INTRAMOLECULAR INFLUENCE OF FIELD EFFECTS PROPAGATED WITHIN THIA, SULFINYL AND SULFONYL GROUPS[1]

Sir:

The importance of the electronic stability of sulfinyl- and sulfonylcarbanions as a factor determining reaction rates and configurational stability of the carbanion is receiving increased attention.[2] We have now observed, with electronically analogous systems, that the anionic stability gained by means of the electron-withdrawing character of thia, sulfinyl and sulfonyl groups may be influenced directly by the electric fields propagated within these groups. As the influence of these fields may be quite large in specific, rigid systems, we feel this report may be of immediate value in related studies.

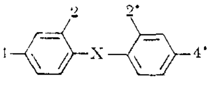
It is well known that the acidity of phenol is increased by *m*- and *p*-substitution with these groups[3]; however, the direct influence of the groups' electric fields on the acidity of the *o*-phenols has been implied only recently.[4] While inductive-conjugative effects are operative at *p*- and *o*-positions, the influence of the electric field surrounding the group is many times greater at the *o*-position.[5] A first approximation of this field effect should be suggested, then, by the difference in acidity between *p*- and *o*-isomers of phenols so substituted. We now have sufficient data to allow a preliminary evaluation of this effect (Table I).[6]

Each of these groups is clearly electron-withdrawing, the order being S < SO < SO_2. In the thia systems this results in the propagation of a slightly negative field surrounding the sulfur atom (d-orbital participation is suggested) which is probably responsible for the slightly lower acidity of the 2-isomers relative to the 4-isomers.[7] This effect should be enhanced in the diphenates and is, in fact, confirmed by the corresponding data.[8]

The sulfonyl group assumes a greater negative charge which is distributed between its oxygen atoms and further strengthens the negative field, *viz.*, 2-OH acidity is substantially decreased. The most stable conformations of diaryl sulfones are those in which both aryl planes are perpendicular to the C—S—C plane.[9] If a stable conformation is retained, then, the 2-O^- cannot escape the influence of the negative field even by rotation (*cf.* Ia and Ib). In the 2,2′-dianion (II) the total negative field of the sulfonyl oxygens is effective.

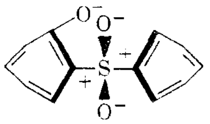
TABLE I

RELATIVE ACIDITIES OF SOME ISOMERIC *o*- AND *p*-SUBSTITUTED PHENOLS

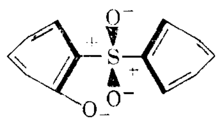


Substituents	pKa^a (phenol, 10.95), when X =			
	S	SO	SO_2	CH_2
4-OH	10.22	9.17	8.69^c	11.08
2-OH	10.27	9.04	9.10	11.15
4-OH-4′-NO_2	9.86	8.97	8.37^d	
2-OH-4′-NO_2	9.91	8.57	8.52	
4,4′-di-OH^b	10.80	9.93	9.41	11.22
2,2′-di-OH^b	11.03	10.79	11.06	11.15

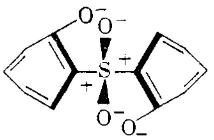
[a] At 25°; 0.001 *M* solutions in 48% (vol.) aq. ethanol; p*K*a values taken as *p*H at half-neutralization point using 0.010 *N* NaOH (in solvent as above) as titrant and Beckman Model G *p*H meter [*cf.* ref. 3a and H. H. Szmant and G. Suld, *J. Am. Chem. Soc.*, 78, 3400 (1956)]. Determinations were in duplicate or triplicate, the average values (in Table) usually varying no more than ±0.02 unit from an individual determination. [b] These are pKa_2 values and *have been corrected* by applying the statistical factor to the observed values (see ref. 3c, pp. 622 ff.). [c] H. H. Szmant and G. Suld, ref. *a*, reported p*K*a 8.64 under essentially the same conditions. [d] Szmant and Suld reported 8.28.



Ia



Ib



II

The electron-withdrawing influence of the sulfonyl group here is *completely compensated* by its negative field effect: the 2,2′-di-OH isomer has a resultant acidity equal to that of the 2,2′-di-OH sulfide.

