148–151°,, neutralization equivalent 102, 0.168 g., 17% yield of methylphenylmalonic acid.

(2) A suspension of 1.17 g. of VII in 2.42 g. of the amine was allowed to stand for 5 days and was then treated with acid and ether. The ether solution led to an oil, 1.014 g., apparently acidic to bicarbonate from which was obtained the di-acid, 0.296 g., 30%, m.p. 146–149° dec.

Infrared Absorption Spectra.—Spectra were determined in 1% solution in chloroform on a Perkin–Elmer model 21 double beam spectrophotometer. One spectrum, #14, below, was obtained in potassium bromide pellet; all units are micron.

(1) Isopropylidene malonate: 2.83(w), 3.42(w), 5.40-(shoulder), 5.55–5.70(s), 5.75(shoulder), 5.94(shoulder), 6.38(w), 6.85(w), 7.20(s), 7.40(s), 7.58–7.77(s), 9.28(s), 9.89(s), 10.28(s) 10.52(m), 11.17(w), 11.94(s).

(2) Isopropylidene phenylmalonate: 2.84(w), 5.58(s), 5.70(s), 6.67(w), 6.87(w), 7.16(m), 7.22(m), 7.44(m), 7.63–7.72(s), 9.10(w), 9.28–9.31(m), 9.88–9.91(m), 10.90-(w), 11.30(m), 11.55(w).

(3) Isopropylidene ethylphenylmalonate: 2.88(w), 3.42(w), 5.62(s), 5.75(s), 6.43(w), 6.70(w), 6.85(shoulder), 6.90(m), 7.19(m), 7.24(m), 7.50(s), 7.78–7.85(s), 9.07(w), 9.28(m), 9.37(ms), 10.05(ms), 10.53(w), 10.97(m), 11.25(w).

(4) Isopropylidene methylphenylmalonate: 2.87(w), 3.41(w), 5.61(s), 5.73(s), 6.24(w), 6.68(m), 6.90(m), 7.18(m), 7.25(s), 7.71(s), 9.07(m), 9.40–9.50(s), 10.07(m), 10.23(s), 11.48(w).

(5) Cyclopentylidene methylphenylmalonate: 3.38(w), 5.60(s), 5.73(s), 6.23(w), 6.72(w), 6.89(m), 7.24(ms), 7.44(s), 7.72(s), 8.93(s), 9.27(w), 9.42(w), 9.98(s), 10.41(w), 11.46(w).

(6) β-Phenylglutaric anhydride: 2.82(w), 3.25–3.37(w), 3.45(w), 5.49(s), 5.64(s), 6.23(w), 6.67(w), 6.87(w), 7.08(w), 7.28(w), 7.52(w), 7.85(w), 8.58(m), 9.05(m), 9.32–9.39(s), 10.52(s).

(7) Diethyl ethylphenylmalonate: 3.38(m), 4.18(w), 5.72(shoulder), 5.76–5.81(s), 5.90(shoulder), 6.23(w), 6.30(w), 6.67(m), 6.82(m), 6.91(m), 7.20(m), 7.30(m), 7.50(w), 7.67(s), 8.05–8.48(s), 8.89(s), 9.13(s), 9.77(s), 10.40(w), 10.70(w), 10.83(w), 11.67(m), 12.23(w).

(8) Methylene diacetate: 2.83(w), 3.35(w), 4.87(w), 5.63–5.69(s), 6.87(m), 7.07(m), 7.28(s), 8.00–8.45(m), 9.85–9.90(s), 10.15(s).

(9) Methyl hydrogen ethylphenylmalonate: 2.88(w), 3.39(m), 5.68(s), 5.76(s), 5.92(s), 6.25(w), 6.68(w), 6.95–7.00(m), 7.10–7.77(m), 7.52(m), 7.61(m), 8.25–8.42(s), 8.80(m), 9.95–10.02(w), 10.85–10.90(w).

(10) Isopropyl hydrogen ethylphenylmalonate: 2.87(w), 3.42(m), 5.69(s), 5.81(s), 5.96(s). 6.26(w), 7.11–7.16(m), 7.22(m), 7.28(m), 7.39(m), 7.62(m), 8.00–8.43(m), 8.77(m), 9.12(s).

