[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DREXEL INSTITUTE OF TECHNOLOGY, PHILADELPHIA, PENNA.]

Steric Effects of *m*-Methyl Groups on the Conjugative Abilities of Thia, Sulfinyl and Sulfonio Functions in *p*-Substituted Phenols[1a]

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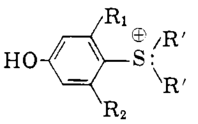
RECEIVED JUNE 25, 1959

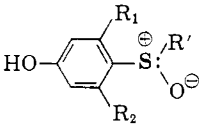
Several di- or polymethyl substituted derivatives of bis-(4-hydroxyphenyl) sulfides, sulfoxides and tris-(4-hydroxyphenyl)-sulfonium chlorides were prepared. Attempts to synthesize tris-(2,6-dimethyl-4-hydroxyphenyl)-sulfonium chloride led to the formation of either bis-(2,6-dimethyl-4-hydroxyphenyl) sulfide or sulfoxide. While methyl groups in the 3- and 5-positions of a 4-arylthio substituted phenol exhibit a significant effect on its *p*Ka value, a methyl group in the 3-position of a 4-diaryl-sulfonio substituted phenol or two methyl groups in the 3- and 5-positions of a 4-arylsulfinyl substituted phenol have relatively little effect on either *p*Ka values or ultraviolet spectra. The infrared spectra of substituted bis-(4-hydroxyphenyl) sulfoxides indicate rather strong intermolecular hydrogen bonding between the hydroxy and sulfoxide groups.

Numerous investigations concerning the nature of the electron pair accepting conjugative ability of the sulfone group have been reported. Evidence for resonance between the sulfone group and the double bond, where such resonance is presumed to involve vacant 3*d*-orbitals of the sulfur atom, has been deduced from dipole moments of various aliphatic and aromatic sulfones,[2] sulfonamides,[3] and sulfonyl chlorides,[4] dissociation constants of sulfonylphenols and sulfonylbenzoic acids,[5] ultraviolet spectra[6] and other properties.[7]

Earlier work (*i.e.*, studies of the dissociation constants and ultraviolet spectra of hindered sulfones[8] as well as theoretical considerations) has led to the conclusion that there is little angular requirement for *p-d* overlap of the C–S.[9]

In a study of the acid dissociation of 3-methyl-, 3,5-dichloro- and 3,5-dibromo-4-dimethylsulfoniophenols, we have shown that there is little or no steric effect on the electron-accepting resonance of the dimethylsulfonio group by these *o*-substituents.[10,11] It is interesting to note that Stuart molecular models of both the dichloro and the dibromo compounds show that these two *o*-substituents block free rotation of the sulfonio group and prevent the two methyl groups of the dimethylsulfonio group from coming into the plane of the benzene ring. However, the rather small steric effect of *o*-dichloro, as well as *o*-dibromo groups, found recently in the ultraviolet spectra of substituted dimethylanilines,[12] prompted us to prepare and study some more sterically hindered compounds of this type. This could be achieved either by introducing bulky substituents, R_1 and R_2, in the benzene ring or by making sulfonium salts having bulky groups, R′. We chose a system where R_1 was methyl and R_2 was either methyl or hydrogen while R′ was a substituted aryl group.





We have undertaken a similar study on the sulfoxide, using a similar approach.

The action of thionyl chloride on aromatic compounds has been known to give diaryl sulfoxides and triarylsulfonium chlorides in the presence of aluminum chloride.[13] It has been reported that the reaction between phenols and thionyl chloride gives bis(4-hydroxyphenyl) sulfides and tris-(4-hydroxyphenyl)-sulfonium chlorides as the main reaction products.[14] Thus, in one step, this reaction could give the desirable sulfoxides as well as sulfonium chlorides and sulfides. In the cases of *o*- and *m*-cresols, the reaction was successfully applied for the preparation of both sulfoxides and sulfonium chlorides. However, no noticeable amount of sulfonium chloride formation was observed in the case of 3,5-xylenol, under various experimental conditions, probably because of the instability of the resulting highly strained sulfonium ion.

Experimental

Diphenyl sulfoxide and di-*p*-anisyl sulfoxide were prepared by the same method employed by previous workers,[13] using benzene or anisole, thionyl chloride and aluminum chloride. Both were recrystallized from ethyl acetate. Colorless crystalline compounds, m.p. 70–71° for diphenyl sulfoxide and m.p. 93–94° for di-*p*-anisyl sulfoxide, were used.

