1-chlorosulfonyl-3,5-dihydro-4,5-dimethyl-2-pyridone (**52**) was hydrolyzed and worked up in a manner similar to **43** → **49**. γ lactam **56** crystallized from the hydrolysis mixture after 2 weeks standing in a freezer (−15°). Several sublimations at 80° (0.3 mm) afforded analytically pure **56**: mp 96–98°; ir (KBr) 1325 (7.55) and 1660 cm^{-1} (6.02 μ) (C=O); nmr ($CDCl_3$) δ 8.65 (mound, 1, NH), 3.87 (mound, 2, CH_2NH), 2.89 (mound, 2, CH_2CO), 1.67 (s, 6, CH_3). Unlike lactam **49**, the signals did not sharpen up after a D_2O wash.

Anal. Calcd for $C_7H_{11}NO$: C, 67.17; H, 8.86; N, 11.19. Found: C, 66.76; H, 8.81; N, 10.94.

With the isolation and identification of lactones **53** and **55** and lactam **56**, it was possible to run a material balance on the reaction between CSI and **13** to form **14** and its thermal rearrangement to **51**, **52**, and **54**. Thus on a 0.20 *M* scale, the reaction between CSI and **13** afforded a mixture of **51**, **52**, and **54** which was hydrolyzed to give 17.7 g (0.140 mol based on an average mol wt 126 (70% conversion) of an oil containing **53**, **56**, and **55**, respectively, in a ratio (nmr) of 8:24:38.

Alkaline Hydrolysis of *N*-Chlorosulfonyl-2-azetidinones in Methanol.—The general procedure used was as follows. A solution of the *N*-chlorosulfonyl-2-azetidinone in ether was treated with a saturated solution of NaOH in CH_3OH to pH 9 at 5–20°. Sufficient water was added to clarify the reaction mixture which was then extracted with five 50-ml portions of ether. The combined extracts were dried ($MgSO_4$) and filtered and the solvent was removed *in vacuo* to give the bis esters of β-amino(*N*-sulfonic acid)carboxylic acids of nmr purity.

Methyl 3-methoxysulfonylamino-3,4-dimethylpent-4-enoate (**61**) was obtained from **8** as a red oil (64%): ir (neat) 3300 (NH) and 1735 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.20 (s, 1, NH), 6.31–5.83 (four peaks, 1, CH=), 5.43–5.00 (four peaks, 2, CH_2=), 3.77 and 3.65 (two s, each 3, SO_3CH_3 and CO_2CH_3), 2.76 (s, 2, CH_2), 1.52 (s, 3, CH_3).

Methyl 3-methoxysulfonylamino-3,4-dimethylpentanoate (**62**) was obtained from **17** as a light yellow oil (72%): bp 135–140° (0.2 mm); ir (neat) 3300 (NH) and 1735 cm^{-1} (C=O); nmr ($CDCl_3$) δ 5.67 (s, 1, NH), 3.77 and 3.66 (two s, each 3, SO_3CH_3 and CO_2CH_3), 2.66 (AB pattern, 2, J_{gem} = ~16 Hz, CH_2), 2.15 (heptet, 1, *J* = 7.0 Hz, CH), 1.31 (s, 3, CH_3), 0.96 and 0.90 [two d, 6, *J* = 7.0 Hz, $CH(CH_3)_2$].

Methyl 3-methoxysulfonylaminohex-4-enoate (**63**) was obtained from **20** as an orange–red oil (46%): ir (neat) 3275 (NH) and 1730 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.34 (mound, 1, NH), 5.73–5.45 (m, 2, CH=CH), 4.40–3.92 (m, 1, CH), 3.72 and 3.64 (two s, each 3, SO_3CH_3 and CO_2CH_3), 2.56 (d, 2, *J* = 6.5 Hz, CH_2), 1.68 (d, 3, *J* = 5.0 Hz, CH_3).

Methyl 3-methoxysulfonylaminohexanoate (**64**) was obtained from **23** as an orange oil (36%): ir (neat) 3290 (NH) and 1735 cm^{-1} (C=O); nmr ($CDCl_3$) δ 5.98 (mound, 1, NH), 3.96–3.52 (m, 1, buried under the methyl singlets, CH), 3.78 and 3.68 (two s, each 3, SO_3CH_3 and CO_2CH_3), 2.62 (d, 2, *J* = 6.0 Hz, CH_2), 1.73–0.73 [m, 9, $(CH_2)_3CH_3$].