(11) Methyl hydrogen methylphenylmalonate: 2.88(w), 3.41(w), 5.66(shoulder), 5.75–5.79(s), 5.89, 5.92(shoulder), 6.25(w), 6.70(w), 6.87(w), 6.92–7.00(m), 7.17(w), 7.30(w), 7.90–8.45(s), 8.95(s), 9.34(w), 9.74(w), 10.26(w).

(12) *l*-Menthyl β-phenylglutarate,[3] m.p. 107–109°: 2.88-(w), 3.44(m), 5.81(s), 6.23(w), 6.70(w), 6.87(m), 7.29(m), 7.89(m), 8.73(m), 9.24(w), 9.30(w), 9.65(w), 9.95(w), 10.17(m), 10.40(w), 11.00(w).

(13) N-Benzyl hydrogen methylphenylmalonamide: 2.92(w), 3.44(w), 3.78(w), 5.11(w), 5.71(s), 5.98(m), 6.14(s), 6.60(m), 6.90–6.98(s), 7.25(w), 7.35(w), 7.95–8.45(w). 8.75–8.95(w), 9.25(w), 9.32(w), 9.73(w).

(14) Methyl N-benzyl methylphenylmalonamide: 3.01-(s), 3.27(m), 3.33(m), 3.39(m), 5.10(w), 5.27(w), 5.75(s). 6.07(s), 6.23(m), 6.29(m), 6.49(s), 6.66(s), 6.86(m), 6.91-(m), 6.97(m), 7.03(m), 7.21(m), 7.33(m), 7.86(s), 8.06(s), 8.36(m), 8.80(m), 8.92(s), 9.02(m), 9.28(m), 9.36(m). 9.70(m), 10.00(m), 10.26(m), 10.92(w), 11.41(m), 11.80(w), 12.15(w), 12.45(w), 13.27(m), 13.57(m), 13.72(m), 14.30(s).

(15) N-Benzyl hydrogen methylphenylmalonamide: 2.93(w), 3.44(w), 3.75(w), 5.11(w), 5.30(w), 5.71(s). 5.93(m), 6.14(s), 6.61(m), 6.93(s), 7.35(w), 8.00–8.45(w), 8.75–8.95(w), 9.25(w), 9.33(w), 9.73(w).

(16) Methyl ethylphenylmalonanilide: 3.03(m), 3.40(w), 5.14(w), 5.35(w), 5.81(s), 5.91(m), 6.23(s), 6.50(s), 6.66-(m), 6.93(s), 7.23(w), 7.60(m), 8.02–8.40(m), 8.81(s), 9.26(w), 9.96(w), 10.13(w), 11.11(w), 11.51(w).

Acknowledgment.—We are pleased to acknowledge generous support of this work by the Division of Research Grants, National Institutes of Health, by a Frederick Gardner Cottrell Grant of Research Corporation, and (for P.J.S.) a travel allowance from the Honolulu Community Foundation.

WALTHAM 54, MASS.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA AND DREXEL INSTITUTE OF TECHNOLOGY]

The Effect of *m*-Dichloro and *m*-Dibromo Groups on the Dissociation and Ultraviolet Spectra of *p*-Dimethylsulfoniophenols

BY SHIGERU OAE AND CHARLES C. PRICE

RECEIVED MARCH 21, 1958

The incorporation of two chlorine or bromine atoms *ortho* to the dimethylsulfonio group in *p*-dimethylsulfoniophenol seems to cause only additive effects on pK_a and ultraviolet spectra. This indicates that the interaction between the sulfonio group and the phenol function is not sensitive to steric factors at the former.

There have been many reports of the conjugative ability of sulfone,[1] sulfonic acid,[2] sulfoxide[3] thiosulfonate[4] and sulfonio groups[5] and it has become a well-established fact that a sulfur atom may stabilize unshared electrons on an adjacent carbon atom, perhaps in part through conjugation using its *d*-orbital.