Bis-(3,5-dimethyl-4-anisyl) sulfoxide was prepared by the same procedure,[13] using 60 ml. of 3,5-dimethylanisole, 10 g. of anhydrous aluminum chloride and 5 g. of thionyl chloride. The crude sulfoxide, 6 g., corresponding to about 45% yield, was recrystallized from ethyl acetate and colorless crystals, m.p. 153–154°, were analyzed.

Anal. Calcd. for $C_{18}H_{22}SO_3$: C, 67.92; H, 6.92. Found: C, 68.17; H, 7.05.

[1a] Presented at the 135th Meeting of the American Chemical Society, Boston, Mass., April 10, 1959, Abstracts of Papers, p. 88-O.

[1b] Radiation Center of Osaka Prefecture, Sakai, Osaka, Japan.

[2] C. W. N. Cumpa, G. H. Jefferey and S. Walker, *Trans. Faraday Soc.*, **52**, 193 (1956).

[3] E. N. Gur'yanova, *Zhur. Fiz. Khim.*, **21**, 633 (1947); *C. A.*, **42**, 2147 (1948).

[4] E. N. Gur'yanova, *Zhur. Fiz. Khim.*, **21**, 411 (1947); *C. A.*, **41**, 6786 (1947).

[5] (a) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952); (b) C. C. Price and J. J. Hydock, *ibid.*, **74**, 1043 (1952).

[6] (a) E. A. Fehnel and M. Carmack, *ibid.*, **71**, 231 (1949); (b) H. P. Koch, *J. Chem. Soc.*, 408 (1949); (c) G. Lendri, A. Mangini and R. Passerini, *Gazz. chim. ital.*, **84**, 73 (1954).

[7] See reference in previous papers[10,11] and also Chapter 2, in forthcoming book, "Sulfur Bonds," by C. C. Price and S. Oae, Ronald Press Co.

[8] (a) H. Kloosterziel and H. J. Baker, *Rec. trav. chim.*, **72**, 185 (1953); (b) W. v. E. Doering and L. K. Levy, THIS JOURNAL, **73**, 509 (1955); (c) E. A. Fehnel and M. Carmack, *ibid.*, **72**, 1291 (1950).

[9] (a) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940); (b) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

[10] S. Oae and C. C. Price, THIS JOURNAL, **80**, 3425 (1958).

[11] S. Oae and C. C. Price, *ibid.*, **80**, 4938 (1958).

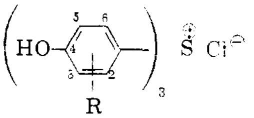
[12] B. M. Wepster, *Rec. trav. chim.*, **76**, 335, 357 (1957).

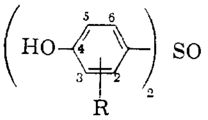
[13] (a) S. Smiles and R. L. Rossignol, *J. Chem. Soc.*, 745 (1908); (b) C. Courtat and P. Chiffert, *Compt. rend.*, **194**, 986 (1932).

[14] A. Lüttringhaus and K. Hauschild, *Ber.*, **72B**, 887 (1939).

TABLE I

TRIS-(4-HYDROXYPHENYL)-SULFONIUM CHLORIDE



Starting substance	R	Yield, %	M.p., °C.	Formula	Analyses, % Calcd. C	Calcd. H	Calcd. S	Found C	Found H	Found S
Phenol	H	65	266	$C_{18}H_{15}SO_3Cl$	62.24	4.32	9.22	62.41	4.54	9.09
o-Cresol	3-CH_3	65	246	$C_{21}H_{21}SO_3Cl$	64.88	5.40	8.22	64.71	5.86	8.18
m-Cresol	2-CH_3	25	260	$C_{21}H_{21}SO_3Cl$	64.88	5.40	8.22	64.19	5.64	8.64
3,5-Xylenol	2,6-DiCH_3									
BIS-(4·HYDROXYPHENYL) SULFOXIDE 										
Phenol	H	25	205	$C_{12}H_{10}SO_3$	61.54	4.27	13.67	61.73	4.40	13.62
o-Cresol	3-CH_3	35	199	$C_{14}H_{14}SO_3$	64.12	5.34	12.21	64.40	5.48	12.02
m-Cresol	2-CH_3	35	211	$C_{14}H_{14}SO_3$	64.12	5.34	12.21	64.15	5.69	12.03
3,5-Xylenol	2,6-DiCH_3	85	175	$C_{16}H_{18}SO_3$	66.20	6.21	11.03	66.14	6.30	10.85

Bis-(4-hydroxyphenyl) sulfide was prepared by a known procedure[15] involving the reaction of phenol and thionyl chloride in chloroform solution. The crude sulfide, obtained in 40% yield, was recrystallized repeatedly from ethanol; colorless needles, m.p. 150°, were obtained (Table I).

