TABLE VII

PERTINENT INFRARED ABSORBANCES USED IN THE IDENTIFICATION OF SOME PREVIOUSLY UNREPORTED COMPOUNDS PREPARED FOR THIS INVESTIGATION

Compd.	Wave length region, μ				
	0.0–3.0	5.5–6.0	6.0–7.0	8.0–10.0	10.0–11.0
γ-Benzylidenebutyryl peroxide		5.55–5.64 (s) (doublet)		9.38 (s)	10.32 (s)
γ-(*p*-Chlorobenzylidene)butyric acid		6.82 (s)	6.67 (s)		10.33 (s)
γ-(*p*-Chlorobenzylidene)butyryl peroxide		5.50–5.60 (s) (doublet)	6.70 (s)	9.13–9.40 (s) (doublet)	10.32 (s)
α-(*p*-Fluorophenyl)allyl alcohol	2.30 (m) 3.40 (s)		6.22 (s) 6.62 (s)	8.13 (s) 8.63 (s)	10.10 (s) 10.75 (s)
p-Fluorocinnamyl bromide			6.22 (s) 6.62 (s)	8.11 (s) 8.31 (s) 8.61 (s)	10.37 (s)
γ-(*p*-Fluorobenzylidene)butyric acid		5.61 (s)	6.20 (m) 6.60 (s)	8.10 (s) 8.60 (s)	10.33 (s)
γ-(*p*-Fluorobenzylidene)butyryl peroxide		5.5–5.59 (s) (doublet)	6.22 (m) 6.62 (s)	8.21 (s) 8.62 (m)	10.35 (m)
γ-(*p*-Methylbenzylidene)butyric acid		5.86 (s)	7.10 (m)		10.36 (s)
γ-(*p*-Methylbenzylidene)butyryl peroxide		5.51–5.61 (s) (doublet)		9.43 (m)	10.35 (m)
γ-(*p*-Methoxybenzylidene)butyric acid		5.98 (s)	6.28 (m)	8.07 (s)	10.25 (m)
δ-(*p*-Methoxyphenyl)valeryl peroxide		5.54–5.61 (s) (doublet)	6.64 (s) 6.22 (m) 6.86 (m)	8.04 (s) 8.56 (m) 9.67 (m)	

acid separated as a white, creamy solid. It was extracted into ether; the latter was washed with water and dried over magnesium sulfate, and the ether was removed. The resulting solid was recrystallized from toluene. The over-all yield of γ-(*p*-methoxybenzylidene)butyric acid from the ethyl ester of the keto acid was 67%. Some chemical and physical properties of this acid are listed in Table VI; its infrared spectrum is described in Table VII.

BDPA was synthesized by the method of Koelsch[8a] as modified by Solar and Lindquist,[8b] and also by the simpler procedure of Kuhn and Neugebauer.[8d]

Kinetic Runs.—The techniques used in the spectrophotometric kinetics runs have been described in previous papers.[9a,b] The same wave length (λ_{max} 490 mμ) was used for runs in benzene and in propylene carbonate. The difficulty in obtaining precise values of the extinction coefficient of BDPA has been discussed.[9b] The values 26,300 and 24,100 were used throughout for benzene and propylene carbonate runs, respectively.

Values of f were calculated from the formula $f = (D_0 - D_\infty)/2\epsilon(\text{In})_0$, where D = absorbance, ϵ = extinction coefficient, and $(\text{In})_0 = (\text{P})_0$ = initial molar concentration of peroxide.

Rate constants were obtained by least-squares adjustment of the absorbance–time data to the formula

$$\log 100(D - D_\infty) = -\frac{k_d}{2.303}t + \log 100(D_0 - D_\infty)$$

The standard deviations in k_d were calculated by standard statistical procedures.

Nitrobenzenesulfonyl Peroxides as Reagents for Aromatic Substitution[1]

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The three isomeric bis(nitrobenzenesulfonyl) peroxides have been prepared in 22–45% yield and found to be quite stable at room temperature. The thermal decomposition of *m*-nitrobenzenesulfonyl peroxide in benzene, fluorobenzene, chlorobenzene, and toluene produces 1 mole of *m*-nitrobenzenesulfonic acid and a 56–70% yield of the phenolic esters resulting from substitution in the aromatic substrate. The exclusive *ortho–para* substitution leads to the following orientations: fluorobenzene, 11% *ortho*, 89% *para;* chlorobenzene, 22%, 78%; and toluene, 35%, 65%. From the relative yields and orientations of the esters obtained from mixtures of benzene or toluene with chlorobenzene, the following partial rate factors were obtained: benzene, 1; chlorobenzene, *ortho* 0.5, *para* 3.7; and toluene, 17, 65. These data are most consistent with the classification of the reaction as an electrophilic substitution.