---

(1) (a) E. P. Kohler and H. Potter, THIS JOURNAL, **57**, 1316 (1935); (b) F. G. Bordwell and W. H. McKellin, *ibid.*, **72**, 1985 (1950); (c) R. H. Eastman and R. M. Wagner, *ibid.*, **71**, 4089 (1949); (d) H. Heymann, *ibid.*, **71**, 260 (1949); (e) A. Kotch, L. H. Krol, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **71**, 108 (1952); (f) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952); (g) H. Kloosterziel and H. J. Backer, *Rec. trav. chim.*, **71**, 295 (1952); (h) H. H. Szmant and G. Suld, THIS JOURNAL, **78**, 3400 (1956); (i) C. C. Price and J. J. Hydock, *ibid.*, **74**, 1043 (1952); (j) F. G. Bordwell and H. M. Anderson, *ibid.*, **75**, 6019 (1953); (k) E. A. Fehnel and M. Carmack, *ibid.*, **71**, 231 (1949); **72**, 1292 (1950); (l) H. P. Koch, *J. Chem. Soc.*, 2892 (1950); (m) W. v. E. Doering and L. K. Levy, THIS JOURNAL, **77**, 509 (1955); (n) S. Oae, *Bull. Chem. Soc., Japan*, **28**, 41 (1955); (o) H. Kloosterziel and H. J. Backer, *Rec. trav. chim.*, **72**, 185 (1953); (p) J. Toussaint, *Bull. Soc. Chim. Belg.*, **54**, 319 (1945) (*C. A.*, **41**, 2297 (1947)).

(2) (a) H. Zollinger and W. Buchler, *Helv. Chim. Acta*, **36**, 1711 (1953); (b) E. E. Sagar, M. R. Schooley, H. S. Carr and S. F. Acree, *J. Research Natl. Bur. Standards*, **35**, 521 (1945); (c) K. B. Whetsel, G. E. Hawkins and F. E. Johnson, THIS JOURNAL, **78**, 3360 (1956).

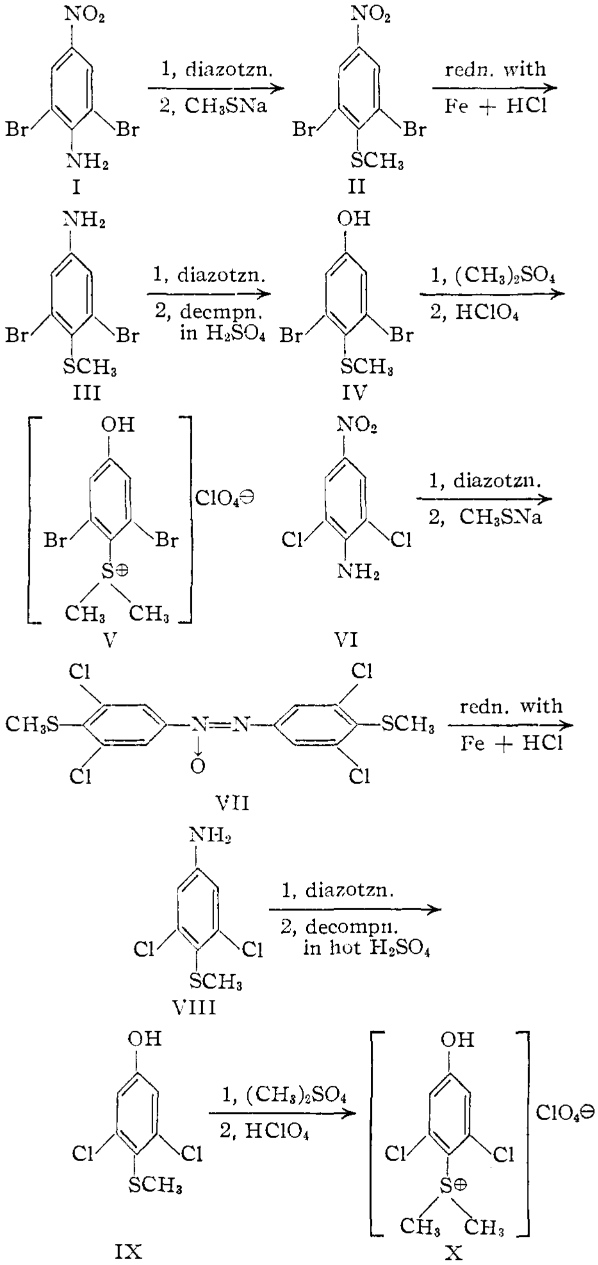
(3) (a) F. G. Bordwell and P. J. Boutan, *ibid.*, **79**, 717 (1957); (b) G. Leandri, A. Mangini and R. Passerini, *J. Chem. Soc.*, 1386 (1957); (c) E. D. Amstutz, J. M. Hunsberger and J. J. Chessick, THIS JOURNAL, **73**, 1220 (1951).

