however, the reaction mixture contained about 40% unchanged 4-en-3-one (**22**). As in dehydrogenations with DDQ, addition of *p*-toluenesulfonic acid facilitated dehydrogenation of 4-androstene-3,17-dione (**22**). Within 24 hr the reaction had gone to completion, affording approximately equal parts of 4,6-dien-3-one (**22a**) and 1,4-dien-3-one (**22b**). Except for the absence of small amounts of steroid 1,4,6-trien-3-ones[22] from dehydrogenations with quinone **3** and except for the failure of quinone **15** to effect dehydrogenations in the absence of an acid catalyst, it appears that dehydrogenations of steroid 4-en-3-ones by quinones **3** and **15** are essentially analogous to dehydrogenations by DDQ and chloranil, respectively; that is, only the higher potential quinones **3** and DDQ are capable of abstracting C-1 hydride ions from steroid 4-en-3-ones.

Oxidation of Trifluoromethyl Sulfides to Sulfones.—Turning next to a study of the oxidation of CF_3S-substituted quinols and quinones as potential routes to CF_3SO_2-substituted quinones, we found that, under conditions severe enough to effect oxidation of CF_3S groups by nitric acid, chromic acid, or trifluoroperacetic acid, quinone **15** or the corresponding quinol **14** underwent extensive decomposition to give gaseous products or products which could not be extracted from water. However, stabilization of quinol **14** by conversion to the dimethyl ether **16** permitted oxidation of **16** to tetrasulfone **17** under carefully controlled conditions. Although dimethyl ether **16** was inert toward warm (60°) fuming nitric acid, boiling concentrated nitric acid (in which it dissolved), chromium trioxide in boiling glacial acetic acid, or a solution of chromium trioxide in 60% nitric acid, it was smoothly oxidized to the tetrasulfone **17** in 60% yield by a solution of chromium trioxide in fuming nitric acid when the reaction mixture was slowly warmed from 0 to 60° over a period of about 17 hr.[23]

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[18] The failure of CF_3SH to add to a quinone as active as **10** in the absence of basic catalyst implies that the sulfur atom of CF_3SH is not sufficiently nucleophilic for reaction until the thiol is converted to the thiolate anion. Furthermore this suggests that the uncatalyzed addition of hydrocarbon aliphatic thiols occurs by direct nucleophilic attack of the sulfur atom of RSH.

[19] The success of this Michael addition depended on the *rapid* addition of about 0.1 equiv of pyridine and the use of excess CF_3SH, presumably because CF_3SH decomposes rapidly in the presence of base.

[20] E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p 501.

[21] E. J. Agnello and G. D. Laubach, *J. Am. Chem. Soc.*, **79**, 1257 (1957).

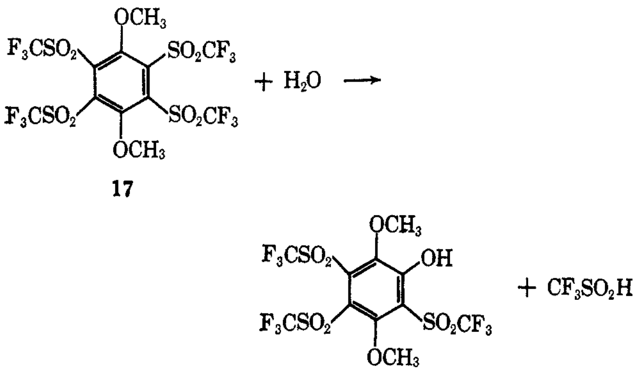
[22] H. J. Ringold and A. Turner, *Chem. Ind.* (London), 211 (1962).

[23] If, instead, the tetrasulfide **16** was added to the oxidizing mixture preheated to 50°, copious amounts of the oxides of nitrogen were evolved and no organic product could be isolated after dilution with water.

Stuart–Briegleb models indicated that rotation of the methoxyl groups in tetrasulfone **17** should be completely inhibited. Yet only one isomer of **17** was obtained, judging by its sharp melting point (214.0–215.0°), its proton nmr spectrum, which shows only a single sharp peak at 4.38 ppm, and its F^{19} nmr spectrum, which also shows only a single sharp peak at 1.86 ppm (upfield from $CFCl_2$–$CFCl_2$).

Catalytic hydrogenolysis of tetrasulfone **17** gave the trisulfone **18**. Methylation of phenol **9** followed by oxidation with trifluoroperacetic acid[24] gave the sulfone–sulfoxide **19**. Further oxidation of **19** with CrO_3–acetic acid gave the disulfone **20**. Of the hydroquinones and hydroquinone dimethyl ethers substituted with one, two, three, or four CF_3SO_2 groups which were thus prepared, tetrasulfone **17** was studied most thoroughly.

Although tetrasulfone **17** could be recovered unchanged from its solutions in boiling fuming nitric acid, in acetone at room temperature it reacted rapidly with water. Titration of the reaction mixture with dilute caustic and sodium hypochlorite demonstrated that the reaction of tetrasulfone **17** with water gave two acids, one of which was CF_3SO_2H, the other presumably being phenol **23**.



17

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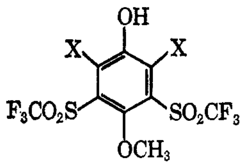
The ease with which tetrasulfone **17** underwent nucleophilic substitution was encountered again when efforts were made to convert **17** to the corresponding hydroquinone. Heating it with concentrated hydrobromic acid at 175° or with concentrated hydrochloric acid in refluxing acetic acid gave, respectively, the dihalophenols **24** and **25**. Prolonged treatment with hydrobromic acid in refluxing acetic acid gave tetrabromohydroquinone.



24, X = Br
25, X = Cl

Physical Measurements

Polarographic Reduction.—Polarographic reductions of the new quinones were carried out in anhydrous acetonitrile at a dropping mercury electrode or graphite[25] electrode. Lithium perchlorate and tetrabutylammonium perchlorate were examined as supporting electrolytes. In almost all cases the former gave better defined and more reproducible reduction waves. Table I lists the half-wave potentials ($E_{1/2}$, *vs.* the standard calomel electrode) and diffusion constants (I_d) observed for the first and second reduction waves in anhydrous acetonitrile with $LiClO_4$ electrolyte. The quinones are arranged in order of increasing magnitude of their first (most positive) reduction waves. Quinone **6**, it can be seen, has a significantly higher potential than 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), a compound which has recently been described[5a] as having an oxidation potential greater than that of any other known quinone. It should be noted, however, that, on the basis of the substituent effects to be described, tetracyano-*p*-benzoquinone[6] is expected to have the highest oxidation potential of all known quinones. Though the polarographic half-wave reduction of this quinone has not been reported, we estimate it (*vide infra*) to be about +0.77 v under conditions corresponding to those of Table I.

TABLE I

POLAROGRAPHIC REDUCTIONS OF QUINONES IN ANHYDROUS ACETONITRILE WITH 0.1 *M* LITHIUM PERCHLORATE SUPPORTING ELECTROLYTE

Quinone[a]	$E_{1/2}$, v,[b] 1st wave	Calcd $E_{1/2}$, v, 1st wave	$E_{1/2}$, v,[b] 2nd wave	I_d,[c] 1st wave	I_d,[c] 2nd wave
p-Benzoquinone	−0.15	. . .	−0.89		
2,6-Bis(trifluoromethylthio)-*p*-benzoquinone (**10**)	−0.01	+0.05	−0.43[d]	4.5	5.0
2,3,5-Tris(trifluoromethylthio)-*p*-benzoquinone (**17**)	+0.15	+0.15	−0.09[d]	3.1	3.0
Trifluoromethylsulfonyl-*p*-benzoquinone (**8**)	+0.15	+0.15	−0.12[e]	3.9	1.0
Chloranil	+0.20[d]	+0.25	+0.04[d,f]	1.2	5.0
Tetrakis(trifluoromethylthio)-*p*-benzoquinone (**15**)	+0.23	+0.25	None	5.1	None
2,3-Dicyano-*p*-benzoquinone	+0.31	+0.31	+0.05[d]	3.7	. . .[d]
2,3-Dicyano-5-chloro-*p*-benzoquinone	+0.41	+0.41	+0.08	3.2	1.9
2,3-Dichloro-5,6-dicyano-*p*-benzoquinone	+0.50	+0.51	+0.12	3.3	3.1
2,3-Dicyano-5-phenylsulfonyl-*p*-benzoquinone (**3**)	+0.52[g]	+0.51	+0.20	2.9[h]	2.0[h]
2,3-Dicyano-5-chloro-6-phenylsulfonyl-*p*-benzoquinone (**6**)	+0.62[i]	+0.61	+0.20	2.9[j]	2.8[j]

[a] Quinones 1–5 × 10^{-4} *M*. [b] *Vs.* standard colomel electrode. [c] $I_d = id/\mathrm{cm}^{2/3}t^{1/6}$. [d] Poorly defined wave; $E_{1/2}$ estimated. [e] A third reduction was noted at $E_{1/2} = -0.38$ v ($I_d = 1.2$). [f] Well-defined reduction wave $E_{1/2} = -0.57$ v. [g] For graphite electrode $E_{1/2}$ is also 0.52 v. [h] A third reduction wave was noted at $E_{1/2} = -1.6$ v ($I_d = 3.0$). [i] Graphite electrode. [j] Additional reduction waves at $E_{1/2} = 1.3$ v ($I_d = 2.8$) and −1.5 v ($I_d = 2.8$).

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[24] In this and several other instances trifluoroperacetic acid has been found in this laboratory to be an excellent reagent for the oxidation of sulfide groups which are resistant to oxidation by peracetic acid but which are in molecules too sensitive for oxidation by CrO_3 or nitric acid.

