Anal. Calcd. for $C_6H_{12}Br$: C, 44.2; H, 6.8; Br, 49.0. Found: C, 44.8; H, 6.9; Br, 48.2.

3-Ethylcyclopentyl bromide. In a similar procedure 0.62 mole (71.0 g.) of 3-ethylcyclopentanol was converted into 65.0 g. (59.3%) of 3-ethylcyclopentyl bromide boiling at 172.0–177.0° and having n_D^{24} 1.4780.

Anal. Calcd. for $C_7H_{14}Br$: C, 47.5; H, 7.4; Br, 45.1. Found: C, 48.6; H, 7.5; Br, 45.0.

2-Methylcyclopentyl bromide. 1-Methylcyclopentanol, 1.19 moles (119.0 g.), was treated with equivalent quantities of the reagents described in the preceding experiment. The displacement was allowed to proceed for 24 hours. Workup yielded 36.0 g. (18.6%) of product boiling at 45.5–49.5° at 20 mm. and having n_D^{25} 1.4757; reported[9] boiling at 150–151°.

School of Pharmacy
Purdue University
West Lafayette, Ind.

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Reaction of Ditolylethane with Gallium Bromide–Hydrogen Bromide in Benzene

A. Streitwieser, Jr., and W. J. Downs

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On the basis of stereochemical and isotope tracer experiments a new mechanism has recently been proposed for the Lewis acid catalyzed transalkylation of ethylbenzene in benzene.[1] In this mechanism a small amount of oxidation to α-phenethyl cation initiates a carbonium ion chain process: The α-phenethyl cation alkylates benzene to form 1,1-diphenylethane, which is rapidly cleaved by acid under the experimental conditions to regenerate an α-phenethyl cation and benzene in which the two aromatic rings may have been interchanged. This mechanism has an obvious extension to related disproportionation reactions; it has the further necessary corollary that 1,1-diarylethanes react rapidly under these conditions.

To test this corollary, a solution of 1,1-di-*p*-tolylethane in benzene was treated with gallium bromide and hydrogen bromide at 50°. Aliquots of the mixture were examined at intervals by v.p.c. analysis after quenching with water. Even by the time the first aliquot was removed (15 seconds), the ditolylethane was converted completely to 1,1-diphenylethane. Toluene and a lesser amount of ethylbenzene were also identified as products. Hence, the reaction

$$Ar_2CHCH_3 + 2\ C_6H_6 \xrightleftharpoons[]{\substack{HBr\\GaBr_3}} (C_6H_5)_2CHCH_3 + 2\ ArH$$

is orders of magnitude faster than the transalkylation studied earlier and is an allowable sequence as required in the proposed reaction mechanism. The ethylbenzene also produced in the experiment undoubtedly arises by hydride transfer to the α-phenethyl cation with concommitant formation of other by-products. Small amounts of other compounds were found by v.p.c. but could not be identified.

EXPERIMENTAL

The experimental technique was similar to that used in the earlier report.[1] A stock solution was prepared from 8.5 g. of sublimed gallium bromide and 101 g. of sodium-dried benzene and stored in a flask carrying a side arm closed with a serum cap. Fifty milliliters of the stock solution was transferred with a syringe to a one necked flask closed with a stopcock and a serum cap. Hydrogen bromide (0.49 g.) was admitted with a syringe needle and the flask was brought to temperature in a 50° thermostat. 1,1-Di-*p*-tolylethane[2] (0.50 ml.) was syringed in and 10 ml. aliquots were removed after 15 sec., 5 min., and 1.5 hr. Each aliquot was quenched with water and the organic layer was separated, dried, and examined by v.p.c. (70°, silicone). In each aliquot, the toluene peak was 1% of the benzene peak; ethylbenzene increased from 1/4 to 1/2% during the run. A sample analyzed in the v.p.c. column at 200° showed six additional peaks, the largest of which was 1,1-diphenylethane. The remaining peaks were small and could not be identified; however, 1,1-ditolylethane was found to be absent.