(4) G. Leandri, A. Mangini and A. Tundo, *J. Chem. Soc.*, 52 (1957).

(5) (a) F. G. Bordwell and P. J. Boutan, THIS JOURNAL, **78**, 87 (1956); (b) S. Oae and C. C. Price, *ibid.*, **80**, 3425 (1958); (c) W. v. E. Doering and K. C. Schreiber, *ibid.*, **77**, 514 (1955); (d) W. v. E. Doering and K. Hoffman, *ibid.*, **77**, 521 (1955).

Many reports concerning the nature of the angular requirement for p,d-overlap of C–S bond for resonance,[1k,1m,1o,1p,5b,5d,5e,6] seem to indicate that there is little angular requirement for p,d-overlapping.

In a previous communication,[5b] we have shown that a methyl group adjacent to a dimethylsulfonio group *meta* or *para* in phenol, has relatively little effect on the nature of the dissociation of the phenol or of its ultraviolet spectra. We now wish to report an extension to *m*-dichloro- and *m*-dibromo-substituted *p*-dimethylsulfoniophenol, for which we have measured both dissociation constants and ultraviolet spectra. 3,5-Dibromo- and 3,5-dichloro-4-dimethylsulfoniophenols were made according to the scheme shown.



Experimental

2,6-Dibromo-4-nitrophenyl Methyl Sulfide (II).—2,6-Dibromo-4-nitroaniline (I)[7] (70 g.) was diazotized according to the procedure developed by Schoutissen,[8] using 280 ml. of concentrated sulfuric acid, 23 g. of sodium nitrite and 200 ml. of 85% phosphoric acid. The diazotized solution was poured onto 2 kg. of ice and excess nitrous acid was decomposed by adding 25 g. of urea.

Methyl mercaptan, 100 g., was dissolved with cooling in 1.5 l. of alkali containing 920 g. of sodium hydroxide. Into this solution, the above diazotized solution was added dropwise with vigorous stirring and cooling to 10°. Vigorous reaction occurred as soon as the dropping started, giving a heavy yellow precipitate. After the addition was over, the mixture was heated to 90°, then acidified with hydrochloric acid. While the mixture was still very hot, the yellow precipitate was collected, washed and dried. The crude product weighed 68 g., yield 88.3%. Recrystallization from benzene gave yellow prisms, m.p. 204–206°.

Anal. Calcd. for $C_7H_5O_2SBr_2N$: C, 25.53; H, 1.51; S, 9.70. Found: C, 25.03; H, 1.91; S, 10.10.

2,6-Dibromo-4-aminophenyl Methyl Sulfide.—To 20 g. of 2,6-dibromo-4-nitrophenyl methyl sulfide, dissolved in 400 ml. of dioxane, was added 35 g. of iron. While refluxing gently and stirring, 180 ml. of concentrated hydrochloric acid was added in six hours. One-half of the dioxane was removed by distillation, the residue was diluted in 4 l. of ice-water. The precipitate was collected and recrystallized from dilute hydrochloric acid. Pale brown crystals, 10 g., were obtained; yield 55%. Recrystallization from petroleum ether gave crystalline needles, m.p. 100–101°.

Anal. Calcd. for $C_7H_7SBr_2N$: C, 28.11; H, 2.36; Br, 54.45; S, 10.72. Found: C, 28.46; H, 2.42; Br, 53.56; S, 11.41.