[25] C. Olsen and R. N. Adams, *Anal. Chim. Acta*, **22**, 582 (1960).

Substituent constants, $\Delta E_{1/2}$, can be assigned to each of the substituents represented in the quinones of Table I such that $\Delta E_{1/2}$ corresponds to the additive effect of each substituent on the first half-wave reduction potential. Thus, if *p*-benzoquinone is selected as an arbitrary standard[26] so that $\Delta E_{1/2}$ for hydrogen is 0.00, the other substituent values $\Delta E_{1/2}$ are, for Cl, 0.10 v; for CF_3S, 0.10 v; for $C_6H_5SO_2$, 0.20 v; for C≡N, 0.23 v; and, for CF_3SO_2, 0.30 v. Using these values, half-wave reduction potentials were calculated[29a] for each quinone and compared with observed values (Table I). Whereas the calculated reduction potential of the only quinone (**8**) containing a CF_3SO_2 group must by definition agree with the observed value, excellent agreement between the observed and calculated reduction potentials for all of the other quinones as well shows that, *at least within the small group of benzoquinones studied*, the contribution $\Delta E_{1/2}$ of each of the substituents Cl, CF_3S, $C_6H_5SO_2$, and C≡N toward quinone polarographic reduction potentials is constant, regardless of the nature or number[29b] of other substituents attached to the quinone ring.

As might be expected, some correlation[30] exists between the substituent parameters $\Delta E_{1/2}$ and the corresponding Hammett substituent parameters (Table II). Thus, CF_3SO_2, which on the basis of σ parameters is one of the strongest uncharged, electron-withdrawing groups known,[7b] has the highest $\Delta E_{1/2}$ value among those measured. Chlorine with a σ_{meta} value close to that of CF_3S has the same $\Delta E_{1/2}$ value as CF_3S. However, the marked difference between the σ_{para} parameters for Cl and CF_3S, in contrast to the equality of their $\Delta E_{1/2}$ values, suggests that substituent inductive effects play a more important role than substituent resonance effects in determining quinone first half-wave reduction potentials.

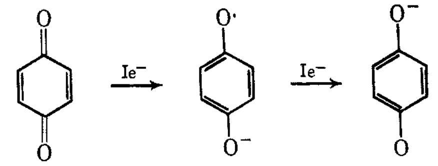
TABLE II

COMPARISON OF $\Delta E_{1/2}$ WITH HAMMETT-SUBSTITUENT PARAMETERS[a]

Group	$\Delta E_{1/2}$, v	σ_{meta}	σ_{para}
Cl	0.10	0.37[b]	0.23[b]
CF_3S	0.10	0.40[c]	0.50[c]
$C_6H_5SO_2$	0.20	(0.60)[d]	0.70[e]
N≡C	0.23	0.56[b]	0.66[b]
CF_3SO_2	0.30	0.79[f]	0.93[f]

[a] Based on the ionization of substituted benzoic acids. [b] See ref 7a; see also footnote 30a. [c] W. A. Sheppard, ref 7b. [d] Since σ_{meta} for $C_6H_5SO_2$ is not available in the literature, the value of σ_{meta} for CH_3SO_2 has been used here as an approximation. These two values are expected to be fairly close especially since the σ_{para} values for $C_6H_5SO_2$ and CH_3SO_2 have been found to be 0.70 and 0.72, respectively: ref 7a and H. H. Szmant and G. Suld, *J. Am. Chem. Soc.*, **78**, 3400 (1956). [e] H. H. Szmant and G. Suld, footnote *d*. [f] See ref 7b.

Previous workers[27] have shown that polarographic reductions of quinones can occur in a stepwise manner to afford semiquinones and hydroquinone dianions when the reductions are carried out in aprotic solvents such as acetonitrile. The magnitudes of the first wave diffusion constants (I_d) for the quinones of Table I indicate that all but two of them undergo a one-electron reduction in the first step.



Evidence for the intermediacy of the semiquinone ion radical in the polarographic reduction of quinones in aprotic solvents has been deduced[27] from the marked effect of added acids on the second polarographic reduction wave. Such an effect has been observed in the one case we have examined. Reduction of a 3×10^{-4} *M* solution of quinone **3** in acetonitrile, 0.1 *M* in $LiClO_4$, and 1×10^{-3} *M* in benzoic acid, occurred with a single two-electron reduction wave ($I_d = 4.7$) at a half-wave potential of +0.50 v and showed the absence of the usual second reduction wave at +0.20 v.

Polarographic reduction of tetrasulfone **17** in anhydrous acetonitrile with lithium perchlorate (0.1 *M*) as the supporting electrolyte occurred in two, well-defined, reversible, reduction waves at $E_{1/2} = +0.34$ and +0.06 v, with $I_d = 2.70$ and 2.81, respectively. Thus, this substituted benzene has an electron affinity greater than that of chloranil or even 2,3-dicyano-*p*-benzoquinone.[31a] The ease with which tetrasulfone **17** undergoes reduction is also reflected in its reaction with iodide ion.

Reduction of tetrasulfone **17** by tetrakis(*n*-hexyl)ammonium iodide dissolved in benzene gave a transient, dark green, ion-free radical formulated as **26**. The epr

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[26] Unfortunately the first reduction wave of *p*-benzoquinone was not well defined and the exact value of $E_{1/2}$ for *p*-benzoquinone may be subject to greater error than the other $E_{1/2}$ values listed in Table I. However, such an error would effect only the absolute $\Delta E_{1/2}$ values without effecting their arithmetical differences. In connection with this, it should be pointed out that a variety of significantly different polarographic reduction potentials for *p*-benzoquinone in acetonitrile are reported in the literature, apparently resulting from the use of different supporting electrolytes; *cf.*, for example, ref 27 and 28.

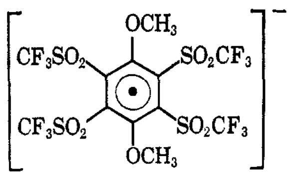
[27] A. Wawzonek, R. Berkey, E. W. Baka, and M. E. Runner, *J. Electrochem. Soc.*, **103**, 456 (1956).

[28] (a) F. A. Matsen, "Proceedings of the 1957 Conference on Carbon," Pergamon Press Inc., New York, N. Y., 1957, p 21, and references cited therein; (b) M. E. Peover [*J. Chem. Soc.*, 4540 (1962)] has shown that $E_{1/2}$ values for the polarographic reduction of quinones in aprotic solvents are linearly related to the calculated energies of the lowest unoccupied orbitals. Peover [*Trans. Faraday Soc.*, **58**, 1656 (1962)] has also shown that the energy of the longest wavelength charge-transfer band of the complexes of an aromatic donor molecule with a series of quinones is linearly related to the reversible, one-electron $E_{1/2}$ of the quinones.

[29] (a) For example, 2,3-dicyano-5-phenylsulfonyl-*p*-benzoquinone (**3**) is calculated to have a first half-wave reduction potential which exceeds that of *p*-benzoquinone by $+0.23 + 0.23 + 0.20 = +0.66$ v. Since $E_{1/2}$ of *p*-benzoquinone is about −0.15 v, the calculated value for $E_{1/2}$ of **3** is about +0.51 v. (b) Although among these π acids of closely related structures it has not been necessary to take into account the relative positions and interaction of substituents, this simplification would not be expected to apply to the effects of multiple substituents on π acids in general; see A. R. Lepley and J. P. Thelman [*Tetrahedron*, **22**, 101 (1966)] for a general theory of structure *vs.* strength of charge-transfer acceptor molecules.

[30] (a) The reversal of order of σ parameters and $\Delta E_{1/2}$ constants of the cyano group in Table II may be a consequence of some discrepancies in the literature regarding the σ parameters of the cyano group. Although we have listed what we consider the most reliable σ parameters for the cyano group, the published value $\sigma_{meta} = +0.68$ is in much better agreement with the observed value for $\Delta E_{1/2}$; see for example R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13, and H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953); (b) P. R. Hammond[2a] has observed a nearly linear relationship between the Hammett σ_{para} constants for the substituents of a series of monosubstituted *p*-benzoquinones and the charge-transfer absorption peaks of these quinones complexes with hexamethylbenzene.

[31] (a) The effectiveness of the CF_3SO_2 groups in imparting electron-acceptor properties to **17** can be better appreciated when it is recognized that the effect of aromatic electron delocalization is to diminish electran affinity.[29b] For example, 1,2,4,5-tetracyanobenzene ($E_{1/2} = -0.73$ v in CH_3CN) undergoes one-electron reduction not only much less readily than tetracyano-*p*-benzoquinone but, in fact, less readily than *p*-benzoquinone ($E_{1/2} = -0.15$ v). (b) The author is indebted to Dr. M. T. Jones of these laboratories for the epr spectra and calculations involved. Details of these spectra will be published later by Dr. Jones.



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spectrum of this green solution exhibited seven lines which could be counted, but the lines at the ends of the pattern were so weak as to be barely detectible. However, the relative intensities of these seven lines were close to those calculated for a 13-line spectrum.[31b] Thirteen-line multiplicity would arise from paramagnetic species **26** by transmission of electron spin through the sulfur and carbon atoms of the SO_2CF_3 groups[32] to each of 12 identical fluorine atoms.

Tetrakis(trifluoromethylthio)-*p*-benzoquinone (**15**) also underwent reduction[33] by iodide ion in benzene to afford a dark green, ion radical, the color of which persisted for several hours in a test tube open to air. The epr spectrum of the fresh solution showed a single peak with no detectible splitting at maximum resolution. The green color of the anion radical was slowly discharged by the addition of water and was rapidly discharged by the addition of trifluoroacetic acid.

