Arylsulfonoxylation of Aromatic Compounds.
II. Partial Rate Factors for the Nitrophenylsulfonoxylation of Alkylbenzenes[1a-c]

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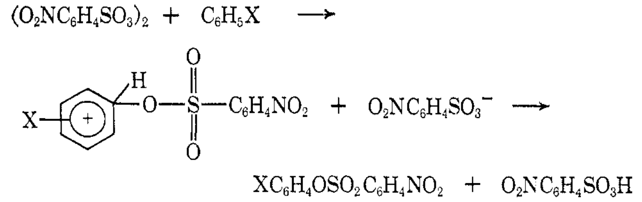
Ethyl acetate is resistant to attack by nitrobenzenesulfonyl peroxides and is a suitable solvent for sulfonoxylations. In the thermal decomposition of *o*- and *m*-nitrobenzenesulfonyl peroxides in alkylbenzenes there are no products resulting from a side-chain hydrogen abstraction characteristic of a homolytic reaction. Competitive *o*- and *m*-nitrophenylsulfonoxylations gave, respectively, for k_{Ar}/k_B: benzene, 1.0; toluene, 13.3, 19.0; ethylbenzene, 11.5, 17.6; cumene, 9.0, 13.5; *t*-butylbenzene, 6.0, 11.9. The *ortho*, *meta*, and *para* orientations (partial rate factors) for *o*-nitrophenylsulfonoxylations follow: toluene, 35.3, 2.7, 62.0% (14.1, 1.1, 49.5); ethylbenzene, 30.6, 4.4, 65.0% (10.5, 1.5, 44.8); cumene, 22.3, 8.9, 68.0% (6.0, 2.4, 36.8); *t*-butylbenzene, 9.0, 19.8, 71.2% (1.6, 3.4, 25.6). The corresponding figures for *m*-nitrophenylsulfonoxylations are: toluene, 31.8, 3.5, 64.7% (18.1, 2.0, 73.8); ethylbenzene, 29.9, 4.3, 65.8% (15.8, 2.3, 69.4); cumene, 23.5, 6.5, 70.0% (9.5, 2.6, 56.7); *t*-butylbenzene, 7.4, 18.1, 74.5% (2.6, 6.5, 53.3). These data are all consistent with an electrophilic classification of the substitution reaction. *m*-Nitrophenylsulfonoxylation is somewhat more selective than *o*-nitrosulfonoxylation.

In the first paper of this series, the partial rate factors obtained for the substitution of toluene and chlorobenzene by *m*-nitrobenzenesulfonyl peroxide led tentatively to an electrophilic ionic classification of the mechanism of the reaction. Confirmation of this ionic classification is needed, however, for heterolytic dissociations of symmetrical peroxides are not common in the absence of strong Lewis acids. In the present work, the decompositions of *o*- and *m*-nitrobenzenesulfonyl peroxides in toluene, ethylbenzene, cumene, and *t*-butylbenzene were studied to determine first, whether higher order side-chain hydrogens would undergo abstraction such as is common in the presence of free radicals; second, the degree of steric hindrance encountered toward *ortho* substitution with increasing bulk of the alkyl group; third, the relation of the *meta* and *para* partial rate factors to the Baker–Nathan order; and fourth, whether the position of the nitro group in the peroxide affects the course of the reactions.



