Arylsulfonoxylation of Aromatic Compounds. IV. Nitrophenylsulfonoxylation of Bromobenzene, Methyl Benzoate, Nitrobenzene, and Anisole[1a-c]

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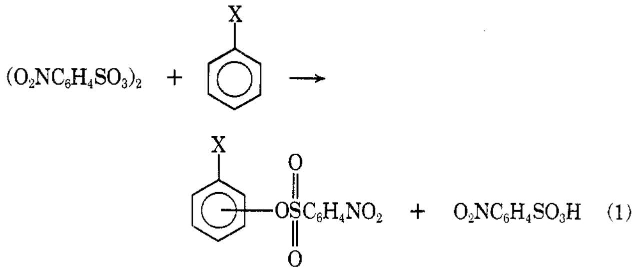
The *m*-nitrophenylsulfonoxylation of methyl benzoate, nitrobenzene, bromobenzene, and anisole follows the familiar pattern of orientation and activation or deactivation influences appropriate to an electrophilic substitution. The k_{Ar}/k_B's determined by competitive reactions (and by direct kinetics) are, respectively, methyl benzoate, 8.3×10^{-2} (10.6×10^{-2}); nitrobenzene, 2.4×10^{-3}; bromobenzene, 0.47 (0.56); anisole, 7.0×10^3 (7.5×10^3). The ortho, meta, and para orientations (partial rate factors based on competitive k_{Ar}/k_B) are, methyl benzoate, 24, 67, 9% (0.059, 0.17, 0.043); nitrobenzene, 24, 65, 11% (0.0017, 0.0046, 0.0015); bromobenzene, 21, 3, 76% (0.29, 0.042, 2.1); anisole, 14, –, 86% (2,940, –, 36,100). The *p*-nitrophenylsulfonoxylation of bromobenzene gave a k_{Br}/k_B of 0.49 by a competitive reaction and the following orientations (partial rate factors): ortho, 22.8% (0.366); meta, 4.7% (0.068); para, 72.5% (2.1). The orders of the reactions with respect to arene were essentially first order within experimental error: methyl benzoate, 0.97: bromobenzene, 0.99; anisole, 1.00. A good Hammett σ^+ plot of these values and those previously reported gave a ρ value of -4.4. The enthalpies (entropies) of activation are, bromobenzene, 19.1 (-13.1); methyl benzoate, 19.6 (-14.7); anisole, 12.3 (-22.7). The larger negative entropies with the more active aromatic substrates correspond to more complete bond formation in the transition state with these electron-rich aromatics.

In the preceding papers[1b] of this series, the nitrophenylsulfonoxylation of aromatic nuclei (eq 1) was



(1)

tentatively classified as an electrophilic reaction. This conclusion was based, however, on experiments involving only alkylbenzenes and two halobenzenes.

The present paper consists of several distinct units of work which were planned to establish more clearly the validity of the electrophilic classification. The thermal decomposition of *m*-nitrobenzenesulfonyl peroxide in nitrobenzene and methyl benzoate was studied to determine, first, whether arylsulfonoxylation would occur with such deactivated nuclei; second, whether any such substitution would be predominantly meta in orientation as predicted for an electrophilic process; and, third, the magnitude of the partial rate factors for reactions at the available positions. A similar reaction with anisole was planned to determine: first, whether its reactive nucleus would undergo substitution and not oxidation; second, the orientations and partial rate factors for any such substitution. A Hammett correlation of the partial rate factors would be particularly valuable in classifying the mechanism of arylsulfonoxylation. A study with bromobenzene as a substrate was proposed particularly to study the magnitude of the para partial rate factor. Finally, kinetic studies were projected to measure the activation parameters needed for a quantitative treatment of the mechanism.

Results and Discussion

Orientation of Substitution.—*m*-Nitrophenylsulfonoxylation occurred in yields of 65-70% with all four of the benzene derivatives neat or in ethyl acetate solution at room temperature (Table I). Inasmuch as nitrobenzene and methyl benzoate were converted into sulfonate esters, arylsulfonoxylation must be included with nitration, halogenation, and sulfonation as one of the few electrophilic aromatic substitutions applicable to strongly deactivated nuclei. It is the mildest of these substitution reactions for it occurs at room temperature in the absence of strong Lewis acids. The substitution of anisole in high yield instead of oxidation of its reactive nucleus gives even wider scope to this new reaction of aromatic substitution.

The predominant meta substitution (Table I) with nitrobenzene (65%) and methyl benzoate (67%) is critical confirmation of the electrophilic classification of the reaction. In contrast, classical homolytic substitutions of these same aromatics such as the phenylation of methyl benzoate[2] and nitrobenzene[3] or the hydroxylation of nitrobenzene with Fenton's reagent[4] all occur with predominant ortho–para orientation.

The magnitude of the meta orientation for the arylsulfonoxylation of methyl benzoate (67%) is similar to that for the nitration of ethyl benzoate (68%).[5] The *m*-nitrophenylsulfonoxylation of nitrobenzene (65%), however, is much less selective than the chlorination (81%)[6] or nitration (93%)[5] of this substrate.