Bis-(4-hydroxy-3,5-xylenyl) sulfide was also prepared in the same way by adding 35 g. (0.85 mole) of thionyl chloride to 100 ml. of a well-cooled chloroform solution containing 100 g. of 3,5-xylenol (0.3 mole). After standing at room temperature for a few hours the deep green reaction mixture deposited white crystals of crude sulfide. This crude sulfide, 80 g., corresponding to a yield of 67%, was recrystallized from either dilute aqueous ethanol or chloroform; colorless crystals, m.p. 153°, were collected and used (Table II).

Anal. Calcd. for $C_{16}H_{18}O_2S$: C, 70.07; H, 6.57; S, 11.68. Found: C, 69.48; H, 6.63; S, 11.55.

General Method for the Preparation of Bis-(4-hydroxyphenyl) Sulfide and Tris-(4-hydroxyphenyl)-sulfonium Chloride and their Methyl Derivatives.—Ten grams of anhydrous aluminum chloride was added to 60 ml. of ice-cooled phenol with vigorous stirring. Then 0.5 g. of freshly distilled thionyl chloride was added dropwise during the course of 5 minutes. When the addition was complete, the reaction mixture was kept standing at room temperature for several hours, and was then decomposed by pouring it into about 200 ml. of ice-water. The mixture separated into two layers. Approximately 300 ml. of ether was added to the non-aqueous layer to precipitate crude tris-(4-hydroxyphenyl)-sulfonium chloride. The sulfonium salts thus obtained were collected and repeatedly recrystallized from an ethanol–ether mixture.

After the ether was evaporated from the mother liquor, the residue was steam distilled until no more phenol came over and the remaining material began to solidify. The solid residue, crude sulfoxide, was collected and repeatedly recrystallized from ethyl acetate.

In the case of 3,5-xylenol, the only compound isolated was the sulfoxide. Several unsuccessful attempts were made to synthesize the sulfonium chloride, either by varying the concentrations of the reactants or by changing the reaction conditions such as reaction time and heat. In all cases no compound corresponding to the sulfonium chloride could be isolated. The results obtained are given in Table I.

Acidity Constant Measurements.—The acidity constants of the substituted phenols were determined potentiometrically, as previously described,[10,11] using a Beckman glass electrode *p*H meter, model H-2, standardized against Beckman buffers. In the present investigation aqueous ethanol (38.9% by weight or 46.20% by volume) had to be used, since most of the phenols were sparingly soluble in water.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra of the substituted phenols were measured in the usual manner.[10,11] Due to the small solubilities of the substituted phenols in water, each compound was first dissolved in ethanol and the solution was then diluted with water to a constant ethanol concentration of 6% by volume.

Infrared Spectra.—The spectra of the substituted phenols were taken on a Perkin–Elmer model 21 auto-recording spectrophotometer. Potassium bromide disks, containing the compounds, were used.

Results and Discussion

Sulfides.—The first dissociation constants of the *p*-substituted mercaptophenols are summerized in Table II. The relatively large increase in acid strength of *p*-hydroxyphenylmercaptophenol (III) over *p*-methylmercaptophenol (II) can be ascribed to the increase in the electron-withdrawing inductive effect in going from methyl to *p*-hydroxyphenyl as well as to the decrease in the electron-donating resonance effect of the *p*-methylmercapto over the *p*-hydroxyphenylmercapto group because of the cross-conjugation in the latter compound. The large increase in acidity of bis-(4-hydroxy-2,6-dimethylphenyl) sulfide (IV) undoubtedly is due to the steric inhibition of the electron-releasing type of

TABLE II

FIRST DISSOCIATION CONSTANTS OF *p*-SUBSTITUTED SULFENYL(THIA), SULFINYL AND SULFONIO PHENOLS IN 38.9% (BY WEIGHT) OR 46.20% (BY VOLUME) OF AQUEOUS ETHANOL SOLUTION AT 25°