The published chemistry of the bis(arylsulfonyl) peroxides is very limited. After the synthesis of bis(benzenesulfonyl) peroxide in 1903,[2] no further work was reported until 1924 when Fichter and Stock[3] described its decomposition in water to form phenol, sulfuric acid, and presumably benzenesulfonic acid. In 1946 Walter[4] patented the use of *p*-toluenesulfonyl peroxide as a polymerization catalyst. Crovatt and McKee[5] recently attempted unsuccessfully to improve the yields of synthesis of benzenesulfonyl peroxide, investigated its use as a catalyst for vinyl polymerization, and found that its thermal decomposition in benzene produced phenyl benzenesulfonate.

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[1] Supported by the U. S. Army Research Office (Durham) through Grant No. DA-ARO(D)-31-124-G242.

[2] R. F. Weinland and H. Lewkowitz, *Ber.*, **36**, 2702 (1903).

[3] F. Fichter and E. Stocker, *Helv. Chim. Acta*, **7**, 1071 (1924).

[4] H. A. Walter, U. S. Patent 2,467,280; *Chem. Abstr.* **43**, 6002 (1949).

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

TABLE I

MELTING POINTS AND ANALYSES OF ARYL *m*-NITROBENZENESULFONATES (m-$O_2NC_6H_4SO_3R$)

	M.p., °C.		Calcd., %					Found, %				
R	Obsd.	Lit.	C	H	N	S	X	C	H	N	S	X
Phenyl	93–95	91–92[a]	...	...	...	...	...	...	...	...	...	...
o-Fluorophenyl	79–80	...	48.49	2.71	4.71	10.78	6.39	48.44	2.75	4.62	10.76	6.63
m-Fluorophenyl	86–87	90–91[a]	48.49	2.71	4.71	10.78	6.39	48.64	2.75	4.70	10.72	6.46
p-Fluorophenyl	127.5–129	...	48.49	2.71	4.71	10.78	6.39	48.40	2.74	4.59	10.63	6.57
o-Chlorophenyl	91–93	...	45.94	2.57	4.47	10.22	11.30	45.90	2.70	4.48	10.38	11.30
m-Chlorophenyl	111–112	111–112[a]	...	...	...	...	...	...	...	...	...	...
p-Chlorophenyl	102–103	104–105[b]	...	...	...	...	...	...	...	...	...	...
o-Tolyl	61–63	...	53.23	3.78	4.78	10.93	...	53.24	3.80	4.66	11.18	...
m-Tolyl	72–74	...	53.23	3.78	4.78	10.93	...	53.15	3.72	4.74	10.80	...
p-Tolyl	109–110	...	53.23	3.78	4.78	10.93	...	53.18	3.63	4.79	11.22	...

[a] H. H. Hodgson and J. H. Crook, *J. Chem. Soc.*, 1677 (1936). [b] H. R. Slagh and E. C. Britton, *J. Am. Chem. Soc.*, **72**, 2808 (1950).

TABLE II

BISARYLSULFONYL PEROXIDES

			Calcd., %					Found, %				
Peroxide	M.p. (dec.), °C.	% yield	C	H	N	S	Active O	C	H	N	S	Active O
o-Nitrobenzenesulfonyl	97	22	35.64	1.99	6.93	15.86	3.95	35.60	1.85	6.62	15.60	3.90
m-Nitrobenzenesulfonyl	112	30	35.64	1.99	6.93	15.86	3.95	35.72	2.07	6.82	16.10	3.90
p-Nitrobenzenesulfonyl	128	45	35.64	1.99	6.93	15.86	3.95	35.90	2.06	6.82	15.84	

The substitution reaction with an aromatic nucleus is apparently characteristic of sulfonyl peroxides, for Haszeldine, Heslop, and Lethbridge[6] have more recently reported that bis(methanesulfonyl) peroxide reacts with both benzene and toluene to produce aryl sulfonates. Unfortunately, the preparation of bis(methanesulfonyl) peroxide is difficult and somewhat dangerous.

As the substitution in an aromatic nucleus by a sulfonyl peroxide offers promise as a novel synthesis of phenols, the present work was undertaken: first, to develop an improved synthesis of arylsulfonyl peroxides; second, to prepare substituted arylsulfonyl peroxides in which greater thermal stability might be encountered; and third, to determine partial rate factors in selected benzene derivatives for substitution by a typical sulfonyl peroxide.