The *m*-nitrophenylsulfonoxylation of anisole (86% para, 14% ortho) is in the range of orientations for other electrophilic substitutions such as chlorination (79% para, 21% ortho),[7] bromination (96% para, 4% ortho;[8] 98.4% para, 1.6% ortho[9]), or mercuration

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[1] (a) Presented in part at the International Symposium on the Chemistry of Organic Peroxides, Berlin-Aldershof, Sept 1967. Taken in part from the Ph.D. Thesis of W. R. Knipple, Case Western Reserve University, 1968. (b) For the previous paper of this series, see R. L. Dannley, J. E. Gagen, and K. Zak, *J. Org. Chem.*, **38**, 1 (1973). (c) Supported in part by the U. S. Army Research Office (Durham) through Grant No. DA-ARO-(D)-31-124-G42. (d) Standard Oil Company of Ohio Fellow, 1966–1967.

[2] R. L. Dannley and E. C. Gregg, Jr., *J. Amer. Chem. Soc.*, **76**, 2997 (1954).

[3] D. R. Augood, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 2094 (1953).

[4] R. O. C. Norman and G. K. Radda, *Proc. Chem. Soc., London*, 138 (1962).

[5] A. F. Holleman, *Chem. Rev.*, **1**, 187 (1925).

[6] R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 3610 (1961).

[7] P. B. D. de la Mare and C. A. Vernon, *ibid.*, 1764 (1951).

[8] B. Jones and E. N. Richardson, *ibid.*, 3939 (1956).

[9] L. M. Stock and H. C. Brown, *J. Amer. Chem. Soc.*, **82**, 1942 (1960).

TABLE I

ORIENTATIONS, COMPETITIVE RELATIVE REACTIVITIES, AND THE CORRESPONDING PARTIAL RATE FACTORS FOR THE *m*-NITROPHENYLSULFONOXYLATION OF NITROBENZENE, METHYL BENZOATE, BROMOBENZENE, AND ANISOLE AND THE *p*-NITROPHENYLSULFONOXYLATION OF BROMOBENZENE

Arene	Temp, °C	Arylsulfonate yield, %	Isomer distribution, %			k_{Ar}/k_B	Partial rate factor		
			Ortho	Meta	Para		Ortho	Meta	Para
			m-Nitrophenylsulfonoxylation						
Nitrobenzene	20	65	24	65	11	0.0024	0.0017	0.0046	0.0015
Methyl benzoate	20	70	24	67	9	0.083	0.059	0.17	0.043
Anisole	−30	67	14	. . .	86	6200[a]	2600	. . .	32,000
Bromobenzene	20	66	21	3	76	0.47	0.29	0.042	2.1
			p-Nitrophenylsulfonoxylation						
Bromobenzene	20	72	22.8	4.7	72.5	0.49	0.366	0.068	2.1

[a] Competitive reaction run with mesitylene and this k_{An}/k_B calculated from the k_{Mes}/k_B kinetic value reported in Table IV.

(86% para, 14% ortho).[10] Arylsulfonoxylation is therefore usually, but not invariably, as selective in orientation as other electrophilic substitutions.

Relative Reactivities from Competitive Reactions.—From the relative yields of phenolic esters produced by decomposition of *m*-nitrobenzenesulfonyl peroxide in a mixture of the aromatic compound with benzene, the relative reactivities (k_{Ar}/k_B) in Table I were calculated. Unfortunately, these competitive reactions at the selected peroxide concentration usually had to be run in the absence of ethyl acetate (the solvent in the kinetic experiments). The restriction that both aromatic substrates must be present in sufficient quantity to prevent their concentrations from changing appreciably during the course of the reaction and the practical necessity that the ratio of the least reactive substrate to the more reactive substrate must be high to give measurable competition results in such a high molarity of aromatics that little ethyl acetate can be added. The value for anisole is of particularly limited accuracy because it is so reactive that it was necessary to run the competitive reaction with mesitylene at −30° and then calculate the k_{An}/k_B from the previously reported[1b] room temperature value for k_{Mes}/k_B. Inasmuch as the relative reactivities are dependent on temperature, the anisole value could easily be in error by a power of ten at room temperature. This value for anisole (7.0×10^3) is much smaller than the reported k_{An}/k_B for bromination (1.79×10^9),[11] chlorination (9.7×10^6),[11] or acetylation (2.9×10^5)[12] indicating a lower selectivity for the nitrophenylsulfonoxylation reaction. This is to be expected for such a reactive reagent. Only the mercuration of anisole is reported[10] to have a k_{An}/k_B (4.48×10^2) smaller than the value reported here.

The relative reactivities of nitrobenzene (2.4×10^{-3}) and methyl benzoate (8.3×10^{-2}) for *m*-nitrophenylsulfonoxylation are larger than those for other electrophilic substitutions such as the k_{Nit}/k_B for bromination (1.6×10^{-5})[13] or the $k_{PhCOOEt}/k_B$ (3.67×10^{-3})[14] for nitration, which is again consistent with a low specificity for the arylsulfonoxylation. In fact, a comparison of the relative reactivities of nitrobenzene and anisole gives a total range of reactivities for sulfonoxylation of only about 3×10^6.