Compound	*p*Ka
Phenol (I)	10.59
Methylmercaptophenol (II)	10.49
Bis-(4-hydroxyphenyl) sulfide (III)	9.90
Bis-(4-hydroxy-2,6-dimethylphenyl) sulfide (IV)	9.13
Bis-(4-hydroxyphenyl) sulfoxide (V)	8.80
Bis-(2-methyl-4-hydroxyphenyl) sulfoxide (VI)	8.83
Bis-(3-methyl-4-hydroxyphenyl) sulfoxide (VII)	9.19
Bis-(4-hydroxy-2,6-dimethylphenyl) sulfoxide (VIII)	8.89
4-Hydroxyphenyldimethylsulfonium perchlorate (IX)	7.72
Tris-(4-hydroxyphenyl)-sulfonium chloride (X)	7.02
Tris-(3-methyl-4-hydroxyphenyl)-sulfonium chloride (XI)	7.39
Tris-(2-methyl-4-hydroxyphenyl)-sulfonium chloride (XII)	7.11

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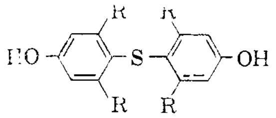
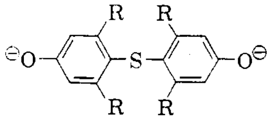
(15) P. Carre and D. Liebermann, *Compt. rend.*, **196**, 275 (1933).

TABLE III

PRIMARY (λ) AND SECONDARY (λ') ULTRAVIOLET ABSORPTION BANDS (mμ) IN 6% ETHANOL IN WATER SOLUTION





R	λ_{max} (log ε)	λ'_{max} (log ε)	λ_{max} (log ε)	λ'_{max} (log ε)
H	250.7 (4.20)	292.5 (3.83)	290 (3.80)	323 (3.30)
CH_3	261.0 (4.30)	....	301 (3.86)	....

TABLE IV

PRIMARY (λ) AND SECONDARY (λ') ULTRAVIOLET ABSORPTION BANDS (mμ) IN 6% AQUEOUS ETHANOL SOLUTION

	Absorption			
	In neutral solution		In alkaline solution[a]	
Compound, sulfoxide	λ_{max} (log ε)	λ'_{max} (log ε)	λ_{max} (log ε)	λ'_{max} (log ε)
Phenol	210.5 (3.79)	270 (3.16)	235 (3.97)	287 (3.41)
Diphenyl (XIII)	232.3 (4.15)	260.8 (3.89)[b]		
Bis-(4-methoxyphenyl) (XIV)	251.3 (4.38)			
Bis-(2,6-dimethyl-4-methoxyphenyl) (XV)	249.7 (4.35)	287.8 (3.93)		
Bis-(4-hydroxyphenyl) (V)	250 (4.05)		279.3 (4.03)	
Bis-(3-methyl-4-hydroxyphenyl) (VII)	249.5 (4.19)[c]	285.0 (3.77)	289 (4.33)[d]	303.5 (4.27)
Bis-(2-methyl-4-hydroxyphenyl) (VI)	249.2 (4.23)	286.3 (3.84)[e]	295 (4.30)	
Bis-(4-hydroxy-2,6-dimethylphenyl) (VIII)	251.0 (3.81)	292 (3.64)	286 (3.95)	

[a] The absorption spectra were measured in 0.01 *N* sodium hydroxide solution containing 6% ethanol. [b] Two other shoulders at 266.8 (3.88) and 273.8 (3.30). [c] E. Ziegler, E. Schauenstein and H. Zima reported 253.5 (4.10) (*Monatsh.*, **84**, 284 (1953)). [d] E. Ziegler, E. Schauenstein and H. Zima reported 295 (4.37) (note *c*). [e] Another shoulder at 276.8 (3.97).

resonance of the divalent sulfide, which counteracts the electron-withdrawing inductive effect.

The ultraviolet spectra of these compounds are listed in Table III. The primary band of diphenyl sulfide is known to be at 250 mμ (log ε 4.08).[16] The substitution of hydroxy groups at both *p*-positions has virtually no effect on this absorption band; in alkaline solution the band shows a substantial shift to a longer wave length. A small red shift and the intensity increase brought about by the substitution of two methyl groups as observed in both neutral and alkaline solutions is caused by the methyl group.