π Acid Strengths.—Though a solution of 2,3-dicyano-5-phenylsulfonyl-*p*-benzoquinone (**3**) in benzene is yellow, its solution in toluene is orange-red, and its solution in xylene is a dark, purple-red. As in the case of tetracyanoethylene,[34] this color phenomenon can be attributed to complexes arising from a Lewis acid–base interaction, a weak dative bond between the components of the complex being formed by partial transfer of a π electron from the aromatic hydrocarbon (the π base) to the quinone (the π acid). Table III lists for the charge-transfer complexes of pyrene with eleven quinones values for the longest wavelengths of maximum absorption (λ_{max}), extinction coefficients at maximum absorption (ϵ_{max}), and association constants (K). The latter two values were calculated from the concentration dependence of the absorption spectra by the method of Keefer and Andrews.[35] Corresponding data for tetracyanoethylene are included to permit comparison. Note that the π acids of Table III are listed in order of increasing λ_{max} of their complexes and that for the nine quinones common to Tables I and II the order is the same in both tables. The relationship between quinone half-wave reduction potentials ($E_{1/2}$) and charge-transfer complex wave numbers ($\tilde{\nu}_{max}$) is more clearly illustrated by Figure 2. Correlation between these values can be rationalized qualitatively by considering that (1) an intermolecular charge-transfer spectrum arises by light absorption causing an electron to jump from π base to π acid;[36] (2) the light energies associated with such transitions in a series of π acids complexed with a given π base should vary in the same order as the molecular electron affinities of

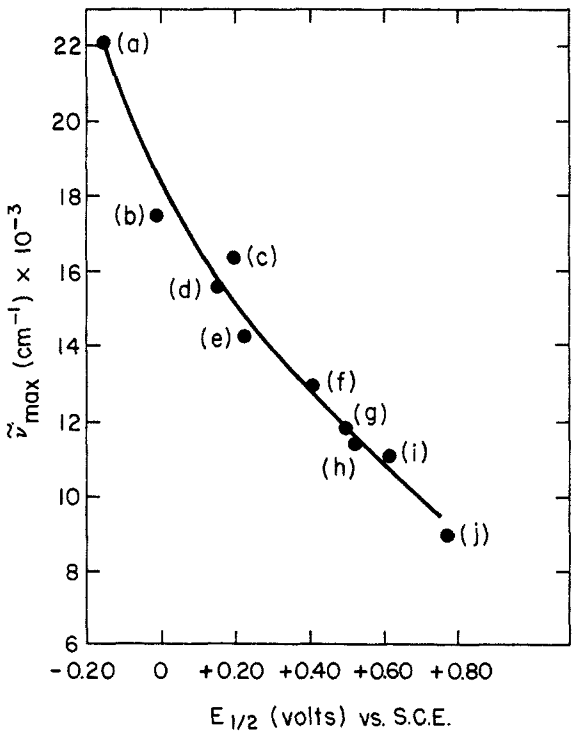

Figure 2.—Variation of quinone polarographic half-wave reduction potentials ($E_{1/2}$, from Table I) with quinone–pyrene π-complex absorption maxima ($\tilde{\nu}_{max}$, calculated from λ_{max} of Table III); quinones: (a) *p*-benzoquinone, (b) 2,6-bis(trifluoromethlthio)-*p*-benzoquinone (**10**), (c) chloranil, (d) 2,3,6-tris(trifluoromethylthio)-*p*-benzoquinone (**12**), (e) tetrakis(trifluoromethylthio)-*p*-benzoquinone (**15**), (f) 5-chloro-2,3-dicyano-*p*-benzoquinone, (h) 2,3-dicyano-5-phenylsulfonyl-*p*-benzoquinone (**3**); (i) 2,3-dicyano-5-chloro-6-phenylsulfonyl-*p*-benzoquinone (**6**), (j) tetracyano-*p*-benzoquinone ($E_{1/2}$ estimated from $\Delta E_{1/2}$ values of Table II and $\tilde{\nu}_{max}$ calculated from ref 6c).

Table III

Comparison of π Complexes of Quinones with Pyrene Measured in CH_2Cl_2 at 22°

π acid	λ_{max}, A	K^a	ϵ_{max},^{a} cm^{-1} mole l.$^{-1}$
p-Benzoquinone	4,530	14	323
2,6-Bis(trifluoromethylthio)-*p*-benzoquinone (**10**)	5,720	15	613
2,3,5-Tris(trifluoromethylthio)-*p*-benzoquinone (**13**)	6,400	21	560
p-Chloranil	6,100	23	943
Tetrakis(trifluoromethylthio)-*p*-benzoquinone (**15**)	7,000	18	480
Tetracyanoethylene	7,240	30	1140
2,3-Dicyano-5-chloro-*p*-benzoquinone	7,730	96	1300
2,3-Dichloro-5,6-dicyano-*p*-benzoquinone	8,500	180	1300
2,3-Dicyano-5-phenylsulfonyl-*p*-benzoquinone (**3**)	8,740	57	175
2,3-Dicyano-5-chlorophenylsulfonyl-*p*-benzoquinone (**6**)	9,050	180	104
Tetracyano-*p*-benzoquinone	11,290^b	...	...

^{a} Calculated according to the method of ref 5. The data indicate that all of these complexes are 1:1. ^{b} See ref 6c.

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(32) D. R. Eaton, A. D. Josey, and W. A. Sheppard, *J. Am. Chem. Soc.*, **85**, 2689 (1963). A small but significant nmr contact interaction shift was observed for the fluorines of a SO_2CF_3 group attached to an aromatic ring of a paramagnetic species.

(33) Tetrakis(trifluoromethylthio)-*p*-benzoquinone (**15**) appeared to undergo a single step, two-electron polarographic reduction under the conditions summarized in Table I. With tetrabutylammonium perchlorate as the supporting electrolyte in anhydrous acetonitrile, polarographic reduction of **15** occurred in three well-defined steps, the first of which appeared to be a one-electron reduction ($E_{1/2}$ = +0.28, −0.47, and −1.68 v; with I_d = 2.4, 1.4, and 1.0, respectively).

(34) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald, and H. E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

(35) L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 462 (1951); see also ref 2b.

(36) R. S. Mulliken, *ibid.*, **74**, 811 (1952).

the π acids;[37] (3) electron affinities (and unknown energies of solvation)[28a] are measured by polarographic reduction potentials.[28b] In general one might expect, as we find, a lack of perfect correlation between $E_{1/2}$ and $\bar{\nu}_{\max}$ because of the effects on $E_{1/2}$ of various energies of quinone solvation. In particular, correlation of the data shown in Figure 2 may to some extent be fortuitous since values for $E_{1/2}$ and $\bar{\nu}_{\max}$ were taken from measurements in different solvents. Nevertheless Figure 2 should be useful in predicting the approximate reduction potential of a given quinone from the absorption maximum of its charge-transfer complex with pyrene.[38]

Experimental Section[39]

2,3-Dicyano-5-phenylsulfonylhydroquinone (1), 2,3-Dicyano-5,6-bis(phenylsulfonyl)hydroquinone (2), and the Monosodium Salt of 2.—A mixture of 130 g (0.63 mole) of benzenesulfinic acid sodium salt dihydrate (Eastman) and 100 ml of distilled water was agitated vigorously while a solution of 35 ml (0.63 mole) of concentrated sulfuric acid in 200 ml of ice–water was added. The resulting suspension of benzene–sulfinic acid was extracted with two 300-ml portions of acetonitrile. The combined acetonitrile extracts were then cooled in an ice bath and stirred vigorously under an atmosphere of nitrogen while a solution of 55 g (0.35 mole) of 2,3-dicyanoquinone[40] in 500 ml of acetonitrile was added dropwise over 30 min. The dark reaction mixture was allowed to stand at room temperature overnight and was then evaporated under reduced pressure until the residue solidified. The resulting solid was triturated with 1 l. of cold water and collected by filtration. It was then mixed with 1.7 l. of fresh water, and solid sodium bicarbonate was added until effervescence ceased. The alkaline solution was heated to boiling and filtered while hot. On standing overnight at room temperature the filtrate deposited 13.0 g (6%) of the monosodium salt of 2,3-dicyano-5,6-bis(phenylsulfonyl)-*p*-hydroquinone (**2**) as yellow needles which were collected by filtration. The filtrate containing hydroquinone **1** was set aside for use as described below. Recrystallization of **2** from dilute aqueous sodium bicarbonate solution gave an analytical sample of the salt: dec pt 240–250°; $\lambda_{\max}^{\text{Nujol}}$ 2.80, 2.95 (OH), 4.49 (C≡N), 6.03, 6.27, 6.51, 6.65 (C═C), and 8.72 μ (sulfonyl); $\lambda_{\max}^{\text{EtOH}}$ 402 mμ (ϵ 9500) and 248 mμ (26,000).

Anal. Calcd for $C_{20}H_{11}N_2NaO_6S_2$: C, 51.94; H, 2.86; N, 6.06; Na, 4.97; S, 13.87. Found: C, 52.07; H, 2.81; N, 6.19; Na, 4.60; S, 13.92.

Action of nitrogen tetroxide on a suspension of this sodium salt in chloroform gave the conjugate acid, 2,3-dicyano-5,6-bis(phenylsulfonyl)hydroquinone, which crystallized as white, chunky crystals from benzene, mp 202–203.5°.

Anal. Calcd for $C_{20}H_{12}N_2O_6S_2$: C, 54.53; H, 2.75; N, 6.37; S, 14.56; neut equiv, 440. Found: C, 54.97; H, 2.83; N, 6.45; S, 14.57; neut equiv, 451 (pK_a = 2.92 in 90% alcohol).