Methyl 3-methoxysulfonylamino-2,3-dimethylbutanoate (**65**) was obtained from **57**[22] as an orange oil (66%): bp 128–136° (0.5 mm); ir (neat) 3300 (NH) and 1730 cm^{-1} (C=O); nmr ($CDCl_3$) δ 5.78 (mound, 1, NH), 3.76 and 3.68 (two s, each 3, SO_3CH_3 and CO_2CH_3), 2.72 (q, 1, *J* = 7.0 Hz, CH), 1.36 [s, 6, $(CH_3)_2C$], 1.22 (d, 3, *J* = 7.0 Hz, CH_3).

Methyl 3-methoxysulfonylamino-2,2,3-trimethylbutanoate (**66**) was obtained from **59**[22] as a yellow oil (74%): ir (neat) 3280 (NH) and 1715 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.12 (mound, 1, NH), 3.76 and 3.71 (two s, each 3, SO_3CH_3 and CO_2CH_3), 1.34 [s, 6, $(CH_3)_2CNHSO_3$], 1.24 [s, 6, $(CH_3)_2CCO_2$].

Registry No.—**3**, 7486-94-4; **6**, 5303-67-3; **8**, 20012-93-5; **9**, 20012-94-6; **12**, 20361-37-9; **14**, 30217-24-4; **15**, 30217-25-5; **18**, 30217-26-6; *cis*-**21**, 22970-43-0; *trans*-**21**, 22970-42-9; **24**, 22937-03-7; **27**, 30217-74-4; **30**, 30217-27-7; *cis*-**33**, 30288-16-5; *trans*-**33**, 30217-75-5; **36**, 30217-76-6; **40**, 22038-80-8; **41**, 22038-79-5; **45**, 10021-22-4; **46**, 30217-28-8; **47**, 2381-87-5; **48**, 30288-18-7; **49**, 20967-57-1; **50**, 30288-19-8; **53**, 22937-02-6; **54**, 30217-32-4; **55**, 30217-33-5; **56**, 30288-20-1; **61**, 30288-21-1; **62**, 30288-22-3; **63**, 30217-34-6; **64**, 30299-80-0; **65**, 30354-61-1; **66**, 30288-23-4; **67**, 30217-35-7; CSI, 1189-71-5; potassium 3-methyl-*cis*-2,4-pentadienoate, 30217-83-5.

Steric Effects of Vicinal Substituents on Redox Equilibria in Quinonoid Compounds

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Received December 8, 1970

The redox potentials of a series of methyl-substituted quinones and hydroquinones having *p*-tolylthio substituents were determined polarographically in 50% methanol at pH 5.37. The substituent effects are not additive, as shown by a break in the plot of $E_{1/2}$ *vs.* $\Sigma\sigma_{p\text{-Me}}$ (summation of Hammett σ-para constants of methyl). The break occurs with those compounds in which the *p*-tolylthio group is flanked by a methyl group, giving half-wave potentials which are more positive than predicted. The fact that the quinone sulfides are more easily reduced than expected suggests steric inhibition of the mesomeric effect of the arylthio substituent. Substituents that show strong electron-withdrawing inductive effects (*e.g.*, phenylsulfonyl and 1-phenyl-5-tetrazolylthio) fail to show a similar break in the linear free-energy relationship. Small, but significant, deviations from strict additivity for certain quinone–hydroquinone couples illustrate that subtle electronic and steric effects can be identified when an internally consistent series of polarographic measurements is obtained.

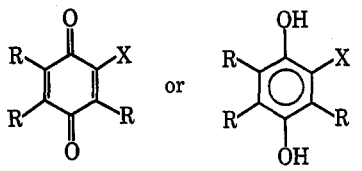
It is well established that the electronic and steric requirements of substituents attached to quinone and hydroquinone rings have important effects on the observed reduction and oxidation potentials.[1] In preparative organic chemistry, the nature of the substituent determines the oxidation state of the product when nucleophiles are added to quinones (eq 1 and 2).[2,3] Thus, when N = $PhNH_2$ and R = H, the substituted hydroquinone (HQ_2) formed initially is oxidized by unreacted Q, and further addition can occur.[2] When N = $PhSO_2H$, no cross oxidation occurs and HQ_2 is isolated.[3]