Partial Rate Factors.—From the competitive relative reactivities and the orientations already discussed, the partial rate factors for *m*-nitrophenylsulfonoxylation were calculated (Table I). These partial rate factors are consistent with an electrophilic classification of the reaction.

One set of values is reported for a *p*-nitrophenylsulfonoxylation. As in previous papers,[1b] the use of *p*- and *m*-nitrobenzenesulfonyl peroxides gave essentially the same results in all respects when used in the substitution of an aromatic substrate, in the present case bromobenzene.

The partial rate factors are those expected for an electrophilic substitution except for the high para partial rate factors for the *m*- (2.1) and *p*-nitrophenylsulfonoxylation ((2.1) of bromobenzene. Similarly, the *m*-nitrophenylsulfonoxylation of chlorobenzene has been reported[15] to give a para partial rate factor of 3.7. Although para partial rate factors over 1.0 are not unknown for the deactivated nuclei of halobenzenes, they are not normally encountered.

π-Complex Formation.—Arylsulfonoxylation can readily be measured kinetically by iodometric titration for the disappearance of the peroxide content of a reaction mixture. The rate of disappearance of the peroxide has been found[1b] to correspond to a pseudo-first-order rate process. In a previous paper,[1b] π-complex formation was excluded as a rate-determining step in nitrophenylsulfonoxylation by comparison of the relative rates of substitution of mesitylene, *p*-xylene, and benzene. The half-life (50 hr) for the disappearance of *m*-nitrobenzenesulfonyl peroxide in an ethyl acetate solution 1 *M* in methyl benzoate at room temperature has now been found to be over twice as great as the corresponding half-life (20 hr) in neat ethyl acetate. A possible explanation for the longer half-life in the presence of methyl benzoate is the formation of a π complex between this substrate and the sulfonyl peroxide, although this π-complex formation need not be rate determining.

Order of the Reaction with Respect to Arene. From the pseudo-first-order rates of reaction (Table II) of *m*-nitrobenzenesulfonyl peroxide with varius concentrations of the arenes, the orders of reaction with respect to the aromatics were found to be, bromobenzene, 0.99; methyl benzoate, 0.97; and anisole, 1.00. The first-order relationships for these compounds are in agreement with all other benzene derivatives.[1b]

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[10] H. C. Brown and M. Dubeck, *J. Amer. Chem. Soc.*, **82**, 1939 (1960).

[11] L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

[12] H. C. Brown and G. Marino, *J. Amer. Chem. Soc.*, **84**, 1658 (1962).

[13] P. B. D. de la Mare and I. C. Hilton, *J. Chem. Soc.*, 997 (1962).

[14] C. K. Ingold and M. S. Smith, *ibid.*, 905 (1938).

[15] R. L. Dannley and G. E. Corbett, *J. Org. Chem.*, **31**, 153 (1966).

TABLE II

DEPENDENCE OF THE PSEUDO-FIRST-ORDER RATE OF DISAPPEARANCE OF *m*-NITROBENZENESULFONYL PEROXIDE (0.01 *M*) ON THE CONCENTRATION OF AROMATIC SUBSTRATE IN ETHYL ACETATE SOLUTIONS

Aromatic substrate	[Aromatic], *M*	$k \times 10^5$, sec^{-1}	*T*, °C
Bromobenzene	1.0	4.76	20
	1.5	7.01	20
	2.0	9.49	20
Methyl benzoate	1.0	0.906	20
	1.5	1.44	20
	2.0	1.93	20
	3.0	2.80	20
Anisole	0.067	15.0	−40
	0.13	31.6	−40
	0.20	47.7	−40
	0.33	74.2	−40

Kinetic Relative Reactivities.—From the pseudo-first-order rate constants (Table III), the relative reactivities given in Table IV were calculated. They differ by from 16 to 21% from the corresponding values obtained from competitive reactions, and similar differences have been found with other benzene derivatives.[1b] This is quite a close check for the competitive values were measured in the neat (or practically neat) aromatics while the kinetics were run in ethyl acetate solution. The solvent change would be expected to have an influence on the relative reactivities. Although both methods of measurement of relative reactivity are subject to certain conceptual as well as experimental errors, the kinetic method is the most reproducible. Therefore, the authors consider the kinetic values the more reliable and partial rate factors based on them are presented in Table V.

TABLE III

TEMPERATURE DEPENDENCE OF THE PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE REACTION OF *m*-NITROBENZENESULFONYL PEROXIDE WITH AROMATICS IN ETHYL ACETATE SOLUTION

Aromatic	*T*, °C	[Peroxide], *M*	[Aromatic], *M*	$k \times 10^5$, sec^{-1}
Benzene	20.0	0.01	1.0	8.56
Bromobenzene	10.1	0.01	1.0	1.48
	20.0	0.01	1.0	4.76
	30.0	0.01	1.0	14.4
	40.0	0.01	1.0	42.0
Methyl benzoate	10.1	0.01	1.0	0.266
	20.0	0.01	1.0	0.906
	30.0	0.01	1.0	2.84
Anisole	−40.0	0.0067	0.067	15.0[a]
	−35.0	0.0067	0.067	28.8[a]
	−30.0	0.0067	0.067	49.4[a]
	−25.1	0.0067	0.067	81[a]
Mesitylene	−30.2	0.0067	0.067	10.0[a]
	−25.1	0.0067	0.067	18.0[a]
	−20.0	0.0067	0.067	32.9[a]
	−15.0	0.0067	0.067	56.2[a]

[a] Second-order calculations were performed and the results then converted into pseudo-first-order rate constants at these concentrations of aromatics.