Experimental Section

Materials.—The benzenesulfonyl chlorides and the solvents were all commercially available and were recrystallized or fractionally distilled when necessary. The benzenesulfonate esters required as reference compounds were synthesized by the following typical procedure. *p*-Fluorophenol (2.3 g.) was dissolved in ethanol (40 ml.) and sodium (0.5 g.) was added. To the resultant solution (heated to boiling) was added a hot solution of *m*-nitrobenzenesulfonyl chloride (5 g.) dissolved in benzene (20 ml.). Water (100 ml.) was added and the mixture was placed overnight in a refrigerator. The product was collected by filtration and recrystallized from ethanol–heptane to produce *p-fluorophenyl m-nitrobenzenesulfonate* (5.0 g., 79%), m.p. 127.5–129°. The esters prepared in this fashion are listed in Table I.

Sulfonyl Peroxide Syntheses.—*m*-Nitrobenzenesulfonyl chloride (22 g., 0.1 mole) dissolved in chloroform (20 ml.) was added with shaking to a cold (−20°) solution of potassium carbonate (20 g.) in water (300 ml.), ethanol (150 ml.), and hydrogen peroxide (5 g., 98%). After a few minutes a precipitate formed, and ethanol (150 ml.) was added to make the liquid phases miscible. The crude product (16.5 g., m.p. 100° dec.) was collected by filtration and extracted with chloroform and/or acetone (*ca.* 200 ml.). The extracts were combined and concentrated under reduced pressure to yield bis(*m*-nitrobenzenesulfonyl) peroxide (6.1 g., 30%), m.p. 112° dec.

TABLE III

REACTION OF *m*-NITROBENZENESULFONYL PEROXIDE WITH BENZENE (100 ML.)

	mmoles	
Compound	Run 1	Run 2
m-Nitrobenzenesulfonyl peroxide	0.99	1.00
m-Nitrobenzenesulfonic acid (by titration)	0.96	1.01
Crude sodium *m*-nitrobenzenesulfonate	1.01	1.02
Crude phenyl *m*-nitrobenzenesulfonate	0.91	0.92
Pure phenyl *m*-nitrobenzenesulfonate	0.75	0.72
Total m-$NO_2C_6H_4SO_3$ accounted for	1.71	1.73

By an essentially identical procedure the *ortho* and *para* isomers were prepared with the results shown in Table II. The infrared spectra of the peroxides and the corresponding acid chlorides did not differ uniformly in any way to permit a spectral method of identification.

In preliminary studies, other peroxides were obtained, but these substances detonated (often spontaneously) when dry, and analytical results could not be obtained. Bolte, Kergomard, and Vincent[7] recently prepared *p*-toluenesulfonyl and *p*-bromobenzenesulfonyl peroxide and similarly found them too unstable to analyze and resorted to the use of crude products. The compounds of unproved purity here obtained were: benzenesulfonyl peroxide, m.p. 66° (lit.[5] m.p. 53–54°); *p*-toluenesulfonyl peroxide, m.p. *ca.* 40° (lit.[7] m.p. 50°); *p*-chlorobenzenesulfonyl peroxide, m.p. 72° (lit.[7] m.p. 75°); *p*-bromobenzenesulfonyl peroxide, m.p. 76°; and 3,4-dichlorobenzenesulfonyl peroxide, m.p. 72°.

Reaction of *m*-Nitrobenzenesulfonyl Peroxide with Benzene.—*m*-Nitrobenzenesulfonyl peroxide (0.404 g., 0.001 mole) was dissolved in dry benzene (100 ml.) and allowed to stand (24 hr.) at room temperature. The mixture was extracted with water until the washings were neutral, the extract was titrated with sodium hydroxide, and the neutralized extract was evaporated to dryness to give crude sodium *m*-nitrobenzenesulfonate, identified as the benzylisothiourea derivative, m.p. 145–146° (lit.[8] m.p. 146.1). The benzene raffinate was dried with Drierite and evaporated to dryness, and the crude ester residue was purified by chromatography on alumina, eluting with chloroform. Admixture with an authentic sample of phenyl *m*-nitrobenzenesulfonate (m.p. 90–92°) showed no depression of melting point. The results are listed in Table III.

Analysis of Isomeric Aryl *m*-Nitrobenzenesulfonate Mixtures.—Infrared and gas chromatographic analyses of the esters

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

[7] J. Bolte, A. Kergomard, and S. Vincent, *Tetrahedron Letters*, **No. 21**, 1529 (1965).