2,6-Dibromo-4-hydroxyphenyl Methyl Sulfide (IV).—2,6-Dibromo-4-aminophenylmethyl sulfide (7 g.) was added to a mixture of 140 ml. of concentrated sulfuric acid and 20 g. of ice. With stirring and cooling in an ice–salt-bath, 3 g. of sodium nitrite was added portionwise, and stirring was maintained for 20 minutes. Then the diazotized yellow solution was poured onto 800 g. of ice and the excess nitrous acid was decomposed by adding 5 g. of urea. Into the well-stirred, boiling solution of the mixture of 100 ml. of sulfuric acid and 50 ml. of water, the above diazotized solution was dropped gradually, while keeping the mixture refluxing. The heavy oil was extracted with ether and the ether extract was dried over Drierite. After removing ether, distillation gave 3.5 g. of pale yellow crystals, b.p. 150° (1 mm.), yield 50%. Recrystallization from ligroin gave colorless crystals, m.p. 104–104.5°.

Anal. Calcd. for $C_7H_6SOBr_2$: C, 28.19; H, 2.01; Br, 53.69; S, 10.74. Found: C, 28.51; H, 2.08; Br, 52.62; S, 10.04.

2,6-Dibromo-4-hydroxyphenyldimethylsulfonium Perchlorate (V).—2,6-Dibromo-4-hydroxyphenyl methyl sulfide (1 g.) and 0.84 g. of dimethyl sulfate were mixed and sealed, and the tube was heated at 100° for 40 hours. The tube was broken and the contents were dissolved in 10 ml. of water. After adding 20 ml. of 70% perchloric acid, it was kept in the refrigerator overnight. The precipitated colorless crystals were collected, washed three times with ether, and then dried. The colorless crystals weighed 1 g.; yield 73%. This compound could be recrystallized from methanol–ether, giving colorless crystals decomposing at 215–217°.

Anal. Calcd. for $C_8H_9SO_5Br_2Cl$: C, 23.3; H, 2.2; S, 7.7; Cl + Br, 47.3. Found: C, 23.3; H, 2.4; S, 7.9; Cl + Br, 47.5.

An Attempt to Make 2,6-Dibromo-4-hydroxyphenyldimethylsulfonium Iodide.—2,6-Dibromo-4-hydroxyphenyl methyl sulfide (1 g.) was mixed with 0.5 g. of methyl iodide in a sealed tube and the sealed tube was heated at 100° for

---

[6] (a) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940); (b) W. E. Moffitt, *Proc. Roy. Soc.* (*London*), **A200**, 409 (1950); (c) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951); (d) P. Cohen-Fernandes, Doctor's Thesis at the Univ. of Leiden, May, 1957.

[7] C. Wurster and E. Nolting, *Ber.*, **7**, 1564 (1874).

[8] H. A. J. Schoutissen, THIS JOURNAL, **55**, 4531 (1933); see also "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 604.

24 hours. No reaction occurred and the starting material was recovered quantitatively.

2,2',6,6'-Tetrachloro-4,4'-dimethylmercapto-azoxybenzene (VII).—Eastman Kodak Co. C.P. 2,6-dichloro-4-nitroaniline (VI, 50 g.) was diazotized according to the procedure developed by Schoutissen,[8] using 280 ml. of concentrated sulfuric acid, 23 g. of sodium nitrite and 200 ml. of 85% phosphoric acid. The diazotized solution was poured onto 2 kg. of ice and excess nitrous acid was decomposed by adding 25 g. of urea.

Methyl mercaptan, 100 g., was dissolved with cooling in 1.5 l. of sodium hydroxide solution containing 920 g. of sodium hydroxide. Into this solution the above diazotized solution was added dropwise with vigorous stirring and cooling under 20°. Vigorous reaction occurred as usual, giving a heavy yellow precipitate. After the addition was over, the mixture was heated up to 90°, then acidified with hydrochloric acid. While the mixture was still hot, the yellow precipitate was collected, washed and dried. The crude product weighed 40 g., yield 83%. Recrystallization from dioxane gave yellow crystals, m.p. 166–166.5°. The infrared spectra had strong bands at 6.87 and 7.3 μ. Since these are close to the positions for the nitro group, perhaps they are characteristic of the azoxy group.