The case of the sulfoxides is different inasmuch as the 2-isomers are *more* acidic than their 4-isomers, in the monophenol series. This difference may be attributed to the geometry of the sulfinyl group which introduces the factor of asymmetry into sulfoxide compounds. This factor becomes important—virtually dominant—in the 2-isomers. Stable conformations of diaryl sulfoxides are similar to those noted above for sulfones.[9b] Unlike sulfones, however, the sulfoxide systems are unique in that the 2-O^- not only can escape the negative-field influence of the sulfinyl oxygen by rotation

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[1] This study is part of a series dealing with the nature of organic sulfur groups and is supported by grants from the Petroleum Research Fund. The preceding paper is by C. Y. Meyers, G. Moretti and L. Maioli, *J. Org. Chem.*, **27**, 625 (1962).

[2] (a) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962); (b) D. J. Cram, R. D. Partos, S. H. Pine and H. Jäger, *ibid.*, **84**, 1742 (1962). See also related studies noted in (a) and (b).

[3] For recent studies and bibliography see (a) S. Oae and C. Zalut, *J. Am. Chem. Soc.* **82**, 5359 (1960); (b) G. Cilento, *Chem. Revs.*, **60**, 147 (1960); (c) H. C. Brown, D. H. McDaniel and O. Häfliger in "Determination of Organic Structures by Physical Methods," edited by E. A. Braude and F. C. Nachod, Academic Press, Inc., New York, N. Y., 1955, Chapt. 14.

[4] C. Y. Meyers, *Ind. chim. belge*, **27**, 538 (1962).

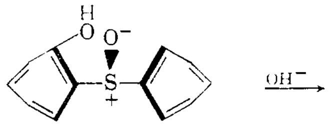
[5] See, for example, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

[6] (a) Molecular models indicate the absence of steric interference in the systems under discussion; moreover, resonance involving d-orbital participation reportedly is more or less independent of the usual geometric requirements (see refs. 2b and 3); (b) in this discussion degree of acidity is related to anionic stability (see ref. 3c and G. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 340 ff.).

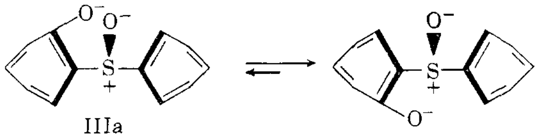
[7] As the —*I* effect is greater at the 2- than 4-position (ref. 5) the true influence of the field effect in the 2-isomers is undoubtedly underestimated from these acidity data alone.

[8] That this effect is not simply caused by the 2,2′-di-O^- field is implied from the almost-equal acidities of the 2-OH, 2,2′-di-OH (Ka_2) and 4,4′-di-OH (Ka_2) compounds with the –CH_2– bridge.

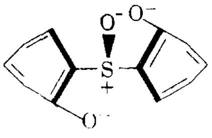
[9] (a) V. Baliah and V. Ramakrishnan, *J. Indian Chem. Soc.*, **35**, 151 (1958); (b) S. C. Abrahams, *Quart. Rev.* (*London*), **10**, 407 (1956); (c) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 369 (1951); T. Okamoto and J. F. Bunnett, *J. Org. Chem.*, **21**, 487 (1956); (d) G. Leandri, A. Mangini and R. Passerini, *Gazz. chim. ital.*, **84**, 73 (1954).



III



IIIa IIIb



IV

but, in so doing, becomes stabilized by the positive field of the sulfur atom. Moreover, a stable conformation is retained (*cf.* IIIa and IIIb).[10] The dianion (IV) of the 2,2′-di-OH sulfoxide also exhibits this type of internal stabilization. This sulfoxide is more acidic than the corresponding sulfone even though the negative-field influence of the sulfinyl oxygen is now effective in reducing the net acidity, *viz.*, it is less acidic than the 4,4′-di-OH sulfoxide.

This paradox, in which a sulfinyl group effects a greater acidity than does a sulfonyl group, is exhibited also by the corresponding 2-OH compounds and arises, apparently, from the opposite field-effect influence exerted in the two systems. This is better illustrated by a comparison of the 4′-NO_2-substituted compounds in which the positive charge at the sulfur atom of both groups is increased[11]: in the sulfoxides the effective positive field is directly enhanced; in the sulfones the effective negative field is indirectly diminished. This is reflected by the larger difference in acidity between the 2- and 4-OH sulfoxides, but smaller difference between the corresponding sulfones, when a 4′-NO_2-group is introduced.