Department of Chemistry,
University of California
Berkeley 4, Calif.

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(1) A. Streitwieser, Jr., and L. Reif, *J. Am. Chem. Soc.*, 82, 5003 (1960).

(2) J. S. Reichert and J. A. Nieuwland, *J. Am. Chem. Soc.*, 45, 3090 (1923).

A Reappraisal Concerning the Variable Character of the Sulfone Group[1]

Cal Y. Meyers, Gianfranco Moretti, and Lillia Maioli

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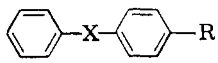
Szmant and Suld[2] reported that, in benzoic acids of type I, a 4-NO_2 group *decreased* the acidity of the parent sulfone derivative but increased that of the corresponding sulfoxide and sulfide derivative, respectively. However, similar substitution of the phenolic sulfone (II. X = SO_2) increased its acidity. In both sulfone series a 4-NH_2 group decreased the acidity, respectively.



I. R = CO_2H; II. R = OH; X = SO_2, SO, S

While it was noted that the decreased acidity of the 4-NO_2-phenylsulfonylbenzoic acid was "entirely unexpected on the basis of additive inductive effects," the combined data were utilized in suggesting that the —SO_2— group varies in character depending upon the electronic nature of the

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(1) This study is part of a series dealing with the nature of the sulfone group. The authors are grateful to the Petroleum Research Fund of the American Chemical Society whose grants are making these studies possible.

(2) H. H. Szmant and G. Suld, *J. Am. Chem. Soc.*, 78, 3400 (1956).

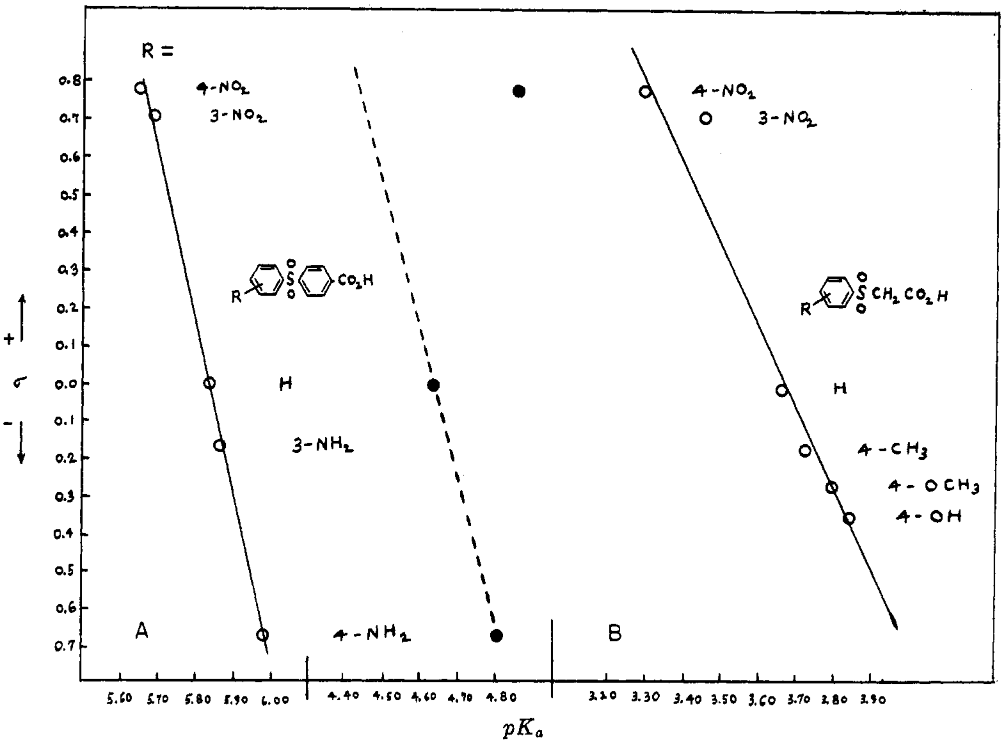

Fig. 1. A. Effect of σ of R on pK_a of p-($R-C_6H_4SO_2$)$C_6H_4CO_2H$, ——— in 80% aq. acetone; - - - - in 48% aq. ethanol (see Table I). B. Effect of σ on R of pK_a of $R-C_6H_4SO_2CH_2CO_2H$ in 48% aq. ethanol (see Table II)