Results and Discussion

In previous work[1b,2] and the first efforts of the present investigations, the sulfonoxylations of benzene derivatives were performed using the aromatic compound as both substrate and solvent. In a general study of the substitution reaction this dual use of the aromatic component is sometimes impossible and always undesirable. It is impossible if the substrate is a crystalline solid. It is undesirable even with liquid aromatics because a change in substrate may also produce major changes (for example, a variation in the dielectric constant) in the reaction mixture. Therefore, in the present work, some of the first efforts were devoted to the selection of an appropriate inert solvent. Ethyl acetate and acetonitrile were found to be more resistant to attack by the nitrobenzenesulfonyl peroxides than other common organic liquids. Ethyl acetate is particularly useful in the nitrophenylsulfonoxylations because it not only ensures reasonable similarity of the reaction mixtures while using different aromatic substrates, but in addition provides homogeneous solutions, for the nitrobenzenesulfonic acids which form are soluble in ethyl acetate, although they are quite insoluble in aromatic hydrocarbons. Essentially identical orientations and relative reactivities were obtained for the nitrophenylsulfonoxylation of several alkylbenzenes in both the absence and presence of ethyl acetate. Therefore, some substitution experiments which already had been completed using an arene as both substrate and solvent were not repeated using ethyl acetate as a solvent.

The ionic classification of the peroxide decomposition is now supported by the absence of any side-chain-attack products in the reactions of both *o*- and *m*-nitrobenzenesulfonyl peroxides with toluene, ethylbenzene, and cumene, although concentrations as low as 1% of such products could be detected. Cumene is normally particularly susceptible to side-chain hydrogen abstraction by free radicals and yields bicumyl when treated with many typical free-radical reagents such as benzoyl peroxide,[3] Fenton's reagent,[4] or diisopropyl peroxydicarbonate.[5] The complete absence of bicumyl in the present work therefore provides strong evidence that the nitrobenzenesulfonyl peroxides are not undergoing any homolytic scission.

Competitive reactions in which *m*-nitrobenzenesulfonyl peroxide decomposed in a mixture of benzene and an arene gave k_{Ar}/k_B as follows: toluene, 19.0; ethylbenzene, 17.6; cumene, 13.5; and *t*-butylbenzene, 11.9. For *o*-nitrophenylsulfonoxylation the figures obtained were: toluene, 13.3; ethylbenzene, 11.5; cumene,

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[1] (a) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, No. S078. Taken in part from the Ph.D. Thesis of J. E. Gagen, Case Western Reserve University, 1967. (b) For the previous paper in this series, see R. L. Dannley and G. E. Corbett, *J. Org. Chem.*, **31**, 153 (1966). (c) Supported in part by the U. S. Army Research Office (Durham) through Grant No. DA-ARO(D)-31-124-G42. (d) NASA Trainee, 1965–1967.

[2] L. W. Crovatt and R. L. McKee, *J. Org. Chem.*, **24**, 2031 (1959).

[3] D. H. Hey, B. W. Pengilly, and G. H. Williams, *J. Chem. Soc.*, 1463 (1956).

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

[5] H. C. McBay and O. Tucker, *J. Org. Chem.*, **19**, 869 (1954).

9.0; *t*-butylbenzene, 6.0. Therefore with both the peroxides the sequence of the reactivities of the hydrocarbons parallels the Baker–Nathan order. The magnitudes of the relative reactivities are similar to those for nitration of the arenes with acetyl nitrate in acetic anhydride.[6] The yields of esters (65–93%, Table VI) compare favorably with those for other electrophilic substitutions.

A comparison of the isomer distributions, Table I, shows a regular decrease in *ortho* substitution with increasing bulk of the alkyl group. However, the *meta/para* ratio also increases markedly, which is characteristic of electronic and not steric influences. The arylsulfonoxy entering group cannot have a much larger steric requirement than a nitronium ion, for the *ortho* substitution of *t*-butylbenzene is fairly similar for introduction of these two substituents.