Addition of thiophenol (N = PhSH) to 1,4-benzoquinone gives the cross-oxidized product Q_2 (R = H).[4,5] In contrast, we find that addition of *p*-toluenethiol to di- and trimethyl-1,4-benzoquinones gives good yields of the *p*-tolylhydroquinone sulfides (HQ_2). Therefore, the presence and number of other substituents in the

(1) P. Zuman, "Substituent Effects in Organic Polarography," Plenum Press, New York, N. Y., 1967, pp 273–308.
(2) H. Suida and W. Suida, *Justus Liebigs Ann. Chem.*, **416**, 113 (1918).
(3) O. Hinsberg, *Chem. Ber.*, **27**, 3259 (1894).
(4) T. Posner, *Justus Liebigs Ann. Chem.*, **336**, 85 (1904).
(5) J. M. Snell and A. Weissberger, *J. Amer. Chem. Soc.*, **61**, 450 (1939).

TABLE I

POLAROGRAPHIC HALF-WAVE POTENTIALS (*vs.* SCE) FOR VARIOUS SUBSTITUTED QUINONES AND HYDROQUINONES[a]

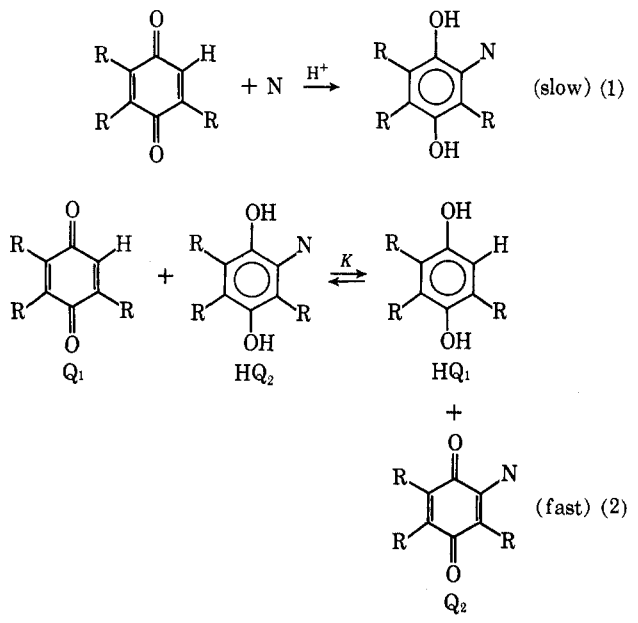


R	X	Registry no. Quinone	Registry no. Hydroquinone	Mp, °C[b] Quinone	Mp, °C[b] Hydroquinone	$E_{1/2}$, mV Quinone	$E_{1/2}$, mV Hydroquinone
H		5831-37-8		106–108		107	
2-Me	6-SC_6H_4Me-*p*	30771-63-2		151.5–152.5		49	
3-Me	6-SC_6H_4Me-*p*	30771-64-3	30771-65-4	84–85.5	103–104	60	63
2,3-Me_2	6-SC_6H_4Me-*p*		30771-66-5		87.5–88.5		0
2,5-Me_2	6-SC_6H_4Me-*p*	30771-67-6	30771-68-7	98.7–99.7	87–88	50	51
3,5-Me_2	6-SC_6H_4Me-*p*		30771-69-8		96–97.5		43
2,3,5-Me_3	6-SC_6H_4Me-*p*		30771-70-1		85–87.5		−15
H	6-SO_2Ph				198–200[c]		267[d]
2-Me	6-SO_2Ph		30771-71-2		189–191		200
2,3-Me_2	6-SO_2Ph		30771-72-3		196–198		154
2,5-Me_2	6-SO_2Ph		30771-73-4		160–161.5		124
3,5-Me_2	6-SO_2Ph		30771-74-5		147.5–149		129
2,3,5-Me_3	6-SO_2Ph		30771-75-6		149.5–150.5		69
H	6-PMT	30771-76-7	1660-27-1			183	181
2,3-Me_2	6-PMT		3308-84-7				64
2,5-Me_2	6-PMT	30771-79-0	3308-83-6			57	57
2,3,5-Me_3	6-PMT	30771-81-4	3237-66-9			−4	−1

[a] pH 5.37 ± 0.02; *t* = ambient laboratory temperature 24 ± 2°; solvent, 50% aqueous methanol (by volume); buffer, acetate, I = 0.090. [b] Corrected. All new compounds had elemental analyses ±0.3% of calculated. [c] Lit.[3] mp 196° uncor. [d] Estimated from $E_{1/2}$ at pH 6.25.

quinone ring also appear to govern the extent of cross oxidation.