The aqueous filtrate remaining from the first isolation of the sodium salt of **2** was acidified with dilute sulfuric acid to pH 1 and then extracted with three 350-ml portions of ethyl acetate. The organic layers were combined, washed with water, and dried over $MgSO_4$. Evaporation under reduced pressure gave 106 g of solid which was crystallized from 9540 ml of water acidified with 95 ml of concentrated hydrochloric acid. This gave 96 g (62% yield) of 2,3-dicyano-5-phenylsulfonylhydroquinone as light-tan needles. Recrystallization again from dilute acid using decolorizing charcoal gave colorless needles, mp 207–211°. An analytical sample was prepared by crystallization from a mixture of ethyl acetate, benzene, and cyclohexane (5:2:1, v/v): $\lambda_{\max}^{\text{KBr}}$ 3.00 (OH), 4.46 (C≡N), 6.20, 6.30 (aromatic C═C), 7.45, 7.62, 7.75, 8.76, and 8.86 μ; $\lambda_{\max}^{\text{CH}_3\text{CN}}$ 235 mμ (ϵ 20,000), 260 (10,600), and 364 (8850).

Anal. Calcd for $C_{14}H_8N_2O_4S$: C, 55.99; H, 2.69; N, 9.33; S, 10.7. Found: C, 55.65; H, 2.82; N, 9.47; S, 11.0.

The anion of this relatively strong acid exhibits blue-green fluorescence in water. A solution of the quinol in acetonitrile cannot be oxidized polarographically at potentials up to 1.14 v (*vs.* sce). It undergoes one-electron reductions at −1.13 and at −1.40 v in acetonitrile ($LiClO_4$ electrolyte).

***2,3-Dicyano-5-phenylsulfonyl-p-benzoquinone* (3).**—This quinone reacted with impurities present in commercial methylene chloride. The solvent was therefore purified prior to use by washing it with concentrated H_2SO_4 and distilling it from P_2O_5 after storage for at least 1 day over the latter. Fifteen grams of dry 2,3-dicyano-5-phenylsulfonylhydroquinone was stirred in 100 ml of purified methylene chloride while about 20 ml of N_2O_4 was added over a period of about 30 min. The mixture was stirred for an additional 15 min and then filtered. The yellow filter cake was washed with two 30-ml portions of ether, giving 13 g (87%) of 2,3-dicyano-5-phenylsulfonyl-*p*-benzoquinone (**3**), mp 222–225° dec. Quinone **3** prepared this way was quite stable if kept dry and out of strong light, but failure to wash the crude quinone with ether left a product that gradually evolved HCN and darkened on storage. Evaporation of the CH_2Cl_2 filtrate gave an additional 2 g of quinone but it was relatively impure and unstable. Recrystallization of the major product from benzene–cyclohexane (5:1) gave an analytical sample as red crystals that on prolonged drying at 78° (0.3 mm) lost benzene, became yellow-orange in color, and melted at 225–235° dec: $\lambda_{\max}^{\text{KBr}}$ 4.47 (C≡N), 5.87 (C═O), 6.10, 6.17, 6.26, 6.30, 6.34, 7.54, 7.72, and 8.56 (SO_2) μ; $\lambda_{\max}^{\text{CH}_3\text{CN}}$ 260 mμ (ϵ 10,400) and 235 mμ (ϵ 13,400).

Anal. Calcd for $C_{14}H_6N_2O_4S$: C, 56.37; H, 2.03; N, 9.39; S, 10.75. Found: C, 56.52; H, 2.14; N, 9.62; S, 10.74.

***2,3-Dicyano-5,6-bis(phenyl)hydroquinone* (2) by Addition of Benzenesulfinic Acid to 2,3-Dicyano-5-phenylsulfonyl-*p*-benzoquinone.**—To a stirred, ice-cold solution of 2.5 g of benzenesulfinic acid in absolute ethanol was added 1.7 g of 2,3-dicyano-5-phenylsulfonyl-*p*-benzoquinone. The mixture was stirred cold for 10 min and then at room temperature for about 35 min. Concentration of the reaction mixture under reduced pressure to about 5 ml gave a yellow, mushy solid that was washed with 140 ml of water and collected by filtration. It was crystallized from 75 ml of hot water almost saturated with sodium bicarbonate, giving yellow needles. Recrystallization from 45 ml of 5% aqueous sodium bicarbonate gave 0.90 g of pure sodium salt of 2,3-dicyano-5,6-bis(phenylsulfonyl)hydroquinone, having an infrared spectrum identical with that of the salt of **2** obtained as described above.

Adduct of 2,3-Dicyano-5-phenylsulfonyl-*p*-benzoquinone and 2,3-Dimethyl-1,3-butadiene (4).—A suspension of 1.2 g (4 mmoles) of 2,3-dicyano-5-phenylsulfonyl-*p*-benzoquinone (**3**) in 13 ml of benzene was stirred while 0.8 g (10 mmoles) of 2,3-dimethyl-1,3-butadiene was added dropwise. The vigorous reaction that ensued was accompanied by dissolution of the quinone. After 0.5 hr, the solution was blown to dryness under a jet of nitrogen. The residual oil was triturated with 15 ml of ether, giving 1.0 g of an orange solid that was collected by filtration. Recrystallization from benzene–cyclohexane gave dark red[41] crystals that softened at 181° and changed color from red

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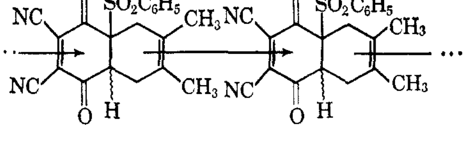
[37] R. S. Mulliken and W. B. Person [*Ann. Rev. Phys. Chem.*, **13**, 107 (1962)] have suggested the relationship: $h\nu = I - E + G_1 - G_0 + X_1 - X_0$, where ν is the frequency of the charge-transfer absorption band, I is ionization potential of the donor, E is the electron affinity of the acceptor, G_1 and G_0 are the interaction energies between donor and acceptor in the dative state and in the ground state, and $X_1 - X_0$ is the resonance energy of interaction between the two states. For less firm complexes this has been reduced to $h\nu = I - E - C$, where C is chiefly the coulombic energy of the charge-transfer excited state: H. McConnell, J. S. Ham, and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

[38] From Table III it can be seen that the association constants K show no simple variation with structure. This is probably because K reflects the combined influence of both quinone electron affinity and steric hindrance toward intermolecular association with the π base;[29] also, see P. R. Hammond [*J. Chem. Soc.*, 479 (1964)] for an analysis of errors inherent in the measurement of low values of K.

[39] Melting points are uncorrected.

[40] A. M. Creighton and L. M. Jackman, *J. Chem. Soc.*, 3138 (1960).

[41] The dark red color of adduct **4** seems to be associated only with its crystalline form, for its concentrated solution in benzene is light yellow. The red color and the unexpected high melting point of **4** may be a consequence of intermolecular charge transfer occurring between electron-deficient and electron-rich double bonds in **4**, *e.g.*



to yellow but did not melt[35] up to 300°: λ_{max}^{KBr} 4.48 ($C{\equiv}N$), 5.79 (carbonyl), 6.30 ($C{=}C$), 7.60, and 8.68 μ (sulfonyl); $\lambda_{max}^{CH_3CN}$ 220 mμ (ϵ 14,800), 261 (11,500), and 367 (202); H nmr ($CDCl_3$, internal TMSi) τ 8.40 (area 6, CH_3), doublet centered at 7.58 (J = 6.8 cps, area 1) 7.42 (broad, area 3), doublet at 6.30 (J = 6.8 cps, area 0.6, vinyl), doublet at 6.09 (J = 6.8 cps, area 0.4, vinyl), 2.27 (area 5, phenyl); no exchange with trifluoroacetic acid.

Anal. Calcd for $C_{20}H_{16}N_2O_4S$: C, 63.2; H, 4.25; N, 7.36; S, 8.46. Found: C, 63.5; H, 4.41; N, 7.40; S, 8.52.

5-Chloro-2,3-dicyano-6-phenylsulfonylhydroquinone.—Gaseous hydrogen chloride was bubbled through a stirred mixture of 2.0 g quinone **3** in 150 ml of benzene maintained at room temperature for 1 hr and then heated at 60° for 15 min. The reaction mixture, which had changed from a cherry red to light orange color, was then allowed to cool to room temperature and filtered. Crystallization of the filter cake from about 100 ml of nitromethane gave 1.3 g of needles, melting at 231–232° dec, which darkened on standing in air. Infrared analyses indicated that this product contained some 2,3-dicyano-5-phenylsulfonylhydroquinone. A final recrystallization of 1 g of the crude product from 2.5 l. of water containing 20 ml of concentrated HCl gave 0.6 g of pure 5-chloro-2,3-dicyano-5-phenylsulfonylhydroquinone as stable, colorless needles; mp 240–241° dec; λ_{max}^{Nujol} 2.94, 3.13 (OH), 4.45 ($C{\equiv}N$), 6.35 ($C{=}C$), 7.40, 8.86 (SO_2), and 11.25 μ (Cl); $\lambda_{max}^{CH_3CN}$ 377 mμ (ϵ 10,000), 270 (8500), and 222 (27,600).

Anal. Calcd for $C_{14}H_7ClN_2O_4S$: C, 50.2; H, 2.11; Cl, 10.6; N, 8.36. Found: C, 50.4; H, 2.35; Cl, 10.6; N, 8.35.