Anal. Calcd. for $C_{14}H_{10}S_2ON_2Cl_4$: C, 39.25; H, 2.33; N, 6.54; S, 14.95; Cl, 33.17. Found: C, 39.64; H, 2.60; N, 6.70; S, 14.37; Cl, 32.48.

2,6-Dichloro-4-aminophenyl Methyl Sulfide (VIII).—2,2',6,6'-Tetrachloro-4,4'-methylmercaptoazoxybenzene (XII, 9 g.) was dissolved in 200 ml. of dioxane, then 17 g. of reduced iron was added. With stirring and refluxing, 75 ml. of concentrated hydrochloric acid was added dropwise in 4 hours. After removing one-half of the solvent, the residue was poured into 3 l. of ice-water. The gray precipitate was collected, dried and recrystallized from dilute hydrochloric acid to give 5 g. of pale yellow crystals, m.p. 122°, yield 56%. Recrystallization from carbon tetrachloride gave colorless crystals, m.p. 124.5–125°.

Anal. Calcd. for $C_7H_7Cl_2NS$: C, 40.38; H, 3.37; N, 6.73. Found: C, 40.56; H, 3.37; N, 6.95.

2,6-Dichloro-4-hydroxyphenyl Methyl Sulfide (IX).—2,6-Dichloro-4-aminophenyl methyl sulfide (VIII, 7 g.) was diazotized as in the case of the dibromo analog, using 200 ml. of 50 volume % sulfuric acid and 3 g. of sodium nitrite. The diazotized solution was poured into 500 ml. of ice-water and excess nitrous acid was decomposed by urea. Then this solution was dropped gradually into 400 ml. of boiling 25% sulfuric acid. The mixture was extracted with ether, the ether was removed and the residue was distilled in vacuum to yield 1.5 g., b.p. 120–130° (0.5 mm.), yield 22%. It solidified and the crude material melted at about 93°. Recrystallization from petroleum ether gave colorless prisms, m.p. 96–97°.

Anal. Calcd. for $C_7H_6Cl_2SN$: C, 40.22; H, 2.89; Cl, 33.93. Found: C, 40.32; H, 3.31; Cl, 34.49.

2,6-Dichloro-4-hydroxyphenyldimethylsulfonium Perchlorate (V).—2,6-Dichloro-4-hydroxyphenyl methyl sulfide, 0.4 g., and 0.5 g. of dimethyl sulfate were mixed, sealed in an ampoule and heated at 100° for 40 hours. The mixture was dissolved in 25 ml. of water then 20 ml. of 70% perchloric acid was added. After standing 3 days in a refrigerator, the colorless crystals were collected; yield 0.4 g. (63%). Recrystallization from a methanol–ether mixture gave colorless crystals decomposing at 200°.

Anal. Calcd. for $C_8H_9SO_5Cl_3$: C, 29.68; H, 2.78; Cl, 32.89. Found: C, 29.68; H, 3.19; Cl, 32.35.

Hydroxyphenyldimethylsulfonium Perchlorate.—Hydroxyphenyl methyl sulfide, 1.4 g., and 2.6 g. of dimethyl sulfate were mixed in a sealed tube and heated at 100° for two hours. The mixture was poured into 50 ml. of water and 40 ml. of 70% perchloric acid was added. After three days in a refrigerator, colorless crystals (2.6 g.) were obtained in almost quantitative yield, m.p. 153–154°.

Anal. Calcd. for $C_8H_{11}ClSO_4$: C, 37.72; H, 4.32. Found: C, 38.27; H, 4.60.

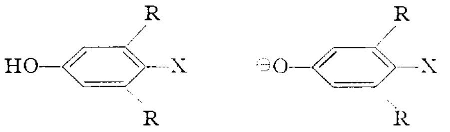
3,5-Dichlorophenol and 3,5-dibromophenol were prepared by conventional methods[9] and both compounds were recrystallized from ligroin. The resulting snow white crystals of m.p. 68 and 81°, respectively, were used for the experiments.

Acidity Constant Measurements.—The acidity constants of the substituted phenols were determined potentiometrically with a Beckman glass electrode *p*H meter, model H2, standardized against Beckman buffers, as in the previous case[5b] and were computed in the same way as before.[5b]

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra of the substituted phenols were measured in the same ways as before[5b] and the results are listed in Table I.