We have measured the reduction potentials of methyl-substituted quinones and their *p*-tolyl sulfides to determine the equilibrium constants for equilibria 2. An earlier polarographic study of the methyl-substituted quinones and hydroquinones[6] provides some of the needed data. We have also measured oxidation potentials of hydroquinones obtained by addition of 1-phenyl-5-mercaptotetrazole (HPMT)[7] and benzenesulfinic acid to methyl-substituted quinones.



(slow) (1)

(fast) (2)

Results

All of the quinone and hydroquinone sulfides were prepared by the addition of *p*-toluenethiol to the appropriate quinone in alcohol solution. The sulfones were prepared by the addition of an aqueous solution of sodium benzenesulfinate to a solution of the appropriate quinone in glacial acetic acid. The corrected melting points of these compounds are given in Table I. The structures of the sulfides and sulfone resulting from addition to 2-methyl-1,4-benzoquinone were assigned on the basis of the coupling constants of the two protons attached to the quinone and hydroquinone. The alkyl-substituted quinones and hydroquinones were sublimed or recrystallized to the literature melting points.

Conventional dc polarography was carried out in a three-electrode cell.[8] The solvent was 50% aqueous methanol buffered with sodium acetate (I = 0.090), which was similar to the solvent used by Smith, *et al.*[6] The pH of the solutions was measured with a glass electrode which had been standardized using a similar buffer.[9] We repeated the published polarographic measurements for 1,4-benzoquinones[6] in our system and obtained half-wave potentials that agreed with the published values to within ±4 mV. The half-wave potentials are listed in Table I.

The wave for 2-phenylsulfonylhydroquinone occurs at such a positive potential[10] that at pH 5.37 it is more positive than the mercury dissolution wave and could not be measured. We determined the half-wave potentials of the other sulfones at both pH 5.37 and 6.25 as shown in Table II. The average change in $E_{1/2}$ for

(6) L. I. Smith, I. M. Kolthoff, S. Wawzonek, and P. M. Ruoff, *J. Amer. Chem. Soc.*, **63**, 1018 (1941).

(7) H. S. Wilgus III, E. Frauenglass, E. T. Jones, R. F. Porter, and J. W. Gates, Jr., *J. Org. Chem.*, **29**, 588 (1964).

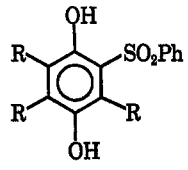
(8) W. M. Schwarz and I. Shain, *Anal. Chem.*, **35**, 1770 (1963).

(9) M. Paabo, R. A. Robinson, and R. G. Bates, *J. Amer. Chem. Soc.*, **87**, 415 (1965).

(10) All of the potentials in this report are in the European convention; *i.e.*, a more negative potential represents a better reducing agent.

TABLE II

HALF-WAVE POTENTIALS OF PHENYLSULFONYLHYDROQUINONES AT pH 5.37 AND 6.25



R	$E_{1/2}$, mV (pH 5.37)[a]	$E_{1/2}$, mV (pH 6.25)[a]
H	267[b]	216
2-Me	195	142
2,3-Me_2	157	104
2,5-Me_2	120	72
3,5-Me_2	126	74
2,3,5-Me_3	77	28

[a] *Vs.* sce; t = ambient laboratory temperature 24 ± 2°; solvent, 50% aqueous methanol (by volume); buffer, acetate (I = 0.090). [b] Estimated from $E_{1/2}$ at pH 6.25.

the five compounds measured is 51 mV; the expected theoretical change is 52 mV for a change in pH of 0.88. We used 51 mV to estimate the $E_{1/2}$ for 2-phenylsulfonylhydroquinone at pH 5.37 from the measured value at pH 6.25.

A number of the half-wave potentials listed in Table I were also determined by ac polarography. The $E_{1/2}$ values determined by both methods agreed within ±3 mV.