5-Chloro-2,3-dicyano-6-phenylsulfonyl-*p*-benzoquinone (**6**).—In the lower bulb of a crystallization assembly[42] was placed 5 ml of purified methylene chloride (*vide supra*) and 0.5 g of the 5-chloro-2,3-dicyano-6-phenylsulfonylhydroquinone. A solution of about 1 ml of nitrogen tetroxide in 1 ml of methylene chloride was then forced into the lower bulb under nitrogen pressure. After 15 min the crystallization assembly was inverted, and the yellow quinone was collected by filtration under nitrogen pressure. The quinone was washed with 2–3 ml of fresh methylene chloride and then with about 3 ml of dry ether. After drying over P_2O_5 at 78° (0.3 mm), the bright yellow quinone melted at 231–233° dec: λ_{max}^{KBr} 4.47 ($C{\equiv}N$), doublet 5.89, 5.92 ($C{=}O$) 6.30, 6.42, 6.15 ($C{=}C$), 7.56, and 8.86 μ (sulfone).

Anal. Calcd for $C_{14}H_5ClN_2SO_4$: C, 50.4; H, 1.51; Cl, 10.7; N, 8.42. Found: C, 50.0; H, 1.76; Cl, 10.7; N, 8.61.

The quinone was stable only if kept in a dry atmosphere away from intense light.

Adduct of 5-Chloro-2,3-dicyano-6-phenylsulfonyl-*p*-benzoquinone with 2,3-Dimethyl-1,3-butadiene (**7**).—2,3-Dimethyl-1,3-butadiene (0.08 g, 1 mmole) was added to a suspension of 0.10 g (0.3 mmole) of quinone **6** in 5 ml of benzene, and the reaction mixture was warmed at about 40° for about 10 min until the quinone dissolved. Evaporation of the benzene solution under a jet of nitrogen afforded an oil that was taken up in 5 ml of ether and centrifuged to remove a trace of insoluble material. Evaporation of the ether and crystallization of the residue three times from benzene–cyclohexane gave yellow crystals: λ_{max}^{KBr} 4.46 ($C{\equiv}N$), 5.81 ($C{=}O$), 6.32, 6.36, 6.47 ($C{=}C$), 7.48, 8.64 (SO_2), 12.2, 13.18, and 14.62 μ; $\lambda_{max}^{CH_3CN}$ 220 mμ (ϵ 15,000), 263 (12,100), and 350 (200).

Anal. Calcd for $C_{20}H_{15}ClN_2O_4S_2$: C, 58.3; H, 3.64; N, 6.74. Found: C, 58.4; H, 3.91; N, 6.53.

Trifluoromethylsulfinic Acid, Potassium Salt.—The following preparation of potassium salt is convenient and gave better yields than the published[13] synthesis of the corresponding sodium salt, which has been reported to be hygroscopic.

Trifluoromethylsulfonyl chloride (73 g, 0.43 mole), was added dropwise over about 1 hr to a stirred solution of 270 g (1.7 moles) of potassium sulfite in 450 ml of water. The reaction mixture was cooled in an ice bath during this addition and for 2 hr afterwards, and then allowed to stand at room temperature for 2 hr longer. The mixture was cooled again to about 5° and was quickly filtered through coarse porosity sintered glass. Evaporation of the filtrate to dryness in a rotating evaporator gave a mixture of salts that was extracted with three 225-ml portions of boiling acetone. The combined acetone extracts were cooled to room temperature and filtered. Evaporation of the acetone filtrate to dryness in a rotating evaporator, followed by drying at 40° over P_2O_5 under high vacuum for 18 hr, gave 50 g (68%) of almost pure, nonhydroscopic, trifluoromethanesulfinic acid potassium salt ($\cdot 0.5H_2O$): λ_{max}^{Nujol} 8.3–8.9 broad (CF) 9.3, and 9.9 μ.

Anal. Calcd for $CF_3SO_2K \cdot 0.5H_2O$: C, 6.63; H, 0.55. Found: C, 6.68; H, 0.39.

Titration of the salt with 0.06 N sodium hypochlorite solution[43] ("Zonite" diluted approximately 1:2) using starch–iodide paper as an external indicator showed that this salt was 98–99% pure. Traces of sulfite salts were removed by precipitation with $BaCl_2$ before the titration was undertaken.[43]

Trifluoromethylsulfonylhydroquinone.—A solution of 14.3 g (80 mmoles) of trifluoromethanesulfinic acid potassium salt in 45 ml of cold water containing 5.0 ml (90 mmoles) of concentrated sulfuric acid was stirred while 6.0 g (55 mmoles) of *p*-benzoquinone was added in portions over a 10-min period. The reaction mixture was stirred at room temperature for 1 hr and then diluted to 100 ml. After filtration to remove unchanged benzoquinone (about 3 g), the brown solution was cooled in an ice–salt bath, and 1.5 g of sodium bisulfate was added, whereupon the color faded from a dark amber-red to straw yellow and a voluminous precipitate appeared. Collection of the precipitate by filtration and washing with 5 ml of ice–water gave 5 g of the crude sulfonyl quinol. Recrystallization from 25 ml of water containing 1 ml of concentrated hydrochloric acid gave 3.15 g of colorless crystals. (The quinol exhibited a remarkably large temperature coefficient of solubility, being very slightly soluble in water at 0° and quite soluble at about 25°.) Sublimation gave colorless cubes, mp 84.0–85.0°, that gradually hydrated on exposure to the atmosphere.

Anal. Calcd for $C_7H_5F_3O_4S$: C, 34.8; H, 2.08. Found: C, 35.1; H, 2.21.

Trifluoromethylsulfonyl-*p*-benzoquinone (**8**).—Trifluoromethylsulfonylhydroquinone (0.50 g) and 1.5 g of magnesium sulfate in 25 ml of purified dichloromethane were stirred with 2.0 g of freshly prepared silver oxide for 15 min and then filtered through sintered glass under a nitrogen atmosphere. The filter cake was washed with three 10-ml portions of dry ether, and the combined filtrates were evaporated under reduced pressure, giving a yellow solid that was sublimed at 80° (0.1 mm). The crystalline sublimate, trifluoromethylsulfonyl-*p*-benzoquinone, quickly changed to a brown oil on exposure to atmospheric moisture, λ_{max}^{KBr} 7.5, 8.2, and 9.0 μ.

Anal. Calcd for $C_7H_3F_3O_4S$: C, 35.0; H, 1.26. Found: C, 35.1; H, 1.49.

2,6-Bis(trifluoromethylthio)-4-methoxyphenol (**9**).—A 2-l., round-bottomed flask was equipped with a magnetic stirrer, a gas inlet tube extending to within about 1 in. of the bottom of the flask, and an efficient Dry Ice condenser. One liter of chloroform was added, followed by 200 g (1.62 mole) of *p*, methoxyphenol and 430 ml (420 g, 5.33 mole) of pyridine. While the mixture was maintained at 0–5° by an ice bath, pure trifluoromethanesulfenyl chloride[44] (bp −2°) was distilled from a graduated cold trap into the reaction mixture over about 2.5 hr until a total of 490 g (288 ml at −78°, 3.56 moles) of CF_3SCl had been added. When the addition was completed, the gas inlet tube was replaced by a stopper, and the mixture was stirred for about 15 hr. The mixture was cooled by an ice bath during the first 1.5 hr, and Dry Ice and acetone were maintained in the condenser during the first 6–8 hr. The chloroform solution was then extracted once with a solution of 500 ml of concentrated hydrochloric acid in 1.5 l. of water and once with a solution containing 100 ml of the acid in 500 ml of water. After a final washing with water, the chloroform solution was dried over $MgSO_4$ and evaporated to dryness under reduced pressure (temperature not exceeding 50°). The solid residue was crystallized from 450 ml of *n*-hexane. The first crop of crystals weighed about 180 g and melted at 78–81°. The second crop, obtained by cooling the mother liquor in an ice bath, weighed 123 g and melted at 70–77°. Recrystallization of the first crop from 360 ml of *n*-hexane gave about 136 g of colorless crystals of 2,6-bis(trifluoromethylthio)-4-methoxyphenol, melting at 82.3–84.0°. Cooling the mother liquor from the second crystallization gave additional solid (10–15 g) which was combined with the crop having mp 70–77° and sublimed giving 90 g

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(42) N. D. Cheronis in "Technique of Organic Chemistry," A. Weissberger, Vol. VI, Ed., Interscience Publishers, Inc., New York, N. Y., 1954, p 36.

(43) L. Ackerman, *Ind. Eng. Chem., Anal. Ed.*, **18**, 243 (1946). Sodium benzenesulfinate is determined by titration with standard sodium hypochlorite.

(44) C. W. Tullock, U. S. Patent 2,884,453 (1959).

of a white solid, mp 75-80°. Recrystallization of the sublimate from 220 ml of *n*-hexane gave 73 g of 2,6-bis(trifluoromethylthio)-4-methoxyphenol, mp 80-82°. The total yield of 2,6-bis(trifluoromethylthio)-4-methoxyphenol melting about 80° was 209° (40%). An analytical sample, prepared by recrystallization of the crop melting at 82.3-84.0° from *n*-hexane, consisted of colorless needles, mp 83.0-84.0°.

Anal. Calcd for $C_9H_6F_6O_2S_2$: C, 33.4; H, 1.87; F, 35.2; S, 19.8. Found: C, 33.7; H, 2.07; F, 34.9; S, 19.9.

The proton nmr spectrum of a solution of this compound in CCl_4 (TMSi internal standard) showed a single peak at τ 2.69 with a relative area of 2, a single peak at 3.58 of area 1, and a single peak at 6.17 with a relative area of 3. The fluorine nmr spectrum in CCl_4 showed a single peak at −1430 ±5 cps (56.4 Mcps) with respect to $Cl_2CF-CCl_2F$ external standard.