TABLE I

ISOMER DISTRIBUTIONS FOR THE NITROPHENYLSULFONOXYLATIONS OF ALKYLBENZENES

	o-Nitrophenylsulfonoxylation			*m*-Nitrophenylsulfonoxylation		
Substrate	% *o*	% *m*	% *p*	% *o*	% *m*	% *p*
Toluene	35.3	2.7	62.0	31.8	3.5	64.7
Ethylbenzene	30.6	4.4	65.0	29.9	4.3	65.8
Cumene	22.3	8.9	68.0	23.5	6.5	70.0
t-Butylbenzene	9.0	19.8	71.2	7.4	18.1	74.5

The partial rate factors calculated from these data (Table II) strongly support the heterolytic classification of the substitution. They are numerically in the same general range as those for nitration, bromination, etc.[7] The magnitude of all of the partial rate factors, but particularly the *para* values (25.6–73.8), are much greater than the comparable figures (*para*, 1.4[3]) for the phenylation of alkyl benzenes, a well-established free radical process. Again support for an electrophilic mechanism is obtained.

TABLE II

PARTIAL RATE FACTORS FOR THE NITROPHENYLSULFONOXYLATION OF ALKYLBENZENES

	o-Nitrophenylsulfonoxylation			*m*-Nitrophenylsulfonoxylation		
Substrate	*o*	*m*	*p*	*o*	*m*	*p*
Toluene	14.1	1.1	49.5	18.1	2.0	73.8
Ethylbenzene	10.5	1.5	44.8	15.8	2.3	69.4
Cumene	6.0	2.4	36.8	9.5	2.6	56.7
t-Butylbenzene	1.6	3.4	25.6	2.6	6.5	53.3

There is a regular decrease in the *para* partial rate factors using both peroxides when the branching of the alkyl group increases. This parallels the Baker–Nathan order and, in agreement with the series of relative reactivities, substantiates a σ complex formation as the rate-determining step. The *meta* partial rate factors, in contrast, increase in the progression from toluene to *t*-butylbenzene for both *o*- and *m*-nitrophenylsulfonoxylation. This is expected from the inductive effect of the alkyl substituents, for resonance influences are not predominant for the *meta* substitutions.

The orientations and partial rate factors demonstrate qualitatively a slightly greater selectivity for *m*-nitrophenylsulfonoxylation than for *o*-nitrophenylsulfonoxylation. This selectivity difference perhaps might have been anticipated because the *ortho* peroxide is less stable (more reactive) than its *para* isomer. The selectivity factors, S_f, are about 1.6 for both reactions but are of limited accuracy because they are dependent on the precision of measurement of very small quantities of the *meta* isomers.

In summary, all of these data are consistent with an electrophilic substitution reaction with no evidence of any free-radical characteristics.

The potential use of this substitution as a synthesis of phenols leads to a comparison with the similar substitution using a peroxydicarbonate and aluminum chloride.[8] The nitrophenylsulfonoxylation is preferred in that it is successful with both activated and deactivated nuclei,[9] while peroxydicarbonate substitution essentially has the Friedel–Crafts limitations. The nitrobenzenesulfonyl peroxides are also safer to work with than the unstable peroxydicarbonate esters. The nitrophenylsulfonoxylation is the less attractive synthesis, however, in that the nitrobenzenesulfonate esters produced are much more difficult to hydrolyze than carbonate esters. The reactions are therefore probably best described as competitive in value.

Experimental Section

Materials.—Spectroquality reagent grade benzene and reagent grade toluene, ethylbenzene, cumene, and *t*-butylbenzene were all redistilled before use. Ethyl acetate was purified by the method of Hurd and Strong.[10] Bicymyl- and *meso*- and DL-2,3-diphenylbutanes[11] were prepared by treatment of the proper alkylbenzene with *t*-butyl peroxide. In the experiments determining the half-lives of the *m*-nitrobenzenesulfonyl peroxide in various solvents, the highest grade commercially available solvents were used as received.