TABLE IV

PSEUDO-FIRST-ORDER RATE CONSTANTS AND RELATIVE REACTIVITIES AT 20° FOR THE REACTION OF *m*-NITROBENZENESULFONYL PEROXIDE WITH ARENES IN ETHYL ACETATE

Arene	[Peroxide], *M*	[Arene], *M*	$k \times 10^5$, sec^{-1}	k_{Ar}/k_B, kinetic	k_{Ar}/k_B, competitive
Benzene	0.01	1.0	8.56[a]	1.00	1.00
Anisole	0.0067	0.067	4300[b]	7500[c]	7000[e]
Bromobenzene	0.01	1.0	4.76	0.56	0.47
Methyl benzoate	0.01	1.0	0.906	0.106	0.083
Mesitylene	0.0067	0.067	1500[b]	2600[c,d]	. . .

[a] Value of 8.65×10^5 previously reported[1c] indicates reproducibility between different investigators using different samples of peroxides, etc. [b] Extrapolated from the values at lower temperatures. [c] Calculated by correcting the rate constant to 1.0 *M* using a first-order dependency on arene concentration. [d] A value of 2400 was reported[1c] previously by a similar extrapolation procedure. [e] Based on the k_{An}/k_{Mes} competitive values and k_{Mes}/k_B kinetic value of 2600 reported in this paper.

TABLE V

PARTIAL RATE FACTORS CALCULATED FROM KINETIC AND COMPETITIVE RELATIVE REACTIVITIES FOR THE *m*-NITROPHENYLSULFONOXYLATION OF ARENES

	Partial rate factors from— Kinetic k_{Ar}/k_B	Partial rate factors from— Competitive k_{Ar}/k_B
Anisole		
Ortho	3,150	2,940
Meta	. . .	. . .
Para	38,800	36,100
Bromobenzene		
Ortho	0.35	0.29
Meta	0.050	0.042
Para	2.6	2.1
Methyl benzoate		
Ortho	0.076	0.059
Meta	0.21	0.17
Para	0.057	0.043

The para partial rate factor for the *m*-nitrophenylsulfonoxylation of anisole (3.4×10^4) is similar to many other partial rate factors for reactions of anisole such as bromination (1.6×10^5),[16] acetylation (1.8×10^4),[12] mercuration (2.31×10^3),[10] deboronation (2.24×10^4),[17] etc. Ortho partial rate factors are less frequently given because of the low percentage of ortho substitution, but of the above substitutions the ortho partial rate factor for the mercuration of anisole (1.86×10^2)[10] is in the same range as the corresponding value for *m*-nitrophenylsulfonoxylation (2.8×10^3).

The partial rate factors for the *m*-nitrophenylsulfonoxylation of methyl benzoate (Table V) are all somewhat larger than the corresponding values (ortho, 0.26×10^{-2}; meta, 0.79×10^{-2}; para, 0.9×10^{-3}) for the nitration of ethyl benzoate[18] in acetic anhydride. Similarly, the meta partial rate factor for the *m*-nitrophenylsulfonoxylation of nitrobenzene (4.6×10^{-3}, Table I) is much larger than the 4.8×10^{-5} meta partial rate factor reported[19] for its bromination. The magnitude of these partial rate factors all point to a low selectivity for nitrophenylsulfonoxylation.

Hammett Correlation.—A least-squares plot of the logs of the partial rate factors against the corresponding σ^+ substituent contents is shown in Figure 1. A ρ value of −4.4 is obtained in contrast to a value of

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(16) G. Illuminati, *J. Amer. Chem. Soc.*, **80**, 4945 (1958).

(17) K. V. Nahabedian and H. G. Kuivila, *ibid.*, **83**, 2167 (1961).

(18) C. K. Ingold and M. S. Smith, *J. Chem. Soc.*, 918 (1938).

(19) L. M. Stock, "Aromatic Substitution Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1968.

−3.38 reported by Kobayashi and Minato[20] based only on toluene, chlorobenzene, and nitrobenzene figures. This fairly large negative value is in the range of the ρ values for mercuration (−4.0),[21] bromination (−5.78),[22] and nitration (−6.22).[23] This ρ value of −4.4 is therefore excellent confirmation of the classification of arylsulfonoxylation as an electrophilic substitution.

Activation Parameters.—From the rate constants given in Table III, the activation parameters in Table VI were calculated. As expected, the $\Delta H^{\ddagger}$ for the *m*-nitrophenylsulfonoxylation of methyl benzoate (19.6) and bromobenzene (19.1) are appreciably larger than the corresponding values for monoalkylbenzenes (15.2–15.5 kcal/mol), while the $\Delta H^{\ddagger}$ for anisole (12.3) is even lower than the value for mesitylene (13.3).[1b] These are all consistent with an electrophilic substitution.