When this reaction was run with less than 3 moles of pyridine for each mole of *p*-methoxyphenol, mixtures of the mono- and di-CF_3S derivatives were obtained. For example, when 2 moles of pyridine, 2 moles of CF_3SCl, and 1 mole of *p*-methoxyphenol were allowed to react, a mixture (mp 55-64°) was obtained which by gas phase chromatography and nmr analysis was shown to be composed of 40% 2-trifluoromethylthio-4-methoxyphenol and 60% 2,6-bis(trifluoromethylthio)-4-methoxyphenol.

2,6-Bis(trifluoromethylthio)-*p*-benzoquinone (10).—A creased, four-necked, 500-ml flask was equipped with a paddle stirrer, a reflux condenser, a thermometer, and a heating mantle. Two hundred milliliters of concentrated (68%) nitric acid was placed in the flask and stirred vigorously while 50 g (0.65 mole) of powdered 2,6-bis(trifluoromethylthio)-4-methoxyphenyl was added in portions over 20-35 min. The temperature of the reaction mixture was maintained at 30-35° by controlling the rate of addition of the solid and, if necessary, by external cooling. When addition of the solid was completed and when the exothermic reaction had subsided, the stirred reaction mixture was heated slowly (30 min) to 50° and maintained at that temperature for 10-15 min. The mixture was allowed to cool to room temperature and then poured into ice-water. The yellow solid was collected by filtration and washed with water until the wash water ceased to be acidic. The air-dried, crude product was crystallized from boiling methylcyclohexane (8-9 ml/g of crude quinone), giving 46.5 g (96%) of 2,6-bis(trifluoromethylthio)-*p*-benzoquinone as bright yellow plates, mp 142.0-143.0°. An analytical sample melting at 143.5-144.5° was obtained by sublimation at 90° (10 mm): λ_{max}^{KBr} 6.00, 6.09 (C═O), 6.23, 6.27 (C═C) 8.5-9.0 (C—F), and 13.17 μ (SCF_3).

Anal. Calcd for $C_8H_2F_6O_2S_2$: C, 31.1; H, 0.65; F, 37.0; S, 20.8. Found: C, 31.3; H, 0.83; F, 37.1; S, 20.9.

2,6-Bis(trifluoromethylthio)hydroquinone (11).—This compound was prepared by reduction of an acetone-water solution of quinone **10** with excess, aqueous sodium hydrosulfite: mp 66-67° after sublimation; λ_{max}^{Nujol} 3.0 broad (OH), 6.25, 6.28 (C═C), 8-9 (CF), and 13.05 (SCF_3) μ.

Anal. Calcd for $C_8H_4F_6O_2S_2$: C, 31.0; H, 1.30; S, 20.7. Found: C, 31.0; H, 1.36; S, 20.8.

2,3,5-Tris(trifluoromethylthio)hydroquinone (12).—Bis(trifluoromethylthio)mercury was prepared by the method of Muetterties.[17] Pure CF_3SH, free of HCl, was generated in about 85% yield by addition of a slight deficiency of standardized (20-25%) HCl in dioxane to $(CF_3S)_2Hg$, heating the reaction mixture at reflux temperature under a water-cooled condenser, and distilling the crude thiol into a trap cooled in Dry Ice-acetone. The light yellow distillate was redistilled through a low-temperature distillation column packed with glass helices and collected as a colorless liquid boiling at −37.5 to −35°. Its density at −78° was about 1.46.

A mixture of 88 g (0.29 mole) of 2,6-bis(trifluoromethylthio)-*p*-benzoquinone and 250 ml of chloroform was stirred in a round-bottomed flask equipped with an efficient Dry Ice condenser and immersed in an ice-salt bath. Trifluoromethanethiol (32 g, 22 ml at −78°, 0.32 mole) was added through a gas inlet tube attached to the flask and then, with vigorous stirring, 2.0 ml (0.025 mole) of pyridine was injected all at once from a hypodermic needle through a rubber septum into the reaction mixture. Reaction was immediate as evidence by rapid dissolution of the quinone and change of color from yellow-orange to amber. The solution was stirred for 2 hr at room temperature and then washed with two 125-ml portions of 7% HCl. After being dried over $MgSO_4$, the mixture was stripped of chloroform under reduced pressure. Distillation of the oily residue through a short-pass column at 0.08 mm with the pot heated at 70-75° gave 110 g (94%) of a light yellow oil. An analytical sample was prepared by distillation through an 18-in. spinning-band column, but this method of purification could not be used for the major portion of the sample because such distillation was invariably accompanied by extensive charring. The proton nmr spectrum of this quinol in CCl_4 showed a single peak at τ 3.47 (area 2) and a single peak a 2.37 (area 1), the former being assigned to the two nonequivalent but rapidly exchanging OH groups, the latter to the single, aromatic hydrogen. The infrared spectrum showed a sharp band at 2.91 (OH), no band in the carbonyl region, and a band at 13.24 μ, believed to be associated with the CF_3S group.

Anal. Calcd for $C_9H_3F_9S_3O_2$: C, 26.3; H, 0.74. Found: C, 26.4; H, 0.85.

Tris(trifluoromethyl)-*p*-benzoquinone (13).—A solution of 106 g (0.259 mole) of 2,3,6-tris(trifluoromethylthio)hydroquinone in 200 ml of methylene chloride was stirred with 20 g of anhydrous magnesium sulfate and cooled in an ice bath. A solution of *ca.* 13 ml (at 20°) of dinitrogen tetroxide in 30 ml of CH_2Cl_2 was added dropwise (0.75 hr) until effervescence ceased and then 1-2 ml more of the solution of oxidant was added. A large excess of oxidant appeared to be deleterious. After addition was completed, the dark mixture was stirred for 10 min longer and then filtered to remove the magnesium sulfate. Removal of solvent under reduced pressure gave crude 2,3,5-tris(trifluoromethylthio)-*p*-benzoquinone as an orange-red oil. The quinone did not have to be purified further prior to use in the subsequent reaction. An analytical sample was prepared by distillation at 80° (0.6 mm) through a short-pass column giving a yellow-red oil that gradually crystallized into an orange solid: mp 29-30°, λ_{max}^{KBr} 5.98 (carbonyl) and 13.17 μ (CF_3S). The proton nmr spectrum (in $CDCl_3$) shows a single peak at τ 2.97.

Anal. Calcd for $C_9HF_9S_3O_2$: C, 26.5; H, 0.25. Found: C, 26.7; H, 0.33.

Tetrakis(trifluoromethylthio)hydroquinone (14).—In a 500-ml round-bottomed flask, equipped as described for the preparation of **12**, was stirred a cold solution of 94 g (0.23 mole) of 2,3,5-tris(trifluoromethylthio)-*p*-benzoquinone in 250 ml of chloroform. Pure trifluoromethanethiol (30 g, 20 ml at −78°, 0.29 mole) was distilled into the reaction vessel, and then 21 g (0.26 mole) of pyridine was injected in four equal portions over a period of about 4 min. The mixture, dark at first and finally amber-yellow in color, was stirred at room temperature for 1 hr and then poured into ice water containing 50 ml of concentrated hydrochloric acid. The water-chloroform mixture was stirred vigorously, and the solid that precipitated was collected by filtration, washed with 5% HCl, and air dried, giving crude tetrakis(trifluoromethylthio)hydroquinone which was almost colorless, weighed 69 g, and melted at 99-100°. The chloroform layer in the filtrate was separated from the aqueous layer, washed with 10% aqueous HCl, and evaporated under reduced pressure giving a dark red, mushy solid. Extraction of this dark red solid with 200 ml of boiling *n*-hexane gave on cooling an additional 27 g of the hydroquinone, mp 99-100° making a total yield of 82%. An analytical sample, mp 105-106°, was prepared by two additional recrystallizations from *n*-hexane and sublimation at 95° (0.1 mm). The proton nmr spectrum in $CDCl_3$ showed a single peak at τ 2.97. The fluorine spectrum in acetone showed a single, sharp peak 26.4 ppm low field from $CFCl_2-CFCl_2$.

Anal. Calcd for $C_{10}H_2F_{12}O_2S_4$: C, 23.6; H, 0.40; S, 25.1. Found: C, 23.6; H, 0.65; S, 25.2.

Tetrakis(trifluoromethyl)-*p*-benzoquinone (15).—A solution of 30 g of the hydroquinone (**14**) in 300 ml of methylene chloride with 10 g of anhydrous $MgSO_4$ in suspension was stirred and cooled in an ice bath while a solution of about 10 ml (at 20°) of dinitrogen tetroxide in 20 ml of methylene chloride was added dropwise until effervescence ceased. An additional 1-2 ml of the solution of oxidant was added, and the dark mixture was filtered. Evaporation under reduced pressure gave an orange solid that was distilled at 67° (0.1 mm) without ebullition onto a cold-finger condenser of a sublimer; giving beautiful orange cubes of tetrakis(trifluoromethylthio)-*p*-benzoquinone: mp 57.0-58.5°; λ_{max}^{KBr} 5.85, 5.94 (C═O), 6.44, 6.56 (conjugated C═C), strong broad bands in the 9-μ region (CF), and 13.18 μ (CF_3S); $\lambda_{max}^{CH_2Cl_2}$ 330 mμ (ϵ 6600).

Anal. Calcd for $C_{10}F_{12}O_2S_4$: C, 23.6; H, 0.0; F, 44.8; S, 25.2. Found: C, 23.7; H, 0.13; F, 44.9; S, 25.3.