The reversibility of the electrode reactions was demonstrated in five cases by the fact that the half-wave potentials for the quinone and hydroquinone were the same within ±3 mV. In cases where both redox forms were not available, reversibility was demonstrated using the dc polarographic current data. A plot of log $(i_d - i)/i$ *vs.* E was linear and had a slope of 30 mV per decade over four log units, where i is the current at the potential E, and i_d is the diffusion-limited plateau current.

The equilibrium constant for eq 2 is given by eq 3,

$$K = \frac{[HQ_1][Q_2]}{[HQ_2][Q_1]} \quad (3)$$

and the standard potentials of the associated redox couples as

$$Q_1 + 2H^+ + 2e^- \rightleftharpoons HQ_1 \qquad E_1^\circ$$
$$Q_2 + 2H^+ + 2e^- \rightleftharpoons HQ_2 \qquad E_2^\circ$$

For reversible couples the difference between the half-wave potentials is equal to the difference between the standard potentials, if one assumes all diffusion coefficients are equal, or nearly so.

$$E_{1/2(1)} - E_{1/2(2)} = E_1^\circ - E_2^\circ$$

The difference in half-wave potentials for a given quinone and a sulfur-substituted hydroquinone can be used to calculate the required equilibrium constant (eq 4) at 25°. The equilibrium constants are listed in

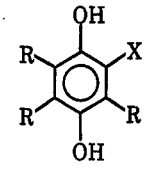
$$E_{1/2(1)} - E_{1/2(2)} = 2.303\,RT/nF \log K \quad (4)$$

$$\log K = \frac{(2)(\Delta E_{1/2})}{59} \quad (5)$$

Table III. The position of the cross-oxidation equilibrium (eq 5) lies to the right when K is greater than unity and to the left when it is less than unity.

TABLE III

EQUILIBRIUM CONSTANTS FOR THE OXIDATION OF SUBSTITUTED HYDROQUINONES BY THE CORRESPONDING UNSUBSTITUTED 1,4-BENZOQUINONE[a]



R	K X = SC_6H_4Me-p	$K \times 10^6$ X = SO_2Ph	K X = PMT
H	9.5	4	0.035
2-Me	19.5	20	
3-Me	6.0		
2,3-Me_2	17.8	10	0.14
2,5-Me_2	0.57	160	0.21
3,5-Me_2	0.68	76	
2,3,5-Me_3	0.57	17	0.076

[a] pH = 5.37, I = 0.090, t = 24 ± 2°.

Discussion

Zuman and his collaborators have shown the utility of linear free-energy relationships of the Hammett type in the correlation and discussion of electrochemical data.[1] The linear plot of the $E_{1/2}$ against the summation of Hammett σ para constants illustrates the additive effect of methyl groups on the reversible thermodynamic half-wave potentials of methyl-substituted 1,4-benzoquinones.[1,11]

We observed a linear shift in $E_{1/2}$ with $\Sigma\sigma_{p\text{-Me}}$, for the methyl-substituted hydroquinone sulfones and PMT derivatives but not for the methyl-substituted quinone or hydroquinone sulfides. The results are plotted in Figure 1. The plot shows that the addition of methyl groups to the sulfides gives a linear shift in $E_{1/2}$ to more negative values until the sulfide substituent is flanked by a methyl group. The potentials of all the quinones or hydroquinones containing methyls and sulfide substituents in vicinal positions are shifted to more positive potentials than expected from the predicted polar effect of added methyls. This gives an abrupt displacement of the plot of $E_{1/2}$ against $\Sigma\sigma_{p\text{-Me}}$ for added methyls, although the displaced plot continues with unchanged slope as still more methyl groups are added.

The occurrence of the break in the linear free-energy relationship (LFER) indicates that, when methyl and arylthio substituents occupy vicinal positions, they prevent the normal polar effect of one or both of the substituents from being exercised. Steric inhibition of a mesomeric effect is clearly indicated. The shift in the LFER plot to positive potentials means that the steric effect is making it easier to reduce the quinones containing vicinal substituents than would be expected if the steric effect were absent and the substituents could exert their normal inductive and mesomeric effects.

The failure of the LFER for the quinone and hydroquinone sulfides explains why the equilibrium constant for the cross-oxidation equilibrium (eq 2) is greater than unity in the absence of the steric effect and less than unity when the steric effect becomes important. As long as the $E_{1/2}$ for the sulfides is more negative than the $E_{1/2}$ for the corresponding quinone (with only methyl substituents), $\Delta E_{1/2}$ and log K of eq 5 are posi-

(11) P. Zuman, *Collect. Czech. Chem. Commun.*, **27**, 2035 (1962).