substituent—*e.g.*, a NO_2 group decreases the positive charge at the S atom ($\overset{-}{O}—\overset{++}{\underset{|}{\overset{|}{S}}}—\overset{-}{O}$) by stabilizing the double-bonded form ($O=\underset{|}{\overset{|}{S}}=O$).[2,3]

During several attempts to confirm the anomalous acidity of this 4-NO_2 derivative, we also studied the 3-NO_2 isomer. Surprisingly, we found that neither compound was sufficiently soluble in 48% aqueous ethanol to allow pK_a determinations under the conditions described by Szmant. It was found, however, that 80% aqueous acetone was very satisfactory and allowed relative acidities to be determined for the series. In addition to the 4-NH_2 derivative, we also studied the 3-NH_2 isomer. The data (Table I and Fig. 1A) indicate that the influence of the —SO_2— group on the benzoic acid acidity is directly related to the electronic nature of the substituent group measured in terms of Hammett's σ constants. The corresponding pK's in 48% aqueous ethanol were then interpolated from the plots. The relative acidity of the 4-NO_2 derivative is in sharp contrast to that reported by Szmant.

To substantiate this observed relationship, the acidities of substituted phenylsulfonylacetic acids were also determined, but directly in 48% aqueous ethanol. Again the data showed that the influence of the —SO_2— group is directly related to the substituent's σ constant (Table II and Fig. 1B).

TABLE I

SUBSTITUENT EFFECTS ON THE ACIDITY OF p-PHENYLSULFONYLBENZOIC ACID

Substituent	σ (of Substituent)[a]	pK_a in 80% Aq. Acetone[b]	pK_a in 48% Aq. ethanol Interpol'd[c]	pK_a in 48% Aq. ethanol Reported[d]
4-NO_2	+0.778	5.64	4.44	4.86
3-NO_2	+0.710	5.68	4.45	—
H	0.000	5.83	4.63	4.63
3-NH_2	−0.161	5.85	4.68	—
4-NH_2	−0.660	5.97	4.80	4.80

[a] J. Hine, *Physical Organic Chemistry*, McGraw-Hill, New York, 1956, p. 72. [b] Determined (in triplicate) by titration of 0.002M solutions with 0.01M NaOH in 48% aqueous ethanol, using a Beckman Model G pH meter; values corrected where necessary by use of the Henderson Equation (S. Glasstone, *Physical Chemistry*, D. Van Nostrand Co., Inc., London, 1947, pp. 1003, ff.). [c] Approximated values from Fig. 1A. [d] Ref. 2.

As, in both types of acids, the degree of acidity increases with the corresponding electronegativity of the —SO_2— group, this electronegativity apparently is *increased* proportionally by 3- and 4-NO_2 substitution, respectively, in both cases. This is contrary to the general conclusion of

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(3) H. H. Szmant and J. M. Dixon, *J. Am. Chem. Soc.*, 78, 4384 (1956).

Szmant. Moreover, a plot of sulfonylphenol acidities[2] against σ reveals a relationship parallel to those reported here for the corresponding benzoic and acetic acids.

TABLE II

SUBSTITUENT EFFECTS ON THE ACIDITY OF PHENYLSULFONYLACETIC ACID

Substituent	σ (of Substituent)[a]	pK_a in 48% Aq. Ethanol[b]
4-NO_2	+0.778	3.29
3-NO_2	+0.710	3.45
H	0.000	3.66
4-CH_3	−0.170	3.72
4-OCH_3	−0.268	3.79
4-OH	−0.357	3.84

[a] Ref. *a* in Table I. [b] Ref. *b* in Table I.