Sulfoxides.—It is known that the sulfoxide group has an electron-withdrawing conjugative effect, though it is smaller in magnitude than that of the sulfone group.[17] Recently Bordwell and Boutan[18] demonstrated the importance of this electron-withdrawing conjugative effect by showing that the acidity of *p*-methylsulfinylphenol is higher than that of its *m*-isomer. Although 2-methyl-4-hydroxyphenylsulfinyl and 2,6-dimethyl-4-hydroxyphenylsulfinyl groups are not identical with the 4-hydroxyphenylsulfinyl group, one could safely assume that their polar effects are identical because only a small fraction of the originally small inductive effect of the methyl group would be transmitted from the second benzene ring. The pK_a values in Table II indicate very clearly that methyl groups have no apparent steric inhibition of the effect of the arylsulfinyl group on the dissociation of phenol. Stuart molecular models of those compounds indicate that one *o*-methyl group in each benzene ring blocks the free rotation of the sulfinyl group. The second methyl group in each benzene ring in VIII has a further, more pronounced effect in blocking free rotation and hence the oxygen atom of the sulfoxide group and two benzene rings have no chance of coming into the same plane. Nevertheless, the two methyl groups do not change the magnitude of the electron-withdrawing resonance interaction of the sulfinyl group with benzene ring where this resonance undoubtedly involves 2p,3d-orbital overlap of the C–S bond.

The ultraviolet spectra of these sulfoxide compounds in aqueous ethanol are listed in Table IV.

Although the acid dissociation constants suggest an electron-withdrawing conjugative effect for the sulfoxide group, the ultraviolet absorption spectra of the sulfoxides appear to resemble those of the sulfide group in which electron-donor type conjugation is present in the photo-excited state.[17b,c,18,19,20] However, unlike the case of the sulfide group, the substitution of hydroxy or methoxy group at both *p*-positions of the diphenyl sulfoxide does enhance the diphenyl sulfoxide chromophore, shifting the maxima as much as 19 mμ toward the longer wave length. This indicates a conjugation between the electron-donating methoxy or hydroxy groups and the *p*-sulfoxide group. The additional substitution of a methyl group on the benzene rings results in virtually no change. This is also consistent with the non-stereosensitivity of the 3d-orbital resonance interaction.

The change of solvent from methanol to dioxane has a rather small effect on λ as well as on λ'. However, in dioxane two peaks appear approximately where there is only one peak in methanol (see Table V). Another interesting feature is the sizable increase in intensity of the absorption bands of all the sulfinylphenols from methanol to dioxane. Perhaps the lack of hydrogen-bond formation in a non-hydroxylic solvent such as dioxane allows the phenolic oxygen atom to interact more effectively with the electron-withdrawing *p*-sulfinyl group.

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[16] (a) E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 84 (1949); (b) H. P. Koch, *J. Chem. Soc.*, 387 (1949); (c) A. Mangini and R. Passerini, *ibid.*, 1168 (1952).

[17] (a) R. L. Shriner, H. C. Struck and W. J. Jorison, THIS JOURNAL, **52**, 2060 (1930); (b) R. H. Eastman and R. M. Wagner, *ibid.*, **71**, 4089 (1949); (c) C. C. Price and J. J. Hydock, *ibid.*, **74**, 1943 (1952).

[18] F. G. Bordwell and P. J. Boutan, *ibid.*, **79**, 717 (1957).

[19] (a) M. Chaix, *Bull. soc. chim.*, **53**, 700 (1933); (b) H. P. Koch, *J. Chem. Soc.*, 2892 (1950).

[20] C. C. Price and H. Morita, THIS JOURNAL, **75**, 4747 (1953).

TABLE V

PRIMARY (λ) AND SECONDARY (λ') ULTRAVIOLET ABSORPTION BAND (mμ) IN DIOXANE

Compound, sulfoxide	λ_{max} (log ϵ)	λ'_{max} (log ϵ)
Diphenyl	232 (4.20)	
Bis-(4-methoxyphenyl)	248.9 (4.48) 254.1 (4.49)	
Bis-(2,6-dimethyl-4-methoxyphenyl)[a]	248.5 (4.27) 253.1 (4.32)	288 (4.08)
Bis-(4-hydroxyphenyl)	248 (4.37) 253.5 (4.37)	
Bis-(3-methyl-4-hydroxyphenyl)[b]	249 (4.40) 254 (4.44)	280 (4.21)
Bis-(2-methyl-4-hydroxyphenyl)[c]	248.7 (4.44) 254.7 (4.41)	279.7 (4.26)
Bis-(2,6-dimethyl-4-hydroxyphenyl)[d]	249.2 (4.42) 254 (4.39)	288.3 (4.26)

[a] Additional shoulder at 258 mμ (4.28). [b] Additional shoulders at 243 mμ (4.30) and 260 mμ (4.36). [c] Additional shoulders at 242.3 (4.33) and 259.7 (4.42). [d] Additional shoulders at 243.2 (4.32) and 260.4 (4.21).