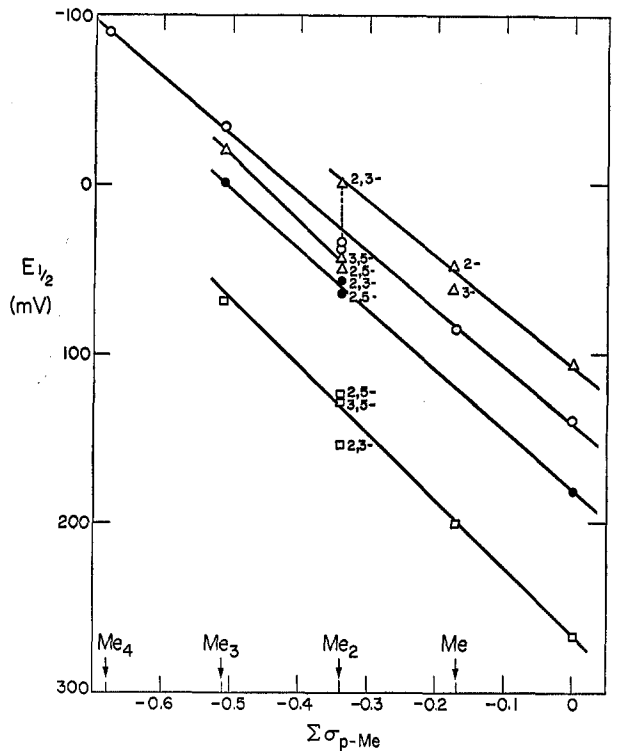


Figure 1.—Linear free-energy relationship of $E_{1/2}$ (*vs.* sce in 50% MeOH at pH 5.37) and $\Sigma\sigma_{p\text{-Me}}$ for various substituted quinone–hydroquinone couples: ○, Me substituents; △, Me and SC_6H_4Me-*p* substituents; □, Me and $PhSO_2$ substituents; ●, Me and PMT substituents.

tive. The incursion of the steric effect changes the sign of $\Delta E_{1/2}$ and log K to slightly negative values.

The failure to find any significant departure from additivity of methyl substituents flanked by phenylsulfonyl and PMT substituents is significant. The fact that the LFER plots for these two classes of redox couples fall at more positive potentials than the corresponding plot for the methyl quinones shows that the $PhSO_2^-$ and PMT groups are electron withdrawing. The σ constant for the *p*-tolylsulfonyl group was estimated by Zuman to be +0.56.[1,11] The polar effect of these two substituents must be almost entirely inductive. It does not seem reasonable that the steric effect of vicinal methyls and arylsulfonyl or PMT groups should be absent in these series of quinones and hydroquinones and present in the sulfides. It is more reasonable to conclude that the steric effect is present in each series, but only results in a shift in the half-wave potential when the steric effect can interfere with a mesomeric effect of a substituent that requires coplanarity with the aromatic or quinonoid ring.

This argument aids in establishing the nature of the steric effect of the vicinal substituents. The fact that successive additions of methyl groups result in more negative values of the $E_{1/2}$'s shows that the methyl groups are electron donating. Comparison of σ_p and σ_m constants for a methyl group[12] shows that much of the electron-donating effect is from hyperconjugation. If the steric effect involved the forcing of a vicinal methyl out of coplanarity with the ring, the steric effect should be seen as a break in the LFER plots for each series of methyl-substituted quinones and hydroquinones. Our results suggest that the steric interaction between vicinal substituents causes the bulkier substituent to be forced out of coplanarity with the ring. When the bulky substituent is an arylthio group, the electron-donating mesomeric effect is reduced. When the substituent is arylsulfonyl or PMT, the electron-withdrawing inductive effect is not reduced.