TABLE VI

ACTIVATION PARAMETERS FOR THE *m*-NITROPHENYLSULFONOXYLATION OF BROMOBENZENE, METHYL BENZOATE, AND ANISOLE

Arene	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}
Bromobenzene	19.1 ± 0.1	−13.1 ± 0.1
Methyl benzoate	19.6 ± 0.1	−14.7 ± 0.1
Anisole	12.3 ± 0.4	−22.7 ± 0.2

The entropies of activation are more interesting. The $\Delta S^{\ddagger}$ for the *m*-nitrophenylsulfonoxylation of anisole (−22.8) is similar to the $\Delta\Delta S^{\ddagger}$ for this substitution obtained for mesitylene (−22.2) and *p*-xylene (−22.3) while all the monoalkylbenzenes have values of about −20.5 cal deg^{-1} mol^{-1}. The $\Delta S^{\ddagger}$ for methyl benzoate (−14.7) and bromobenzene (−13.1) are much less negative. Inasmuch as nitrophenylsulfonoxylation of each of these substrates occurs to only a small extent in the ortho position, steric hindrance can exert only a minor influence on the measured entropies of activation. The magnitudes of these entropies are consistent with more complete σ-bond formation (Wheland intermediate) in the transition state with electron-rich aromatics. A late transition state requires destruction of the aromatic π system, conversion of an sp^2 aromatic carbon into sp^3 configuration together with formation of a σ bond to a peroxidic oxygen, and probably stretching of the peroxide bond to an intimate ion pair and solvation of the ion pair. These influences cumulatively could result in a large negative $\Delta S^{\ddagger}$ for a late transition state with solvation being most significant of course.

The late transition state in electrophilic substitution of activated nuclei and an early transition state with deactivated nuclei may be a general phenomenon and not just characteristic of arylsulfonoxylation. Substitution involving other uncharged reagents, for example, sulfonation with sulfur trioxide, certainly might be expected to follow the same pattern. In addition, reactions such as bromination could behave similarly provided that ion or ion-pair formation from the reagent (*e.g.*, bromine) is not sufficient to lead to extensive solvation.

TABLE VII

MELTING POINTS OF ARYL NITROBENZENESULFONATES $(O_2NC_6H_4SO_3R)$[a]

R	Registry no.	Mp, °C
m-Nitrobenzenesulfonates		
Phenyl		92–93[b]
o-Bromophenyl	36601-36-2	94.5–95.5
m-Bromophenyl		133–134[b]
p-Bromophenyl	36601-37-3	108–109
o-Nitrophenyl		88–89[b]
m-Nitrophenyl		110.5–112[b]
p-Nitrophenyl		132–133[b]
o-Methoxyphenyl	36601-38-4	72.5–73.5
m-Methoxyphenyl	36601-58-9	69–70
p-Methoxyphenyl	36601-39-5	86–88
o-Carbomethoxyphenyl	36601-40-8	95–97
m-Carbomethoxyphenyl	36601-41-9	114–116
p-Carbomethoxyphenyl	36601-42-0	102.5–103.5
2,4,6-Trimethylphenyl	36601-43-1	106.5–108
p-Nitrobenzenesulfonates		
Phenyl		114–115[c]
o-Bromophenyl	36601-44-2	111.5–112.5
m-Bromophenyl	36601-45-3	126–128
p-Bromophenyl	36601-46-4	121.5–122.5

[a] Analysis for the elements gave maximum deviations from the theoretical values as follows: all C values ±0.39, H values ±0.22, N values ±0.17, S values ±0.22 for new compounds. [b] Lit. mp: phenyl, 88–89°; *m*-bromophenyl, 135–136°; *o*-nitrophenyl, 88–89°; *m*-nitrophenyl, 110.5–111.5°; *p*-nitrophenyl *m*-nitrobenzenesulfonate, 131–132.5° [H. H. Hodgson and J. H. Crook, *J. Chem. Soc.*, 1677 (1936)]. [c] Lit. mp 114° [F. Bell, *ibid.*, 2777 (1928)].

TABLE VIII

PROPERTIES[a] OF ARYL TRIMETHYLSILYL ETHERS $[ROSi(CH_3)_3]$

R	Registry no.	Bp, °C (3 mm)	$n^{20}D$
Phenyl		55[b]	1.4784[b]
o-Bromophenyl	36601-47-5	87	1.5136
m-Bromophenyl	76971-28-5	89.5	1.5148
p-Bromophenyl		91.3[c]	1.5153[c]
o-Nitrophenyl		114.5[d]	1.5085[d]
m-Nitrophenyl	34038-80-7	119.0	1.5094
p-Nitrophenyl		130.5[d]	1.5275[d]
o-Methoxyphenyl		86.0[e]	1.4886[e]
m-Methoxyphenyl	33285-71-1	91.0	1.4918
p-Methoxyphenyl	6689-38-9	92.5	1.4909
o-Carbomethoxyphenyl	18001-14-4	83.2[f]	1.4951
m-Carbomethoxyphenyl	27798-50-1	92.0[f]	1.4939
p-Carbomethoxyphenyl	27739-17-9	99.0[f]	1.5014
o-Carbotrimethylsiloxyphenyl	3789-85-3	111.0[f]	1.4797
m-Carbotrimethylsiloxyphenyl	3782-84-1	117.0[f]	1.4778
p-Carbotrimethylsiloxyphenyl	2078-13-9	127.6[f]	1.4854