2,6-Bis(trifluoromethylthio)-3,6-dianilinobenzoquinone (21).—To a solution of 5.08 g (10 mmoles) of quinone **15** in 25 ml of methanol was added 4.0 g (43 mmoles) of aniline dissolved in

25 ml of methanol. An exothermic reaction ensued, accompanied by precipitation of a voluminous orange solid which, after 10 min was collected by filtration and washed with three 25-ml portions of methanol. After air drying, the orange-red needles weighed 4.6 g (94%). Crystallization from benzene twice gave silky needles: mp 265–266°; λ_{max}^{EtOH} 360 mμ (ϵ 12,700) and 240 mμ (ϵ 18,100); λ_{max}^{KBr} 3.12 (NH), 6.07 (C=O), 6.17, 6.29, 6.48, 6.66, 6.74, 9.05 (CF), and 13.26 μ (SCF_3).

Anal. Calcd for $C_{20}H_{12}F_6N_2O_2S_2$: C, 51.1; H, 2.47; N, 5.72; S, 13.1. Found: C, 51.2; H, 2.66; N, 5.30; S, 12.8.

1,4-Dimethoxytetrakis(trifluoromethylthio)benzene (16).—To a solution of 10.0 g (0.02 mole) of the crude (mp 99–100°) quinol **14** in 50 ml of water containing 2.4 g (0.06 mole) of sodium hydroxide was added dropwise with vigorous stirring 7.6 g (5.6 ml, 0.06 mole) of dimethyl sulfate. When addition was completed (5 min), the reaction mixture was heated slowly to 95–100°, and an additional 2.4 g of sodium hydroxide in 12 ml of water was added, followed by 5.7 ml of dimethyl sulfate. Ten minutes later, while the solution was still at 95–100°, an additional 2.4 g of NaOH in 12 ml of water and 2.0 ml of dimethyl sulfate were added. The mixture was heated at reflux temperature for 29 min, cooled to 25°, made alkaline with 10% sodium hydroxide solution, and filtered. The solid obtained was sublimed at 95–100° (0.1 mm), giving 11.5 g of crude 1,4-dimethoxytetrakis(trifluoromethylthio)benzene. One recrystallization from 40 ml of cyclohexane gave 8.0 g (75%) of colorless needles, mp 128.5–130.0°. Fluorine nmr (acetone) showed one sharp peak at −1533 cps (at 56.4 Mc) from $CFCl_2$–$CFCl_2$ internal standard. Proton nmr ($CDCl_3$) shows one sharp peak at τ 5.95.

Anal. Calcd for $C_{12}H_6F_{12}O_2S_4$: C, 26.7; H, 1.12; F, 42.3. Found: C, 26.7; H, 0.87; F, 42.3.

1,4-Dimethoxytetrakis(trifluoromethylsulfonyl)benzene (17).—A mixture of 18 g (0.24 mole) of anhydrous chromium trioxide in 180 ml of fuming (90%) nitric acid was stirred in a round-bottomed flask and maintained at 0–10° by cooling with a large ice bath. Finely powdered 1,4-dimethoxytetrakis(trifluoromethylthio)benzene, 18.2 g (0.034 mole), was added all at once, and the reaction mixture was stirred overnight. During this time, the ice in the cooling bath was allowed to melt. To the resulting homogeneous solution was added an additional 18 g of CrO_3. The stirred reaction mixture was then heated slowly (1 hr) to 50°, held at that temperature for 1 hr, and then heated to 60° (15 min) and maintained at that temperature for 1 hr. The dark green reaction mixture was cooled to 15° and poured into ice water. Collection of the bright yellow solid by filtration gave, after washing with water and drying in air, 21.2 g of crude tetrasulfone, mp 200–209°. Recrystallization from 500–600 ml of benzene gave 13.6 g (60%) of the pure tetrasulfone as bright yellow crystals, mp 214.0–215.0°. An analytical sample (having the same melting point) was prepared by sublimation at 100° (0.1 mm). The proton nmr spectrum of a solution of the tetrasulfone in deuterioacetone showed a single, sharp peak at τ 5.62 at maximum resolution. The fluorine nmr spectrum showed a single peak at +105 cps from $CFCl_2$–$CFCl_2$ internal standard at 56.4 Mc. The infrared spectrum (KBr) of the tetrasulfone showed a doublet at 7.5 and 8.25 (SO_2) and a band at 13.29 μ (SO_2CF_3).

Anal. Calcd for $C_{12}H_6F_{12}O_{10}S_4$: C, 21.6; H, 0.91; F, 34.2; S, 19.2. Found: C, 21.8; H, 1.02; F, 34.2; S, 19.3.

1,4-Dimethoxy-2,3,5-tris(trifluoromethylsulfonyl)benzene (18).—Catalytic hydrogenation of sulfone **17** was carried out at 28° at approximately 1 atm by stirring a suspension of 0.666 g (1 mmole) of the sulfone and 0.10 g of 10% palladium on charcoal in 50 ml of purified dichloromethane. Hydrogen uptake was completed in about 1 hr, whereupon the colorless solution was filtered and evaporated to dryness, giving 0.615 g of a colorless solid, mp 180–181° dec. The impure product gradually evolved HF on storage (decomposition of CF_3SO_2H?). Sublimation of the crude product twice at 140° (0.1 mm) gave colorless, stable crystals of 1,4-dimethoxytris(trifluoromethylsulfonyl)benzene, mp 187.5–188.0°; the proton nmr (CD_3CN) spectrum showed two peaks at τ 4.15 and 4.17 (OCH_3, each of area 3), and a peak at 1.82 (aromatic H, area 1).

Anal. Calcd for $C_{11}H_7F_9O_8S_3$: C, 24.7; H, 1.32. Found: C, 24.8; H, 1.21.

1,4-Dimethoxy-2,6-bis(trifluoromethylthio)benzene.—To a solution of 10.5 g (32 mmoles) of 2,6-bis(trifluoromethylthio)-4-methoxyphenol (**9**) in 40 ml of 1 *N* sodium hydroxide was added 4 ml of dimethyl sulfate. The resulting mixture was heated at reflux for 15 min. An additional 40 ml of 1 *N* sodium hydroxide and 4 ml of dimethyl sulfate were added, and the mixture was heated at reflux for 0.5 hr. The mixture was cooled to room temperature, treated with 10 ml of 1 *N* sodium hydroxide, and extracted with two 100-ml portions of ether. Fractional distillation of the ethereal extract gave 8.2 g of 1,4-dimethoxy-2,6-bis(trifluoromethylthio)benzene as a colorless, mobile liquid: bp 60° (0.08 mm), $n^{24}D$ 1.4794.

Anal. Calcd for $C_{10}H_8F_6O_2S_2$: C, 35.6; H, 2.48; S, 33.7. Found: C, 36.1; H, 2.48; S, 33.4.

1,4-Dimethoxy-2-trifluoromethylsulfonyl-6-trifluoromethylsulfinylbenzene (19).—When 1,4-dimethoxy-2,6-bis(trifluoromethylthio)benzene was treated with chromium trioxide in sulfuric or acetic acid, reagents commonly used for the oxidation of trifluoromethylthio groups to sulfones, extensive decomposition occurred. The desired disulfone **20** could, however, be prepared by oxidation in two stages, as described in the following two paragraphs.

A solution of trifluoroperacetic acid was prepared by adding 46 g (31 ml, 0.22 mole) of trifluoroacetic anhydride to a suspension of 5.0 ml (0.18 mole) of 90% H_2O_2 in 150 ml of methylene chloride cooled in an ice bath. 1,4-Dimethoxy-2,6-bis(trifluoromethylthio)benzene (12.2 g, 0.036 mole) in about 20 ml of CH_2Cl_2 was added dropwise with stirring over a 1-hr period to the ice-cooled per acid. The reaction mixture was stirred at room temperature for 48 hr, and then extracted with five 75-ml portions of saturated aqueous sodium bicarbonate. Drying the organic layer over magnesium sulfate and evaporating it under reduced pressure gave 13.3 g of white solid, mp 61–73°. Recrystallization from *n*-hexane gave 10.7 g of **19**, mp 62–74°. An analytical sample prepared by sublimation melted at 64–67°: λ_{max}^{Nujol} 6.25, 6.45 (C=C), 7.30, 8.76 (SO_2), 9.56 (SO), and 10.2 μ.

Anal. Calcd for $C_{10}H_8F_6O_5S_2$: C, 31.1; H, 2.09; F, 29.5; S, 16.7. Found: C, 31.3; H, 2.18; F, 29.4; S, 16.6.

1,4-Dimethoxy-2,6-bis(trifluoromethylsulfonyl)benzene (20).—A solution of 23.7 g (0.06 mole) of 1,4-dimethoxy-2-trifluoromethylsulfonyl-6-trifluoromethylsulfinylbenzene (**19**) and 10 g of CrO_3 in 100 ml of glacial acetic acid was stirred vigorously. The temperature of the exothermic reaction that ensued was maintained between 55 and 60° by external cooling with an ice bath. When the reaction subsided, an additional 10 g of CrO_3 was added and the temperature was kept within the same limits. After the reaction subsided, the mixture was heated slowly to 100° and, when another exothermic reaction set in at that temperature, the mixture was maintained at 100° by periodic removal of the heating mantle. Finally the reaction mixture was heated at 115° for 45 min, cooled in ice, and poured into water. Collection of the resulting solid by filtration gave 15.8 g of colorless solid. Recrystallization from 100 ml of *n*-hexane gave 9.2 g (37%) of 1,4-dimethoxy-2,6-bis(trifluoromethylsulfonyl)benzene, mp 69.5–71.0°, as large prisms.

Anal. Calcd for $C_{10}H_8F_6O_6S_2$: C, 29.9; H, 2.00; F, 28.4; S, 16.0. Found: C, 30.1; H, 1.93; F, 28.3; S, 16.2.