The substituent constant for the *p*-tolylthio, phenylsulfonyl, and PMT groups can be estimated by the modified Hammett equation (eq 6)[11] where $\Delta E_{1/2}$ is defined as in eq 4.

$$-\Delta E_{1/2} = \rho\sigma_{p\text{-X}} \qquad (6)$$

Using this relationship and our $E_{1/2}$ data, we calculate σ_p values of −0.10, +0.36, and +0.12, respectively, for *p*-tolylthio, phenylsulfonyl, and PMT substituents. The fact that $\Delta E_{1/2}$ for the *p*-tolylthio derivatives changes signs when steric hindrance is introduced shows that this substituent has a weakly electron-withdrawing inductive effect. We cannot estimate the magnitude of this effect without assuming that a vicinal methyl group completely suppresses the electron-donating mesomeric effect.

Figure 1 shows that the $E_{1/2}$ values for the 3-methylquinone sulfide and the 2,3-dimethylquinone sulfone deviate significantly from the LFER plots. Zuman has regarded such deviations as unimportant in correlating $E_{1/2}$ data from different laboratories. The deviations are, however, outside our experimental error and suggest that factors other than those discussed here can have small but significant effects on $E_{1/2}$ values of substituted quinones and hydroquinones.

Experimental Section

Polarographic and pH Measurements.—Dc polarograms were obtained using conventional equipment.[8] In selected cases ac polarograms were also determined using phase-sensitive detection of the resistive component of the ac current.[13] Instrumental compensation of the cell resistance was also employed.[14] The solvent system was selected for easy comparison with half-wave potentials reported in the literature[6] and to accommodate the rather low solubility of the compounds studied.

The buffer in 50% aqueous methanol (by weight) used for standardizing the pH meter was 0.05 M each in HOAc, NaOAc, and NaCl and had a pH value of 5.493.[9] The chemicals were Eastman or Baker and Adamson Reagent Grade.

Most solutions of quinones and hydroquinones for polarography were prepared in deaerated methanol at a concentration of 10^{-3} M. The methanol solution (5 ml) was diluted with 45 ml of deaerated 44.5% aqueous methanol that was 0.100 M in glacial acetic acid and 0.100 M in sodium acetate. It was shown that no observable volume change occurred in this dilution. Half-wave potentials of solutions of selected quinones and hydroquinones or equimolar mixtures of the couple were also determined at concentrations of 10, 2.5, 2.0, and 1.25×10^{-4} M and gave identical $E_{1/2}$ values.

Preparation and Purification of Quinones and Hydroquinones.—Most of the methylquinones and hydroquinones were commercially available and were recrystallized and/or sublimed to the literature melting points. Reduction of quinones with zinc and acetic acid or oxidation of hydroquinones with ferric chloride by well-established procedures provided the rest of the compounds.[5]

The *p*-tolyl sulfides[5] and phenyl sulfones[3] were prepared by published methods and gave combustion analyses within ±0.3%

(12) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N.Y., 1964, pp 410–411.

(13) D. E. Smith, *Anal. Chem.*, **35**, 1811 (1963).

(14) E. R. Brown, T. G. McCord, D. E. Smith, and D. D. DeFord, *ibid.*, **38**, 1119 (1966).

of the calculated values. The PMT-substituted compounds were generously provided by Dr. J. W. Gates, Jr.[7,15]

The position of substitution in the 2-methyl-1,4-benzoquinone addition of *p*-toluenethiol, benzenesulfinate, and HPMT was established by the characteristic nmr pattern, as previously described for the PMT derivative.[15]

We found that the easily oxidized *p*-tolyl hydroquinone sulfides could be recrystallized by solution in a very small volume of chloroform followed by the addition of a large excess of ligroin (63–75°).

(15) H. S. Wilgus III, E. Frauenglass, E. T. Jones, R. F. Porter, and J. W. Gates, Jr., *J. Org. Chem.*, **29**, 594 (1964).

Acknowledgment.—We wish to express our appreciation to Dr. T. H. Regan for the nmr spectra and Mr. D. F. Ketchum for the microanalyses. Mr. G. J. Brien assisted by making several of the electrochemical determinations.

The Condensation of Acetone with Methylcyclopentadiene. The Use of Tetracyanoethylene Adducts for Structure Proofs

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Received March 3, 1971

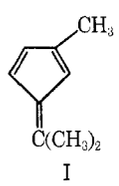
The condensation of methylcyclopentadiene with acetone has been shown to yield 2,6,6-trimethylfulvene as the major product. The structure of the molecule was established uniquely by the nmr spectrum of the tetracyanoethylene adduct. The spectra of several other TCNE adducts were analyzed and found to provide a convenient method for structure assessment of cyclic dienes.