***m*-Nitrobenzenesulfonyl peroxide** was obtained in improved yield using minor modifications of the literature[1b] synthesis. *m*-Nitrobenzenesulfonyl chloride (11.1 g, 0.05 mol) in chloroform (15 ml) was added to a cold (−20°) solution of potassium carbonate (8.5 g) in water (140 ml), ethanol (70 ml), and hydrogen peroxide (20 g, 30%) in a Waring blender cup. Agitation was slowly increased to full power and held there for 1 min. Ethanol (100 ml) was then added and the mixture agitated slowly for a few minutes. The resulting precipitate was collected by filtration, washed thoroughly with water, and dried under vacuum. The crude material (96% yield, 95% pure by peroxide titration) decomposed explosively at 105° (lit.[1b] mp 112° dec). The crude peroxide was dissolved in acetone at room temperature, the solution filtered, and the filtrate concentrated under reduced pressure to yield 97% pure peroxide (5 g, 49.5% yield) which decomposed at 107°.

By an identical procedure, *o*-nitrobenzenesulfonyl peroxide (30% yield, 98% pure) is obtained as crystals which sometimes explode on touching and decompose explosively at 94° (lit.[1b] 97°). If this peroxide is stored at room temperature, it loses about 10% of its active oxygen content in 30 days. The same procedure gives *p*-nitrobenzenesulfonyl peroxide (40% yield, 99% pure) as a white powder which is stable to handling but at 127° decomposes explosively (lit.[1b] mp 128° dec).

Nitrobenzenesulfonate esters were prepared from the phenols and the sulfonyl chloride in alcohol–benzene (procedure A)[12]

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[6] J. R. Knowles, R. O. C. Norman, and G. K. Radda, *J. Chem. Soc.*, 4885 (1960).

[7] L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 36 (1963).

[8] P. Kovacic and M. Kurz, *J. Amer. Chem. Soc.*, **87**, 4811 (1965).

[9] W. R. Knipple, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1968.

[10] C. D. Hurd and J. S. Strong, *Ind. Eng. Chem.*, *Anal. Ed.*, **23**, 542 (1951).

[11] B. Zaremsky, Ph.D. Thesis, Western Reserve University, Cleveland, Ohio, 1954.

[12] G. Leandri, G. Monaco, and L. Spinelli, *Ann. Chim. (Rome)*, **49**, 407 (1959).

or aqueous alkali (procedure B).[13] The physical parameters and yields of these compounds are listed in Tables III and IV.

TABLE III

MELTING POINTS AND SYNTHESIS METHODS[a] OF ARYL *m*-NITROBENZENESULFONATES (m-$O_2NC_6H_4SO_3C_4H_4R$)

R	Registry no.	Mp, °C	Synthesis method
H		92–94[b]	A
o-Methyl		61–62[c]	A
m-Methyl		73[d]	A
p-Methyl		106–108[e]	A
o-Ethyl	25238-10-2	Liq	B
m-Ethyl	25238-11-3	Liq	B
p-Ethyl	25238-12-4	42–44	B
o-Isopropyl	25238-13-5	31–32	B
m-Isopropyl	25238-14-6	Liq	B
p-Isopropyl	25238-15-7	34–36	B
o-*t*-Butyl	25238-16-8	80–82	A
m-*t*-Butyl	25238-17-9	Liq	B
p-*t*-Butyl	25238-18-0	95	A

[a] All C, H, N values within ±0.3% for new compounds. [b] Lit. mp 93–95.[1b] [c] Lit. mp 61–63.[1b] [d] Lit. mp 72–74.[1b] [e] Lit. mp 109–110.[1b]

TABLE IV

MELTING POINTS AND ANALYSES[a] OF ARYL *o*-NITROBENZENESULFONATES (o-$O_2NC_6H_4SO_3C_6H_4R$)

R	Registry no.	Mp, °C	Yield, %
H		55–56[b]	18
o-Methyl	25238-19-1	57–58	50
m-Methyl	25238-20-4	64–65	75
p-Methyl		90–91[c]	75
o-Ethyl	25238-21-5	35–36	19
m-Ethyl	25238-22-6	24.5–26	19
p-Ethyl	25238-23-7	62	60
o-Isopropyl	25238-24-8	Liq	15
m-Isopropyl	25238-25-9	36–37	27
p-Isopropyl	25238-26-0	27–28	40
o-*t*-Butyl	25238-27-1	106.5–108	42
m-*t*-Butyl	25237-68-7	54–56	24
p-*t*-Butyl	252382-57-9	44–46	30

[a] All C, H, N values within ±0.3% for new compounds. [b] Lit. mp 57°: R. Vizgert and E. K. Savchuk, *Zh. Obshch. Khim.*, **26**, 2261 (1956). [c] Lit. mp 88–90°: G. Schetty, *Helv. Chim. Acta*, **32**, 24 (1949).