Infrared studies of aryl sulfones[4] indicate that the S—O force constant also varies regularly with the σ of the substituent, resembling analogous observations with ketones.[5] As both this relationship and that describing the relative acidities within the three series of sulfone derivatives are valid in each case even at either extreme of substituent electronegativity, true variation in the character of the sulfone group, at least to the extent proposed by Szmant, is not evident.

ISTITUTO DI CHIMICA INDUSTRIALE
UNIVERSITÀ DI BOLOGNA
BOLOGNA, ITALY

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[4] C. Y. Meyers, 140th Meeting, Am. Chem. Soc., Chicago, Ill., Sept. 1961, paper No. 12, Div. of Phys. Chem.

[5] N. Fuson, M.-L. Josien, and E. M. Shelton, *J. Am. Chem. Soc.*, **76**, 2526 (1954).

The Oxidation of Anisole and Diphenyl Ether with Trifluoroperoxyacetic Acid

JAMES D. MCCLURE AND PAUL H. WILLIAMS

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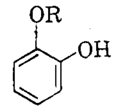
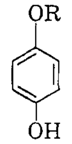
Friess[1] and co-workers studied the reactions of peroxybenzoic acid with the methyl ethers of di- and trihydric monocyclic phenols in chloroform solution. 1,4-Quinones were usually formed, in some cases with the loss of a methoxy group. More recently, the action of peroxyacetic acid[2] on a number of substituted di- and trimethoxybenzenes has been examined. Once again 1,4-quinones, formed by electrophilic 1,4-dihydroxylation and methoxy elimination, were usually the principal products obtained. With neither peroxy acid were the presumed primary products of oxidation, methoxyphenols, isolated. Less reactive monocyclic aryl ethers such as anisole[1–3] were reported to remain unchanged or to give water-soluble unidentified oils.

A recent publication[4] on the oxidation of aromatic hydrocarbons with trifluoroperoxyacetic acid prompts us to report some results of our own. Trifluoroperoxyacetic acid was found to oxidize anisole and diphenyl ether primarily by a process of electrophilic monohydroxylation. Moderate yields of phenols were obtained when an equimolar amount of peroxy acid was added slowly over several hours to a solution of the aryl ether in methylene chloride at 15–25°. Anisole (44% conversion) gave *o*-methoxyphenol (Ia) in 27% yield and *p*-methoxyphenol (IIa) in 7% yield. From diphenyl ether (44% conversion) *o*-phenoxyphenol (Ib) and *p*-phenoxyphenol (IIb) were obtained in 35% and 12% yields, respectively. In neither case were we able to isolate any of the corresponding meta isomer.



Ia. R = CH_3
b. R = C_6H_5



IIa. R = CH_3
b. R = C_6H_5

It was of interest that the phenols isolated from the oxidations of both anisole and diphenyl ether were predominantly the ortho isomers. The modest total yields (34–47%) were explained by noting that the phenols underwent further rapid oxidation, although no specific products were isolated. There was considerable doubt as to whether the observed ortho to para ratio (3:1) was due to a truly selective process or was merely the consequence of a rate of subsequent oxidation greater for the para isomer than for the ortho. In order to determine which of these alternatives was correct, an equimolar mixture of *o*-methoxyphenol and *p*-methoxyphenol was treated with a one-half molar quantity of trifluoroperoxyacetic acid. Analysis of the unchanged methoxyphenol showed that approximately twice as much para as ortho isomer had been consumed. The apparent selectivity of the hydroxylation of anisole can thus be accounted for to a large extent by the more rapid oxidation of *p*-methoxyphenol.

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[2] H. Davidge, A. G. Davies, J. Kenyon, and R. F. Mason, *J. Chem. Soc.*, 4569 (1958).

[3] H. Fernholz, *Angew. Chem.*, **60A**, 62 (1948); *Ber.*, **84**, 110 (1951).

[4] R. D. Chambers, P. Goggin, and W. K. R. Musgrave, *J. Chem. Soc.*, 1804 (1959).