The chemical shift assignments of the ring protons in 6,6-dimethylfulvene are open to question since they are based mainly on arguments regarding long-range couplings between the exocyclic methyls and the ring protons.[2] In an effort to clarify this issue we became interested in preparing the ring-methylated derivatives of 6,6-dimethylfulvene. While the initial goal was not achieved using these compounds as will become evident, the proof of structure of the condensation products proved an interesting exercise.[3]

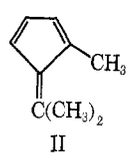
Results and Discussion

The reaction of methylcyclopentadiene with acetone was carried out by the method of Crane, Boord, and Henne.[4] The complex reaction product was fractionated by vpc and gave two compounds which had the proper nmr spectra and mass spectra for trimethylfulvenes. The major isomer was eluted first and was formed in about three times the amount of the minor. The total yield of both was estimated as 40–50% of the starting methylcyclopentadiene by the vpc analysis.

The condensation of acetone with methylcyclopentadiene most reasonably may lead to either I, II, or both. The nmr spectra of both products were made extremely complex by long-range couplings to all methyls on the part of the ring protons. Furthermore, the methyl groups had such similar chemical shifts that no selective decoupling of the methyl protons could be carried out. However, decoupling of all methyl protons gave typical ABC patterns for both major and minor isomers. The major isomer (CCl_4) gave $J_{AB} = 5.2$, $J_{AC} = 1.8$, $J_{BC} = 2.1$ Hz and δ (ppm) 6.00, 6.14, and 6.31, respectively.[5] The minor isomer essentially gave the same coupling constants with chemical shifts at δ 5.99, 6.09, and 6.24, respectively.[5] Consideration of typical fulvene nmr parameters[2] allows no decision between I and II.

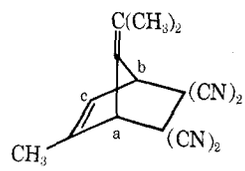


I

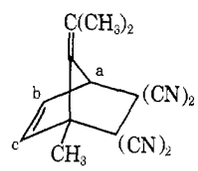


II

Subsequently the major isomer was allowed to react with tetracyanoethylene, and the product was analyzed. Again, the likely structures are III or IV. The TCNE adduct of the major fulvene isomer showed only one olefinic proton but two bridgehead protons, thus ruling in favor of III *vs.* IV and confirming the structure of the major isomer as I. The TCNE adduct of the minor isomer gave an extremely complex nmr spectrum which suggested that polymerization or decomposition had occurred. The minor isomer is tentatively assigned the structure II on the basis of its mass spectrum and nmr evidence.



III



IV

Nmr Spectra of the TCNE Adducts.—The use of TCNE to derivatize dienes has been known for some years.[6] We have found the use of perdeuterioacetonitrile to be particularly convenient as a solvent for these systems and often prepared them *in situ* in the nmr tube.

(1) Taken in part from the Senior Honors paper of S. Biesemeier.

(2) (a) W. B. Smith and B. A. Shoulders, *J. Amer. Chem. Soc.*, **86**, 3118 (1964); (b) M. L. Heffernan and A. J. Jones, *Aust. J. Chem.*, **19**, 1813 (1966).

(3) We have recently arrived at a satisfactory solution to this problem by spin decoupling experiments on 2-(dimethylmethylol)-6,6-dimethylfulvene: W. B. Smith and C. Gonzalez, *J. Org. Chem.*, **28**, 3541 (1963). When the 6,6-dimethyl protons are decoupled, the three ring protons form an ABC pattern which was analyzed to give $J_{13} = 1.73$, $J_{14} = 2.29$, $J_{34} = 5.43$ Hz, and δ_1 (CCl_4) 6.15, δ_3 6.51, δ_4 6.45. The fact that on decoupling only the lines associated with one proton sharpen confirms that long-range coupling of the exocyclic methyls in dimethylfulvene is stronger to H-2 and H-3 than to the nearer H-1 and H-4 in agreement with ref 2b.

(4) G. Crane, E. Boord, and A. L. Henne, *ibid.*, **67**, 1237 (1945).

(5) The results were obtained by J. L. Roark of these laboratories to whom we express our appreciation.

(6) W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Amer. Chem. Soc.*, **80**, 2783 (1958).