[a] Analysis for the elements gave maximum deviations from the theoretical values as follows: all C values ±0.15, H values ±0.24, N values ±0.19 for new compounds. [b] Lit. bp 181.9° (742 mm), $n^{20}D$, 1.4782 [S. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958)]. [c] Lit. bp 126° (25 mm), $n^{25}D$, 1.5123 [L. Speier, *J. Amer. Chem. Soc.*, **74**, 1003 (1952)]. [d] Ortho: lit. bp 84° (1 mm), $n^{20}D$, 1.5090; para: lit. bp 95–96° (0.75 mm), $n^{20}D$, 1.5293 [M. Von Roshdy Ismall, *Z. Naturforsch*, *B*, **18**, 582 1962)]. [e] Lit. bp 217°, $n^{20}D$ 1.4855 [J. Kramer, *Chem. Ber.*, **92**, 2585 (1959)]. [f] Pressure, 1.5 mm.

[20] M. Kobayashi and H. Minato, Symposium on Organic Sulfur, Venice, June 15, 1970.

[21] H. C. Brown and C. W. McGary, *J. Amer. Chem. Soc.*, **77**, 2306 (1955).

[22] Y. Okomoto and T. Inukai, *ibid.*, **80**, 4964 (1958).

[23] H. C. Brown and Y. Okomoto, *ibid.*, **79**, 1913 (1957).

TABLE IX

REACTION OF *m*-NITROBENZENESULFONYL PEROXIDE WITH AROMATICS

Compound or quantity	Bromobenzene[a]		Bromobenzene		Anisole[b]		Methyl benzoate[c]		Nitrobenzene[d]	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Reaction in absence of benzene										
Peroxide, mmol	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Aromatic substrate, mmol	500	500	200	200	10	10	100	100	500	500
Ethyl acetate, ml	0	0	0	0	75	75	0	0	0	0
Sulfonate esters, % yield	71.1	72.5	68.4	62.7	69.5	64.2	74.1	66.5	65.3	65.5
Original ester, mmol										
Ortho	0.184	0.189	0.184	0.154	0.0886	0.0899	0.192	0.177	0.185	0.210
Meta	0.036	0.034	0.023	0.026	...	...	0.484	0.435	0.484	0.472
Para	0.538	0.552	0.526	0.493	0.606	0.552	0.065	0.053	0.086	0.086
Isomer distribution										
% ortho	22.5	22.6	24.7	22.4	12.9	14.0	25.9	26.6	23.8	27.0
% meta	4.8	4.4	3.0	3.6	...	...	65.3	65.4	64.9	61.7
% para	72.7	72.5	72.3	73.9	87.1	86.0	8.8	8.0	11.2	11.3
Competitive reaction										
Peroxide, mmol	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Benzene, mmol	100	100	100	100	0[e]	0[e]	10.	10.	9.	9.
Benzene derivative, mmol	500	500	500	500	25	25	300	300	900	900
Ethyl acetate, ml	0	0	0	0	70	70	51	51	0	0
Sulfonate esters, % yield	77.3	70.9	72.6	70.6	65.4	67.6	55.6	58.3	59.6	69.7
k_{Ar}/k_B	0.495	0.487	0.482	0.462	...[f]	...[f]	0.0815	0.0844	0.00232	0.00245
Original ester, mmol										
Phenyl	0.262	0.238	0.268	0.252	...[g]	...[g]	0.199	0.204	0.644	0.721
Ortho aryl	0.144	0.132	0.116	0.118	0.0672	0.0736	0.083	0.097	0.030	0.050
Meta aryl	0.028	0.024	0.018	0.016	...	...	0.241	0.253	0.088	0.101
Para aryl	0.414	0.384	0.409	0.402	0.4018	0.4254	0.033	0.029	0.014	0.016
Isomer distribution										
Ortho	22.8	22.8	21.1	21.6	14.1	14.8	23.1	24.7	22.6	26.1
Meta	4.7	4.6	3.1	2.9	...	...	67.9	66.8	66.7	62.9
Para	72.5	72.6	75.9	75.5	85.9	85.2	9.0	8.5	10.7	11.0

[a] Reaction with *p*-nitrobenzenesulfonyl peroxide. [b] Reaction run at −30° and analysis performed on a 150 ft × 0.01 in. capillary column of R-Ucon-LB 550-x at 130°. [c] Reaction run at room temperature for 48 hr and analysis performed with a 15 ft × 0.25 in. column at 180° of 5% SE-30 on Chromosorb W, DMCS, washed. [d] Reaction run at room temperature for 5 days and analysis performed on the column used for bromophenyl esters, but at 130°. [e] Mesitylene (25 mmol) used in place of benzene. [f] k_{An}/k_{Mes}: 2.55, 2.81. [g] Yield of 2,4,6-trimethylphenyl ester: 0.1846, 0.1774.