Infrared spectra of several aryl sulfoxides were taken and the results are shown in Table VI.

TABLE VI

CHARACTERISTIC SULFOXIDE AND HYDROXY BANDS OF ARYL SULFOXIDES IN KBr DISKS

Compound, sulfoxide	OH band, μ	SO band, μ
Diphenyl		9.64
Bis-(4-methoxyphenyl)		9.67
Bis-(2,6-dimethyl-4-methoxyphenyl)		9.69
Phenol	2.97	
Bis-(4-hydroxyphenyl)	3.13	10.27–10.37
Bis-(3-methyl-4-hydroxyphenyl)	3.17–3.30	10.45–10.50
Bis-(2-methyl-4-hydroxyphenyl)	3.15–3.20	10.48–10.55 9.58 (small)
Bis-(2,6-dimethyl-4-hydroxyphenyl)	3.05	10.30 9.61 (small)

As other workers[21] have pointed out, the sulfoxide group appears to form a fairly strong hydrogen-bond with hydroxy groups because of the semi-polar nature of the sulfoxide bond. The characteristic S$\rightarrow$O bond of 9.6–9.7 mμ disappears and a broad band of 10.2–10.5 mμ appears in the spectra of p-hydroxy compounds. The latter band would be the hydrogen-bonded sulfoxide band. The OH band also shifts to a longer wave length in these p-hydroxy compounds. However, in the case of bis-(2,6-dimethyl-4-hydroxyphenyl) sulfoxide (VIII), both OH and S$\rightarrow$O bonds appear to survive. Perhaps strong hydrogen-bond formation is inhibited in this molecule because of steric hindrance.

Sulfonium Salts.—The first dissociation constants of p-substituted sulfinylphenols are summarized in Table II. The pK_a data in this table show clearly that methyl groups exert no apparent inhibition of the effect of the aryl sulfonio group on the dissociation of the substituted phenols. when one considers the acid-weakening effect of methyl group *ortho* as well as *meta* to phenolic hydroxy group (pK_a values of o- and m-cresols are 0.27 and 0.15, resp., higher than that of phenol in 48.9% ethanol[22]). Particularly striking is the case of tris-(2-methyl-4-hydroxyphenyl)-sulfonium chloride, where there is no acid-weakening effect by methyl group due to the steric inhibition. The Stuart molecular model of this compound also indicates that the o-methyl groups in XII make this molecule so rigid that the free rotation of all three benzene rings is almost impossible. The effective bulkiness of the 2-methyl-4-hydroxyphenyl group is far greater than that of the methyl group studied previously.[10] The carbon atoms of two benzene rings directly attached to the sulfur group have no chance of becoming co-planar with the third benzene ring. This lack of sensitivity of the sulfonio group to steric inhibition is in accord with theoretical consideration[9] for $3d$-orbital resonance. It is interesting to note that the substitution of two 4-hydroxyphenyl groups for two methyl groups causes a fairly large increase in acidity of p-substituted sulfoniophenols (0.72 in pK_a value). This is understandable in view of the powerful electron-withdrawing inductive effect of the phenyl group noted in many other cases.[22]

TABLE VII

PRIMARY (λ) AND SECONDARY (λ') ULTRAVIOLET ABSORPTION BANDS (mμ) IN 6% AQUEOUS ETHANOL SOLUTION

	Absorption			
	In neutral solution		In alkaline solution[a]	
Compound, sulfonium chloride	λ_{max} (log ϵ)	λ'_{max} (log ϵ)	λ_{max} (log ϵ)	λ'_{max} (log ϵ)
Phenol	210.5 (3.79)	270 (3.16)	235 (3.97)	287 (3.41)
Tris-(4-hydroxyphenyl)-	258.5 (4.59)[b]	277 (4.48)[b]	283 (4.56)[c]	
Tris-(3-methyl-4-hydroxyphenyl)-	258 (4.47)[d]	277 (4.40)[d]	295.5 (4.26)	316.5 (4.21)
Tris-(2-methyl-4-hydroxyphenyl)-	260 (4.50)[e]	277 (4.41)[c]	283–300 (4.61) (286)	

[a] The absorption spectra were measured in 0.01 N sodium hydroxide solution containing 6% ethanol. [b] Determined with added HCl to suppress dissociation; without added HCl, peaks are located at 252.8 (4.39) and 276.8 (4.28) with two additional shoulders at 285.7 (4.18) and 307.8 (3.83). [c] An additional small shoulder at 303 (4.48). [d] Determined with added HCl to suppress ionization; without added HCl, peaks are at 255.0 (4.22) and 287.5 (4.13) with an additional shoulder at 313 (3.78). [e] Determined with HCl added to suppress ionization; without HCl added, there are peaks at 256.7 (4.38) and 286.2 (4.30) together with additional shoulders at 276.7 (4.33) and 306.2 (4.12).