Reaction of Tetrasulfone 17 with Water.—A solution of 0.333 g (0.50 mmole) of the tetrasulfone **17** in 20 ml of pure, dry acetone changed from bright yellow to orange-amber when 10 ml of distilled water was added. The pH of the solution dropped to about 2.2 in about 3 min. Potentiometric titration with 1.00 *N* NaOH required 1.02 ± 0.02 ml to bring the solution to its equivalence point, which was estimated graphically to be at about pH 7.5. These data indicate that the products of the hydrolysis of the tetrasulfone are either two strong acids, or, less likely, a single, strong dibasic acid. The former alternative would result by hydrolysis of the tetrasulfone to afford phenol **23** and trifluoromethanesulfinic acid. The presence of a sulfinic acid was verified in another experiment in which a solution of the tetrasulfone in tetrahydrofuran was brought to pH 11.0 by addition of 0.100 *N* base and then titrated with 0.329 *N* NaOCl solution ("Zonite" diluted about 1:2) using an external KI-starch indicator (*cf.* preparation of trifluoromethanesulfinic acid potassium salt and ref 43). The presence of 0.215 mole of CF_3SO_2Na from the hydrolysis of 0.214 mole (0.142 g) of tetrasulfone **17** was thus demonstrated.

Reaction of Tetrasulfone 17 with Hydrogen Bromide. A.—The tetrasulfone (**17**, 1.0 g, 1.5 mmoles) and 6.0 ml of 48% aqueous hydrogen bromide were heated together in a Carius tube at 175° for 6 hr. The tube was cooled in ice, opened, and allowed to warm to room temperature, whereupon evolution of a gas (bp of CH_3Br 4.5°) was noted. Evaporation of the crude reaction mixture to dryness under reduced pressure gave 0.83 g of a solid, 0.5 g of which was crystallized twice from cyclohexane, giving 0.20 g of almost colorless needles, mp 158–160°. Sublimation of this product at 125° (0.05 mm) gave colorless crystals of 2,6-dibromo-3,5-bis(trifluoromethylsulfonyl)-4-methoxyphenol: mp 159–160°; soluble in 5% aqueous $NaHCO_3$; F^{19} nmr ($CDCl_3$) single peak at +390 cps from $CFCl_2–CFCl_2$ at 56.4 Mc; H nmr ($CDCl_3$) peak at τ 6.05 (area 3) and 2.68 (area 1); λ_{max}^{KBr} (aromatic C=C) 6.62 μ.

Anal. Calcd for $C_9H_4Br_2F_6O_6S_2$: C, 19.9; H, 0.74; F, 21.1; S, 11.9. Found: C, 19.9; H, 1.11; F, 21.3; S, 12.0.

B.—A solution of 0.7 g (1 mmole) of tetrasulfone **17** in 10 ml of glacial acetic acid, and 5 ml of 48% HBr was heated at reflux temperature for 26 hr. Considerable etching of the glass equipment became evident during this time. The reaction mixture, on cooling, deposited 0.27 g of crystalline solid that on recrystallization from glacial acetic acid gave needles of tetrabromohydroquinone, mp 245–247°, with an infrared spectrum identical with that of authentic bromanil.

Reaction of Tetrasulfone 17 with Hydrogen Chloride.—Addition of 1.0 ml (12 mmoles) of concentrated hydrochloric acid to a refluxing solution of 0.50 g (0.75 mmole) of tetrasulfone **17** in 10 ml of glacial acetic acid caused the yellow solution to become almost colorless. An additional 5 ml of concentrated HCl was added, bringing the solution to a point just short of cloudiness, and the mixture was heated at reflux temperature for 20 min. On cooling the solution in ice, it deposited a crystalline solid that weighed 0.3 g after drying in air. Recrystallization twice from cyclohexane gave white needles of 2,6-dichloro-3,5-bis(trifluoromethylsulfonyl)-4-methoxyphenol: mp 150–152°; λ_{max}^{KBr} 3.12 (OH), 6.59, 6.62 (aromatic C=C) μ, and general absorption similar to that observed in the infrared spectrum of 2,6-dibromo-3,5-bis(trifluoromethylsulfonyl)-4-methoxyphenyl (above); H nmr ($CDCl_3$), a strong sharp peak at τ 6.13 and a very weak, broad peak at about 0.8 (exchange with $CDCl_3$?). The compound was soluble in 5% aqueous sodium bicarbonate.

Anal. Calcd for $C_9H_4Cl_2F_6O_6S_2$: C, 23.7; H, 0.83; F, 24.9. Found: C, 23.9; H, 0.44; F, 24.2.

2,5-Bis(ethylsulfonyl)-3,6-bis(ethylsulfinyl)hydroquinone.—Dost[8] claims without citing spectral evidence that oxidation of tetrakis(ethylthio)-*p*-benzoquinone with peracetic acid gives a bis(sulfonyl)bis(sulfonyl)quinone, mp 221–222°. However, the product obtained in this laboratory (mp 218–219°) under similar conditions clearly is the corresponding hydroquinone.

Tetrakis(ethylthio)-*p*-benzoquinone, mp 87–89°, was prepared by the method of Sammis.[45] When, and only when, the chloranil was finely ground prior to use, this procedure worked well and was much more convenient than more recent preparative methods. Oxidation of 1.74 g of tetrakis(ethylthio)-*p*-benzoquinone with peracetic acid by the method of Dost[8] gave on crystallization of the crude product from 15 ml of acetic acid 0.5 g of colorless solid, mp 200–202°. Two more crystallizations from acetic acid gave colorless needles of 2,5-bis(ethylsulfonyl)-3,6-bis(ethylsulfinyl)hydroquinone: mp 218–219°; λ_{max}^{KBr} 2.90 (OH), 6.15, weak (C=C), 7.64, 8.50 (SO_2), 9.76 (SO), 10.5, 12.7, and 13.7 μ; H nmr ($CDCl_3$); τ 2.77 (area 2, OH) quadruplets at 6.42 (area 4, CH_2), and triplets at 8.47 (area 6, CH_3) and 8.65 (area 6, CH_3).

Anal. Calcd for $C_{14}H_{22}S_4O_8$: C, 37.6; H, 4.98; S, 28.7. Found: C, 37.6; H, 5.04; S, 29.0.

Dehydrogenation of Testosterone with Quinone 15.—A solution of 1.00 g (3.5 mmoles) of testosterone and 2.5 g (4.9 mmoles) of tetrakis(trifluoromethylthio)-*p*-benzoquinone in 25.0 ml of *t*-butyl alcohol was heated at reflux temperature for 7 hr, during which time the solution underwent no apparent change in color or color intensity. A 1.00-ml aliquot of the solution was withdrawn and run into 100 ml of ether. The ether solution was washed with three 25-ml portions of sodium hydroxide and then dried over sodium sulfate and evaporated to dryness. The ultraviolet absorption spectrum of the solid residue showed λ_{max} 240 mμ (ϵ *ca.* 10,000). From this and the results of the following experiment it was concluded that under these conditions quinone **15** does not dehydrogenate testosterone.

To the remainder of the *t*-butyl alcohol solution of steroid and quinone **15**, 50 mg of *p*-toluenesulfonic acid monohydrate was added, and the resulting solution was heated at reflux temperature for 5 hr. The dark reaction mixture was cooled, poured into water, and extracted with three 100-ml portions of ether. The extracts were washed with three 50-ml portions of 5% sodium hydroxide, dried, and evaporated. The residue (1.76 g) was chromatographed on 70 g of neutral activity grade III alumina affording on elution with benzene–ether (1:1, v/v) 0.80 g of 6-dehydrotestosterone: mp 205–206° (ethyl acetate) (lit.[46] mp 209–211°); $\alpha^{24}{}_D$ +83° (c 1.3, $CHCl_3$); λ_{max}^{EtOH} 238 mμ (log ϵ 4.32); $\nu_{max}^{CHCl_3}$ 2.78, 2.90 (OH), 6.02 (conjugated C=O), 6.20, and 6.31 μ (conjugated C=C).

Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.71; H, 9.35.

Dehydrogenation of 4-Androstene-3,17-dione with Quinone 3. **A.**—A solution of 0.574 g (2 mmoles) of 4-androstene-3,17-dione and 1.20 g (4 mmoles) of 2,3-dicyano-5-phenylsulfonyl-*p*-benzoquinone (**3**) in 35 ml of benzene was heated at reflux temperature for 24 hr. The mixture was poured into 50 ml of water and extracted with three 20-ml portions of ether. The combined ether extracts were washed three times with aqueous 5% sodium hydroxide and once with saturated sodium chloride solution, and then dried over sodium sulfate. Evaporation of solvent under reduced pressure gave 0.293 g of amber solid which was analyzed by thin layer chromatography on silica gel. Benzene–ethyl acetate (93:7, v/v) was used as the developing solvent and sulfuric acid–ethanol–water (1:1:2, v/v/v) was used as the spray for visualization of spots by charring. Comparison with chromatograms of authentic steroids showed that the reaction mixture consisted of 1,4-androstadiene-3,17-dione, 4,6-androstadiene-3,17-dione, and unchanged 4-androstene-3,17-dione in relative proportions approximating 2:1:2.

B.—Under the same conditions as experiment A, except for 25 mg of added *p*-toluenesulfonic acid, 4-androstene-3,17-dione was dehydrogenated by quinone **3** to afford a mixture of steroids which, by thin layer chromatography according to the procedure described above, consisted of 1,4-androstadiene-3,17-dione and 4,6-androstadiene-3,17-dione in approximately equal parts.

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