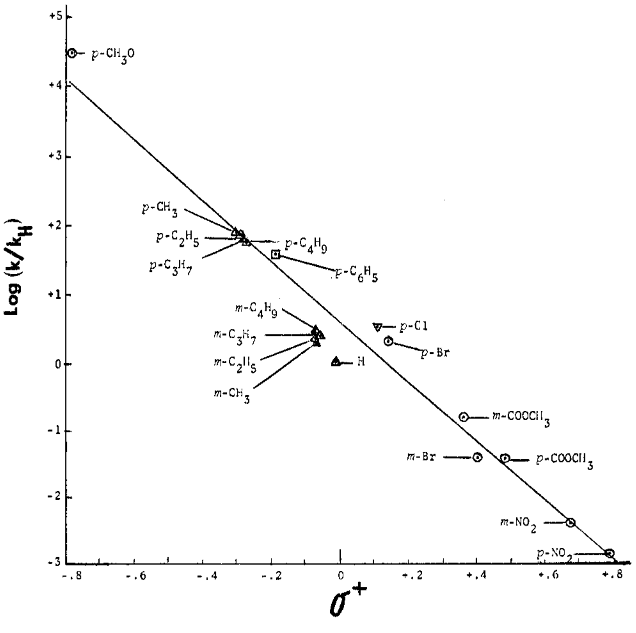

Figure 1.—Correlation of σ^+ and rate of *m*-nitrophenylsulfonoxylation: ⊙, from the present paper; △, from ref 24; ▽, from ref 15; ⊡, from the Ph.D. Thesis of F. Nelson Keeney, Western Reserve University.

Experimental Section

Aryl Nitrobenzenesulfonates.—Sodium (1.0 g, 0.04 g-atom) was dissolved in ethanol (80 ml), and the phenol (0.04 mol) was added. This mixture was added to a hot solution of *m*-nitrobenzenesulfonyl chloride (8.9 g, 0.04 mol) in benzene (40 ml). The mixture was refluxed and water (200 ml) added. The ester often separated as an oil, but crystallized when cooled overnight. Recrystallization from alcohol gave the esters listed in Table VII.

Phenyl Trimethylsilyl Ethers.—The phenol (0.07 mol), hexamethyldisilazane (11.3 g, 0.07 mol), and a trace of sand were mixed and refluxed for several hours. Distillation at reduced pressure gave the ethers listed in Table VIII.

***m*-Nitrobenzenesulfonoxylation of Benzene–Bromobenzene.**—*m*-Nitrobenzenesulfonyl peroxide[24] (0.404 g, 0.001 mol) was dissolved in a mixture of bromobenzene (78.5 g, 0.50 mol) and benzene (7.8 g, 0.10 mol), and the mixture was stirred (24 hr) at room temperature (20°). The excess aromatic solvents were then removed by distillation at reduced pressure leaving a residue of crude esters. This residue was dissolved in a solvent (methylene chloride and/or ethyl ether), transferred to a Fischer-Porter Aerosol tube, and the solvent evaporated *in vacuo*. A small magnetic stirring bar and 6 ml of a 20% potassium hydroxide solution in methanol–water (50:50) were added. The sealed tube was heated (24 hr) at 145° in an oil bath. Hydrochloric acid (3 *N*, 50 ml) was added and the acidic solution extracted three times with chloroform (30-ml portions) and three times with benzene (30-ml portions).

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[24] R. L. Dannley, J. E. Gagen, and O. J. Stewart, *J. Org. Chem.*, **35**, 3076 (1970).

The combined extracts were concentrated by distilling the solvents at atmospheric pressure. When the volume had been reduced to 50 ml, dry benzene (10 ml) was added and the distillation continued until near dryness. The residue was treated with hexamethyldisilazane (5.0 g, 0.031 mol) and a trace of sand. The mixture was refluxed for several hours and then analyzed by glpc using a 15 ft × 0.125 in. column packed with 5% SE-30 on Chromosorb W at 110° (Table IX). Relative yields for hydrolysis of the isomeric esters and conversion into the silyl ethers were determined using authentic samples. Identification of the glpc peaks from the m-nitrophenylsulfonoxylation reaction was accomplished not only by comparison of retention times with authentic esters but also by trapping samples from the chromatographic column and comparing their infrared spectra to those of authentic samples.

Essentially the same procedure was used for the competitive reactions with other substrates with the minor differences given in Table IX.

Kinetics.—The procedure previously described[1b] was followed to titrate iodometrically for the disappearance of the peroxide content of the reaction mixtures.

Registry No.—Bromobenzene, 108-86-1; methyl benzoate, 93-58-3; nitrobenzene, 98-95-3; anisole, 100-66-3; m-nitrobenzenesulfonyl peroxide, 6209-71-8; benzene, 71-43-2; mesitylene, 108-67-8; p-nitrobenzenesulfonyl peroxide, 6209-72-9.