The ultraviolet absorption spectra of the substituted phenols were measured and the results are listed in Table VII. As in the previous cases,[10,11] a methyl group adjacent to the sulfonio group has very little influence on the conjugative characteristics of the group. Here again the conjugative

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(21) (a) D. Barnard, J. M. Fabian and H. P. Koch, *J. Chem. Soc.*, 2442 (1949); (b) E. D. Amstutz, J. M. Hunsberger and J. J. Chessick, THIS JOURNAL, **73**, 1220 (1951).

(22) See Chapter 14, by H. C. Brown, D. H. McDaniel and O. Häfliger, *in* "Determination of Organic Structure by Physical Methods," edited by E. A. Braude and F. C. Nachod, Academic Press, Inc., New York, N. Y., 1955.

interaction of the sulfonio group with the benzene ring in the photo-excited state does not require a preferred steric or angular arrangement. The ultraviolet spectra of these sulfonio phenols when taken in neutral solution contain peaks corresponding to those found in alkaline solution. Since these phenols are comparatively strong acids, they evidently partially dissociate even in neutral solution.

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Neighboring Carbon and Hydrogen. XXXIX.[1] Complex Rearrangements of Bridged Ions. Rearrangement Leading to the Bird-cage Hydrocarbon[1]

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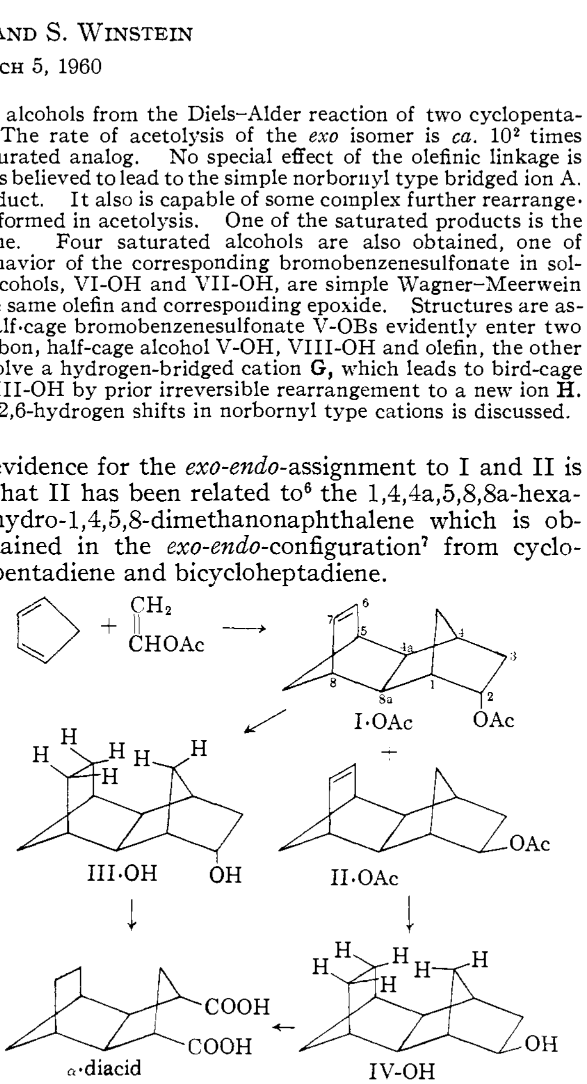
RECEIVED MARCH 5, 1960