Aryl trimethylsilyl ethers were prepared by refluxing for 6 hr the phenol (0.025 mol) and hexamethyldisilazane (0.25 mol) with a little sand and vacuum distilling the product. The physical parameters and yields of these compounds are listed in Table V.

TABLE V

PROPERTIES[a] OF ARYL TRIMETHYLSILYL ETHERS ($RC_6H_4OSi(CH_3)_3$)

R	Registry no.	Bp, °C (1 mm)	$n^{25}D$ (temp, °C)
H		51–51.5	1.4761[b]
o-Methyl	10009-02-5	50–50.5	1.4805 (20)[c]
m-Methyl	17902-31-7	53–53.5	1.4790 (20)[c]
p-Methyl	17902-32-8	53.53.5	1.4755[c]
o-Ethyl	17993-88-3	65.5–66	1.4770[d]
m-Ethyl	17993-89-4	64–64.5	1.4784 (20)[d]
p-Ethyl	17993-90-7	66.5–67	1.4760[d]
o-Isopropyl	25237-75-6	64.5–65	1.4768
m-Isopropyl	25237-76-7	71	1.4785 (20)
p-Isopropyl	25237-77-8	74.5	1.4760
o-*t*-Butyl	25282-58-0	85.5	1.4838
m-*t*-Butyl	25237-78-9	78.0	1.4773 (20)
p-*t*-Butyl	25237-79-0	83.0	1.4807 (20)

[a] All C, H values within ±0.3%. [b] Lit. $n^{20}D$ 1.4782: S. H. Langer, I. Connell, and S. Wender, *J. Org. Chem.*, **23**, 50 (1958). [c] Lit. *ortho* $n^{20}D$ 1.4812, *meta* $n^{20}D$ 1.4796, *para* $n^{20}D$ 1.4738: F. A. Henglein and J. Kramer, *Chem. Ber.*, **92**, 2585 (1959). [d] S. H. Langer, P. Pantages, and S. Wender, *Chem. Ind.* (*London*), 1664 (1958).

Selection of a Suitable Solvent.—Aliquots (5 ml) of solutions (0.03–0.04 *M*) of *m*-nitrobenzenesulfonyl peroxide in various solvents at room temperature were removed at intervals and titrated for the peroxide content.[14] The half-lives in hours at room temperature were: chloroform, 1.5; diglyme, 3; acetone, 4.7; nitroethane, 19; ethyl acetate, 20; and acetonitrile, 23. In dimethylformamide the decomposition was immediate. The decomposition in ethyl acetate was first-order with respect to peroxide but in acetonitrile the order was complex. Ethyl acetate was the solvent of choice because of its inertness to the peroxide, its excellent solvent characteristics for the nitrobenzenesulfonic acids, and because in it the kinetic order for disappearance of the peroxide was the same as for the peroxide in pure aromatic substrates.