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The Reaction of Arylsulfonyl Azides with N-Methylindole

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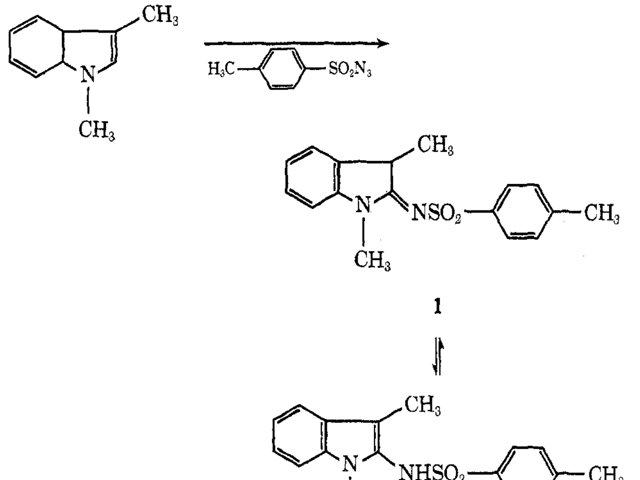
The reaction of several substituted arylsulfonyl azides with N-methylindole using p-dioxane as solvent yielded mixtures of the expected 2-sulfonamido and the unexpected 3-sulfonamido derivatives. In solution (DMSO-d_6) the 2-sulfonamides showed tautomeric equilibrium between the amino and the imino forms, whereas in crystalline form they existed mainly as the imino tautomers. The corresponding 3-sulfonamides existed only in the amino form. Using ethanol as solvent, the reaction of arylsulfonyl azides with N-methylindole afforded N-(3-diazo-1-methyl-2-indolinylidene)benzenesulfonamides. The same diazo compounds were obtained by treating the 2-sulfonamido derivatives with an excess of the appropriate arylsulfonyl azide, thereby providing the first example of a diazo transfer reaction to an amidine.

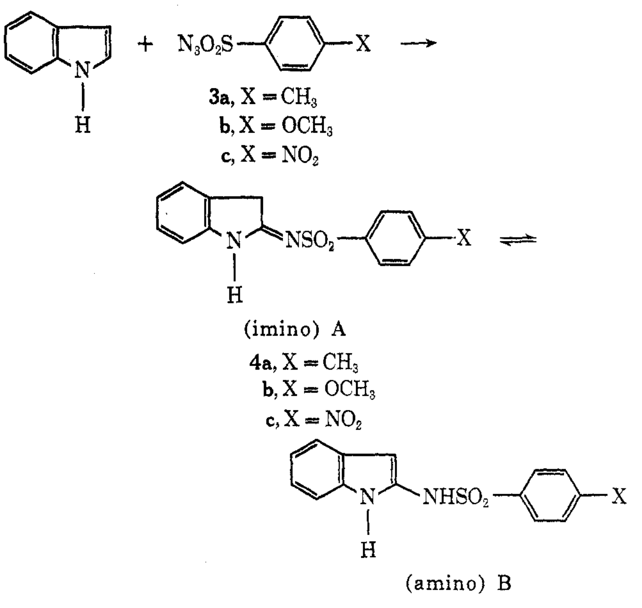
During the past several years Bailey and coworkers[1-5] have reported the results of their investigations on the reaction of arylsulfonyl azides with indole and alkylindoles. According to them the addition of p-toluenesulfonyl azide to 1,3-dimethylindole yielded an equilibrium mixture containing the 2-sulfonamido derivatives **1** and **2**. Bailey, *et al.*,[4] observed by nmr that the equilibrium between the tautomers **1** and **2** was solvent dependent, the imino form **1** predominating in chloroform while in dimethyl sulfoxide the amino form **2** predominates. In mixtures of these two solvents, both tautomers were present in appreciable amounts. We have investigated the above tautomeric equilibrium as a function of substituents on the arylsulfonyl azide. During the course of this study it was found that N-methylindole was more amenable to study the tautomeric equilibrium ratios than indole or dimethylindole used by Bailey, *et al.*[2,4]



1

2

The Reactions of Arylsulfonyl Azides with Indole.—Our preliminary investigation based on the work reported by Bailey, *et al.*,[2] involved the reaction between three arylsulfonyl azides (**3a–c**) and indole. The



3a, X = CH_3
b, X = OCH_3
c, X = NO_2

(imino) A

4a, X = CH_3
b, X = OCH_3
c, X = NO_2

(amino) B

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(1) A. S. Bailey and J. J. Merer, *J. Chem. Soc. C*, 1345 (1966).

(2) A. S. Bailey, N. C. Churn, and J. J. Wedgwood, *Tetrahedron Lett.*, 5953 (1968).

(3) A. S. Bailey, W. A. Warr, G. B. Allison, and C. K. Prout, *J. Chem. Soc. C*, 956 (1970).

(4) A. S. Bailey, R. Scattergood, and W. A. Warr, *Tetrahedron Lett.*, 2979 (1970).

(5) A. S. Bailey, A. J. Holton, and J. F. Seager, *J. Chem. Soc., Perkin Trans. 1*, 1503 (1972).