The solvolysis of the bromobenzenesulfonates of the epimeric alcohols from the Diels–Alder reaction of two cyclopentadiene molecules with one of vinyl acetate has been studied. The rate of acetolysis of the *exo* isomer is *ca.* 10^2 times that of the *endo* and approximately the same as that of its saturated analog. No special effect of the olefinic linkage is evident in the rate-determining ionization step. Ionization is thus believed to lead to the simple norbornyl type bridged ion A. Ion A gives rise to some unrearranged unsaturated solvolysis product. It also is capable of some complex further rearrangements which lead to saturated products, *ca.* 70% of these being formed in acetolysis. One of the saturated products is the bird-cage hydrocarbon, hexacyclo$[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}.0^{5,9}]$dodecane. Four saturated alcohols are also obtained, one of them, V-OH, being unique as regards infrared spectrum and behavior of the corresponding bromobenzenesulfonate in solvolysis. This alcohol has a half-cage structure. Two of the alcohols, VI-OH and VII-OH, are simple Wagner–Meerwein isomers, and two of them, VI-OH and VIII-OH, are related to the same olefin and corresponding epoxide. Structures are assigned to alcohols VI-VIII-OH. The bridged ion A and the half-cage bromobenzenesulfonate V-OBs evidently enter two complex rearrangement paths, one leading to bird-cage hydrocarbon, half-cage alcohol V-OH, VIII-OH and olefin, the other leading to VI-OH, VII-OH and olefin. The first path may involve a hydrogen-bridged cation **G**, which leads to bird-cage hydrocarbon or half-cage alcohol by reaction with solvent, or VIII-OH by prior irreversible rearrangement to a new ion **H**. The analogy between the complex rearrangements of ion A and 2,6-hydrogen shifts in norbornyl type cations is discussed.

The solvolysis of the *endo* and *exo* pair of benzenesulfonates I-OBs and II-OBs was of some interest[2] because of the expected formation of a bridged cationic intermediate **A** and the possibility that it would undergo further more complex rearrangements. Therefore, solvolysis of these two materials and the corresponding saturated analogs III-OBs and IV-OBs has been examined, and some of the results of this study are presented and discussed in the present manuscript.

Results

Materials.—The mixture of *endo-* and *exo*-acetates I-OAc and II-OAc is readily available from the Diels–Alder reaction between cyclopentadiene and vinyl acetate.[3] The *exo-endo*-4a,8a-fusion of the two bicycloheptane nuclei was deduced by Soloway[4] in an excellent analysis of the stereochemistry of fused norcamphane systems. The necessary plausible assumption that the configuration of the carbon skeleton of I and II is identical with that in the bis-adduct of cyclopentadiene to ethylene has since been verified by actual conversion[5] of the vinyl acetate adduct to the ethylene analog. Other evidence for the *exo-endo*-assignment to I and II is that II has been related to[6] the 1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene which is obtained in the *exo-endo*-configuration[7] from cyclopentadiene and bicycloheptadiene.



Saponification of the bis-adduct of cyclopentadiene to vinyl acetate led to a mixture of the *endo*- and *exo*-alcohols I-OH and II-OH. These alcohols were separated by fractional crystallization of the sodium salt of the mixture of corresponding acid phthalates. Saponification of the pure acid phthalates gave rise to the pure alcohols. From these materials, the corresponding alcohols III-OH and IV-OH were obtained in nearly quantitative yield by hydrogenation.

That III-OH and IV-OH, as well as I-OH and II-OH, represent epimeric pairs of alcohols was con-

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(1) (a) Research sponsored by the Office of Ordnance Research, U. S. Army. (b) Abstracted from Ph.D. Thesis of Louis de Vries, U.C.L.A., Jan., 1956. (c) Paper XXXIV: C. F. Wilcox, Jr., S. Winstein and W. G. McMillan, THIS JOURNAL, **82**, 5450 (1960); paper XXXV: S. Winstein, J. Sonnenberg and L. de Vries, *ibid.*, **81**, 6523 (1959); paper XXXVI: S. Winstein, *ibid.*, **81**, 6524 (1959); paper XXXVII: P. Bruck, D. Thompson and S. Winstein, *Chemistry & Industry*, 590 (1960); paper XXXVIII: S. Winstein and C. Ordronneau, THIS JOURNAL, **82**, 2084 (1960).

(2) Much of the material reported in this manuscript was reported in outline at: (a) Symposium on "Dynamic Stereochemistry," Manchester, England, March 31, 1954; see *Chemistry & Industry*, 562 (1954); (b) XIVth International Congress of Pure and Applied Chemistry, Zurich, Switzerland, July 21–27, 1955; S. Winstein, *Experientia Suppl. II*, 137 (1955).

(3) K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939).

(4) S. B. Soloway, THIS JOURNAL, **74**, 1027 (1952).

(5) S. B. Soloway, Thesis, Univ. of Colorado, 1955.

(6) D. Thompson and P. Bruck, unpublished work in these laboratories.

(7) See J. K. Stille and D. A. Frey, THIS JOURNAL, **81**, 4273 (1959).