m-**Nitrophenylsulfonoxylation of Alkylbenzenes.**—To a mixture of alkylbenzene (0.01 mol) and benzene (0.05 mol), diluted to 50 ml with ethyl acetate, was added *m*-nitrobenzenesulfonyl peroxide (0.0005 mol). After 3 hr at room temperature the peroxide content had disappeared. The toluene, benzene, and ethyl acetate were removed by distillation and ether was used to transfer the residue to an aerosol compatibility tube. The ether was removed by gentle warming of the tube which was purged with nitrogen. A solution (15 ml) of 20% potassium hydroxide in methanol–water (50–50) was added and the closed tube was heated to 145° for 19 hr. The tube was cooled, opened, and the mixture acidified with 50 ml of hydrochloric acid (3 *N*) and extracted with benzene (100 ml). The benzene extract was dried with magnesium sulfate and filtered. The benzene was evaporated from the filtrate, and hexamethyldisilazane (4 ml) and a pinch of sand were added to the residue. After this mixture had been refluxed for 2 hr and an internal standard added (Table VI), the mixture was analyzed by glpc using a 10 ft × 0.25 in. column packed with 5% STAP on 80–100 mesh Chromosorb G. From a rough calculation of the composition of the mixture, assuming areas and concentrations were proportional, a mixture of the pure trimethylsilyl ethers of approximately the same composition was prepared and calibration factors were determined. Using these factors, the true composition of the trimethylsilyl ether mixture was determined and using the hydrolysis yields the composition of the original ester mixture calculated.

In no case was a fraction obtained with a retention time corresponding to that of a side-chain coupling product, although a 1% yield would be detected.

In the *t*-butylbenzene run, the glpc analysis was performed using a 150-ft capillary column coated with SE-30 Silicone "Z." Even using this column the resolution of the *ortho* and *meta* peaks was not complete and the reproducibility was poor.

Calibration Factors for the Conversion of Aryl Nitrobenzenesulfonate Esters to Silyl Ethers.—A mixture of pure isomeric alkylphenyl and phenyl nitrobenzenesulfonate esters in the same ratio of composition, calculated roughly from the chromatogram of a substitution reaction, was subjected to the hydrolysis procedure just described. As yields varied appreciably with minor variations in procedure, calibration runs were always performed along with the substitution determinations. Typical overall yields of silyl ethers are given in Table VII.

Although some of these yields are as low as 40.3%, the isomer percentages are considered generally accurate to about 5% of the significant figures. This is confirmed by a comparison of *o*- and *p*-nitrophenylsulfonoxylation figures which show regular relationships although they are based on different conversion figures obtained by two independent experimentalists using somewhat different times of hydrolysis reactions and techniques.

Validity of the Analytical Procedure.—If hydrolysis of some of the sulfonate esters occurred in the reaction mixture before the alkaline hydrolysis, excessively high yields of phenolic esters would be obtained by using the calibration factors. To determine if this were true, *m*-nitrobenzenesulfonyl peroxide (0.0005 mol) was dissolved in benzene (0.05 mol), *t*-butylbenzene (0.01 mol), and enough ethyl acetate to give a total volume of 50 ml.

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[13] H. R. Slagh and E. C. Britton, *J. Amer. Chem. Soc.*, **72**, 2808 (1950).

[14] R. N. Haszeldine, R. B. Hislop, and J. W. Lethbridge, *J. Chem. Soc.*, 4901 (1964).