TABLE I

PRIMARY (λ) AND SECONDARY (λ') ULTRAVIOLET ABSORPTION BANDS (mμ), IN ETHANOL



R	X	λ_{max} (log ϵ)	λ'_{max} (log ϵ)	λ_{max} (log ϵ)	λ'_{max} (log ϵ)
H	H[10]	210.5(3.79)	270(3.16)	235(3.97)	287(3.41)
Cl	H	220(3.86)	278(3.23)	246(3.77)	296(3.47)
Br	H	218(4.02)	280(3.33)	242(3.72)	298(3.51)
H	$SMe_2^{\oplus}$ $ClO_4^{\ominus}$	241(4.01)	266(3.70)[a]	269(4.21)	....
Cl	$SMe_2^{\oplus}$ $ClO_4^{\ominus}$	257(4.04)	292(3.20)[c]	285(4.18)[b]	....
Br	$SMe^{\oplus}$ $ClO_4^{\ominus}$	259(3.85)	293(3.30)[e]	287(4.14)[d]	....

[a] There are additional peaks at 204(4.19) and 330(2.70). [b] There is a sharp peak at 215(4.16) and a shoulder at 230-(4.09). [c] Determined with added HCl to suppress dissociation; there were additional peaks at 218(4.40), 284(3.44), 372(2.79). [d] There is a sharp peak at 219(4.25) and a shoulder at 231(4.17). [e] Determined with HCl added to suppress ionization; there were additional peaks at 218-(4.43), 284(3.44).

The calculations of σ-values from acid dissociation constants were made using log K_0 and ρ of phenol as -9.95 and 2.29, respectively. The values are listed in Table II, together with the acid dissociation constant.

TABLE II

ACID DISSOCIATION CONSTANTS AND σ-CONSTANTS

Phenol	*p*Ka	σ(obsd.)	$\Sigma\sigma$(calcd.)[a]
3,3-Dibromo-	8.01	0.85	0.78[b]
3,5-Dichloro-	8.13	0.79	0.75[b]
p-Dimethylsulfonio-	7.23	1.19	
3,5-Dibromo-*p*-dimethylsulfonio-	5.30	2.03	2.04
3,5-Dichloro-*p*-dimethylsulfonio-	5.41	1.98	1.98

[a] Assuming additivity. [b] Using 2 × σ_m, according to H. H. Jaffé, *Chem. Revs.*, **53**, 222 (1953).

Discussion

The σ-constant data in Table I indicate very clearly that two dichloro or dibromo groups exert no apparent steric inhibition of the effect of the *p*-dimethylsulfonio group on the dissociation of phenol. Stuart molecular models of both the dichloro- and dibromo compounds show that these two *ortho* substituents block the free rotation of sulfonio group and the two methyl groups of the dimethylsulfonio group have no chance of coming into the same plane with the benzene ring. Nevertheless, the sulfur group seems to function as an electron sink for a mesomeric shift through its conjugative ability.

Recently, however, Wepster has shown through ultraviolet spectra data that even one *o*-methyl is more effective in blocking coplanarity of the dimethylamino group than two *o*-iodo groups.[11]

---

(9) H. H. Hodgson and J. S. Wignall, *J. Chem. Soc.*, 2217 (1927).

(10) L. Daub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947).

(11) B. M. Wepster, *Rec. trav. chim.*, **76**, 335, 357 (1957).

If it can be applied equally to the dimethylsulfonio group, then smaller groups such as dibromo and dichloro groups would be certainly less effective in blocking coplanarity of the particular group, even though Stuart models definitely indicate effective hindrance by dibromo groups. This would at least be in accord with our observation that, whereas two *o*-chlorine or bromine atoms have no influence on the acidifying effect of the *p*-dimethylsulfonic group in phenol, one *o*-methyl group[5b] had a definite if small influence in diminishing conjugation.

The ultraviolet spectra of both 3,5-dihalo-4-dimethylsulfoniophenols in neutral solution are the same as those in alkaline solution. Since both phenols are quite strong acids even in neutral solution they evidently dissociate to an appreciable extent, giving the absorption bands characteristic of phenolate. This dissociation was suppressed by addition of hydrochloric acid.