The behavior of other sulfone and sulfoxide systems may be accounted for on the basis of the type of field effects described here.[12]

[10] One cannot rule out the possibility that the undissociated phenol (III) may be already in the conformation denoted by IIIb. This will be considered in a forthcoming publication.

[11] C. Y. Meyers, G. Moretti and L. Maioli, in ref. 1 (*cf.* H. H. Szmant and G. Suld, Table I, ref. *a*).

[12] C. Y. Meyers, *Tetrahedron Letters*, in press.

ISTITUTO DI CHIMICA INDUSTRIALE
UNIVERSITÀ DI BOLOGNA
BOLOGNA, ITALY

CAL Y. MEYERS
GAETANO LOMBARDINI
LUCIANO BONOLI

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HOMOENOLATE ANIONS

Sir:

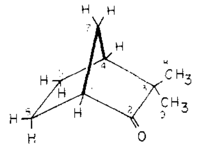
A hydrogen *alpha* to a carbonyl group is acidic and its abstraction by alkali leaves an enolate anion whose charge is stabilized by conjugation with the neighboring pi electrons. We now present evidence that removal of a hydrogen more remote from a carbonyl group can be facilitated by homoconjugation and can lead to a corresponding *homoenolate* anion.

Optically active camphenilone (I, m.p. 38–38.5°, α + 69°; semicarbazone m.p. 224.5–225.5°, α + 255°),[1] which has no ordinarily enolizable hydrogens, was heated at elevated temperature with potassium *t*-butoxide in *t*-butyl alcohol. The ketone was recovered (usually in about 80% yield), was identified by its infrared spectrum and by gas chromatography, and was converted to its semicarbazone. The specific rotation of the purified derivative was recorded to determine its optical purity. The results in Table I are typical and show that (+)-camphenilone is *racemized by the alkaline treatment.* The last run, in which the butoxide was omitted, establishes that the loss of optical activity is not the result of the thermal treatment alone.

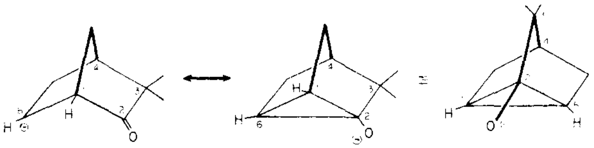
TABLE I[2]

Temp., °C.	Time, hr.	% Racemization
185	12	26
185	36	69
185	48	88
250	4	100
250	113 (alkali omitted)	0

We interpret the racemization as abstraction of a hydrogen from C.6 to form a non-classical anion II, termed a homoenolate anion, whose charge is stabilized by delocalization to the carbonyl group (*cf.* resonance structures IIa and IIb).



I



IIa IIb

Formation of this ion provides an opportunity for the C.2–C.6 bond to become equivalent to the C.2–C.1 bond and hence for the system to lose its optical activity. Recapture of a proton at C.6 regenerates the original (+)-camphenilone, whereas protonation at C.1 leads to the enantiomer.[3]

The mobility of hydrogens in camphenilone was further supported by deuterium-incorporation experiments in which the ketone was heated at 185° with potassium *t*-butoxide in *t*-butyl alcohol-*d*. The deuterium content and the relative distribution of deuterated species in the recovered ketone were determined mass spectroscopically. In separate runs conducted for 12 hr. and for 48 hr. the recovered camphenilone contained mono-, di-

[1] (a) W. P. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952); (b) W. Hückel, *Ann.*, **549**, 186 (1941).

[2] In all the runs reported in this paper the concentrations were not the same. Typically, the potassium *t*-butoxide molar ratio ranged from 2–4 and the *t*-butyl alcohol molar ratio ranged from 20–60, relative to camphenilone.

[3] Protonation of a homoenolate ion on oxygen would give the corresponding *homoenol*. In the present case the homoenol is also a cyclopropyl alcohol.