TABLE VI

REACTION OF *o*- AND *m*-NITROBENZENESULFONYL PEROXIDES WITH ARENES

	Toluene		Ethylbenzene		Cumene		*t*-Butylbenzene	
Compd or quantity	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
o-Nitrophenylsufonoxylation								
Peroxide (mmol)	0.0005	0.0005	0.001	0.001	0.0005	0.0005	0.0005	0.0005
RC_6H_5 (mmol)	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Benzene (mmol)	0.50	0.50	0.50	0.50	0.50	0.50	0.05	0.5
Ethyl acetate	0	0	0	0	0	0	to 50 ml	0
Sulfonate esters, % yield	86	93	84	75	64.6	65.0	76.6	73.8
k_{Ar}/k_B	13.06	13.52	11.5	11.4	8.8	9.2	6.0	6.0
Isomer distribution								
% *ortho*	35.8	34.8	30.4	30.9	21.0	23.7	10.4	7.6
% *meta*	3.15	2.27	3.57	5.18	9.2	8.6	19.8	19.8
% *para*	61.1	62.9	66.0	63.9	69.8	67.7	69.8	72.6
Partial rate factor								
ortho	14.0	14.1	10.5	10.6	5.53	6.6	1.9	1.4
meta	1.2	0.92	1.2	1.8	2.4	2.4	3.6	3.6
para	48.0	51.0	45.7	43.8	36.8	36.0	25.1	26.2
Internal standard	*p*-Trimethylsilyloxyethylbenzene		*o*-Trimethylsilyloxytoluene		*p*-Trimethylsilyloxytoluene		*p*-Trimethylsilyloxytoluene	
m-Nitrophenylsulfonoxylation								
Peroxide (mmol)	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
RC_6H_5 (mmol)	0.01	0.01	0.1	0.01	0.1	0.1	0.01	0.1
Benzene (mmol)	0.05	0.05	0.5	0.05	0.5	0.5	0.5	0.5
Ethyl acetate	To 50 ml	To 50 ml	None	To 50 ml	None	None	To 50 ml	None
Sulfonate esters, % yield	76.1	72.4	89.2	91.6	92.2	77.5	83	53.8
k_{Ar}/k_B	18.8	19.1	18.5	16.7	13.2	13.9	13.2	10.6
Isomer distribution								
% *ortho*	31.7	31.9	30.2	29.6	23.6	23.4	8.4	6.4
% *meta*	3.5	3.5	4.1	4.5	6.3	6.7	18.0	18.2
% *para*	64.8	64.6	65.7	65.9	70.1	69.9	73.6	75.4
Partial rate factors								
ortho	17.9	18.3	16.7	14.8	9.3	9.8	3.3	2.0
meta	2.0	2.0	2.3	2.3	2.5	2.8	7.1	5.8
para	73.0	74.6	72.9	66.0	55.5	58.2	58.2	47.9

TABLE VII

OVERALL YIELDS FOR THE CONVERSION OF NITROPHENYL AND PHENYL SULFONATES TO THE PHENOLIC TRIMETHYLSILYL ETHERS

Ester source		% yield of ether			
Peroxide	Hydrocarbon	Phenyl	*ortho* R	*meta* R	*para* R
m-Nitro	Toluene	39.4	54.1	83.5	57.8
m-Nitro	Ethylbenzene	45.9	64.5	61.5	67.6
m-Nitro	Cumene	42.8	40.3	87.4	90.7
m-Nitro	*t*-Butylbenzene	46.0	64.8	62.0	67.9
o-Nitro	Toluene	96	100	91	92
o-Nitro	Ethylbenzene	87	90	90	100
o-Nitro	Cumene	91	91	97	97
o-Nitro	*t*-Butylbenzene	50.4	36.7	88.9	80.8

After 24 hr at 25°, the solvents were removed by distillation and the residue was refluxed with hexamethylsilazane (4 ml) for 2 hr. Analysis (glpc) showed that the phenyl and all three isomeric *t*-butylphenyl trimethylsilyl ethers were absent. Therefore no hydrolysis of the sulfonate esters occurs in the reaction mixture.

Registry No.—Table V, R = *m*-Me, 17902-31-7; Table V, R = *p*-Me, 17902-32-8; Table V, R = *o*-Et, 17993-88-3; Table V, R = *m*-Et, 17993-89-4; Table V, R = *p*-Et, 17993-90-7; Table V, R = *o*-*i*-Pr, 25237-75-6; Table V, R = *m*-*i*-Pr, 25237-76-7; Table V, R = *p*-*i*-Pr, 25237-77-8; Table V, R = *o*-*t*-Bu, 25282-58-0; Table V, R = *m*-*t*-Bu, 25237-78-9; Table V, R = *p*-*t*-Bu, 25237-79-0; *o*-nitrobenzenesulfonyl peroxide, 5279-06-1; *m*-nitrobenzenesulfonyl peroxide, 5354-00-7.

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