PHILADELPHIA 4, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF GENERAL CHEMISTRY OF THE UNIVERSITY OF ROME]

The ρ–σ^+ Treatment for the Bromination of Substituted Polymethylbenzenes. The Kinetic Effect of the Cyano Group[1]

BY GABRIELLO ILLUMINATI

RECEIVED JANUARY 14, 1958

The relative bromination rates of fluorobromomesitylene, cyanomesitylene and cyanodurene have been measured in nitromethane solution at 30°. A least square value of −8.690 for the reaction constant has been calculated from most *meta* reactivity data available for the present approach. Substituent σ_p^+ constants have then been evaluated and found to be in excellent agreement with Brown and Okamoto's constants. Surprisingly, a discrepancy is observed for the *m*-cyano group. The present data indicate similar values for the σ_m^+ and σ_p^+ constants of the cyano group: the possible link of such data with the orienting effect of this group in bromination with Br_2 is discussed.

In a previous paper,[2] we have shown that the electrical effects of halogens in such overcrowded molecules as halo tri- and tetramethylbenzenes are transmitted to a *meta* or *para* reaction center, on nuclear attack by molecular bromine, without appreciable steric disturbances. Furthermore, anticipation of some of Brown and Okamoto's results on their stimulating ρ–σ^+ treatment[3] of aromatic substitution permitted a preliminary test, which turned out to be quite successful, of the σ^+ constants on our data and a graphical estimation of the reaction constant for bromination.

Our studies on the orientation effects of substituents by what it may be called, for brevity, the "polymethylbenzene approach" to the problem may be considered valuable in the following ways: (1) in the determination of the electrical effects of *m*- and *p*-substituents causing negligible steric interaction; and (2) in the estimation of steric effects in the case of substituents susceptible to deviation from co-planarity with the benzene ring and/or provided with much too large effective sizes.

We wish to treat the first point in this paper by extending the investigations to fluorobromomesitylene, cyanomesitylene and cyanodurene and by broadening the reactivity range from *p*-methyl[4] to Σ(*m*-F, *m*-Br).

Substituents expected to give rise to steric effects, such as the *p*-nitro and *p*-methoxy groups, because of their lower symmetry, will be dealt with in subsequent papers.[5]

Results

Since the reactivities relative to the parent hydrocarbon in the two *m*-polymethylbenzene series, those of mesitylene and isodurene, correspond to each other within a small factor, the *m*-cyano group was only examined in the former series for convenience. The initial rates for cyano- and fluorobromomesitylene and cyanodurene were measured in 0.055 *M* nitromethane solution and the rates relative to durene (= 1000) calculated with the aid of chloromesitylene as the compound of intermediate reactivity. The new kinetic data are reported in Table I. The concentrations used in this work were made relatively high in order to compensate for the low reactivity of the compounds investigated, particularly cyanodurene. For the latter compound, autocatalytic phenomena began to appear as early as 10% changes or even less. Thus the extent of reaction used for the determination of the times at 10% reaction (t_{10}) was carefully chosen in each kinetic run and, whenever necessary, the t_{10} values were obtained by extrapolation (see Experimental). Residual superimposition of concurrent reactions might lead to an apparent relative reactivity (k/k_0) higher than the correct value by a supposedly small factor. Complications of this kind were not observed for cyano and fluorobromomesitylene, for which the reliability of the specific effects of the substituents involved finds a perfect correspondence in chlorination studies in acetic acid solution.[6]

---

[1] This paper is part VIII in the series "Substitution in Polymethylbenzenes"; preceding paper, G. Illuminati, *Nature*, **179**, 780 (1957).

[2] G. Illuminati and G. Marino, THIS JOURNAL, **78**, 4975 (1956).

[3] (a) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957); (b) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

[4] G. Illuminati, *Ric. Sci.*, **26**, 2752 (1956).

[5] For the *p*-methoxy group and other group VIb substituents, see G. Illuminati, THIS JOURNAL, **80**, 4945 (1958).

[6] E. Baciocchi and G. Illuminati, *Ric. Sci.*, **28**, 1159 (1958); part X.