[8] E. Chambers and G. W. Watt, *J. Org. Chem.*, **6**, 376 (1941).

themselves were found not to be possible. The isomeric phenols produced by hydrolysis could be analyzed, however. Conventional hydrolysis in a reflux setup open to the atmosphere led to nonreproducible figures owing to losses of vapors (particularly of *ortho* isomers). Hydrolysis in sealed tubes followed by extraction produced solutions which gave reproducible analyses.

Procedure.—The total yield of crude ester (*ca.* 0.25 g.) was sealed in an ampoule with 0.3 *N* sodium hydroxide–sodium carbonate (5 ml.) and heated to 130° for 3 days. The mixture was transferred to a Dean–Stark apparatus and the water was removed by azeotropic distillation with benzene or cyclohexane. The anhydrous solution of the phenols was then analyzed by gas chromatography on Carbowax 20M at 225°. Pure isomers and mixtures of the pure isomers were subjected to this procedure to check for any isomerization and to provide calibration curves. The total yields of esters from substituted benzenes obtained by this method (56–69%) are somewhat lower than the yield of phenyl *p*-nitrobenzenesulfonate (73%) obtained by chromatography of the reaction mixture from benzene itself as a substrate.

Reaction of *m*-Nitrobenzenesulfonyl Peroxide with Fluorobenzene.—By the isolation procedure described for the decomposition of the peroxide in benzene and the analytical method just described, the results listed in Table IV were obtained. From the application of the procedure to pure isomeric esters, it was found that the reference *ortho* ester gave other products as well as *o*-fluorophenol but did not give *m*- or *p*-fluorophenol. The reference *para* ester gave only *p*-fluorophenol. The reference *meta* ester gave *m*-fluorophenol plus other products. The reaction mixture gave no *m*-fluorophenol, but both the *ortho* and *para* isomers were present. The analytical procedure was therefore appropriate.

TABLE IV

REACTION OF *m*-NITROBENZENESULFONYL PEROXIDE WITH FLUOROBENZENE (100 ML.)

Reagent or product	mmole Run 1	mmole Run 2
Peroxide	1.00	1.00
m-Nitrobenzenesulfonic acid (titration)	0.98	1.00
Crude sodium *m*-nitrobenzenesulfonate	1.10	1.10
Crude ester mixture[a]	0.92	0.92
Total ester (by gas chromatography)	0.61[b]	0.61[b]

[a] Assuming it is all $C_{12}H_8FNO_5S$. [b] 11% *ortho*, 89% *para*.

Reaction of *m*-Nitrobenzenesulfonyl Peroxide with Chlorobenzene.—The pure isomers were found to give a single peak in the gas chromatograph upon hydrolysis. The fraction giving the *meta–para* peak from the reaction mixture was collected, and its infrared spectrum showed only a trace of the *meta* isomer. The results are shown in Table V.

TABLE V

REACTION OF *m*-NITROBENZENESULFONYL PEROXIDE WITH CHLOROBENZENE (100 ML.)

Reagent or product	mmole Run 1	mmole Run 2
Peroxide	1.00	1.00
m-Nitrobenzenesulfonic acid (titration)	0.94	0.95
Crude ester mixture[a]	0.87	0.91
Total ester (by gas chromatography)	0.59[b]	...[c]

[a] Assuming it is all $C_{12}H_8ClNO_5S$. [b] 22.5% *ortho*, 77.5% *para*. [c] Material lost in transference: 19% *ortho*, 81% *para*.

Reaction of *m*-Nitrobenzenesulfonyl Peroxide with Toluene.—Application of the previously described analytical procedures to the pure isomeric cresyl esters showed that no rearrangement of the cresols occurred during analysis. Gas chromatography of the cresols from the substitution reaction gave three peaks. One peak was too small to permit trapping and identification, but its retention time was proper for bibenzyl which would be expected from a radical reaction. The other two peaks proved to be the pure *ortho* and *para* isomers by trapping and identification by the infrared spectra. The results are shown in Table VI.

TABLE VI

REACTION OF *m*-NITROBENZENESULFONYL PEROXIDE WITH TOLUENE (100 ML.)

Reagent or product	mmole Run 1	mmole Run 2
Peroxide	1.00	1.00
m-Nitrobenzenesulfonic acid (by titration)	1.00	1.01
Crude sodium *m*-nitrobenzenesulfonate	1.10	1.14
Crude ester[a]	0.71	...[b]
Total esters (by gas chromatography)	0.56[c]	...[b]

[a] Assuming it is all $C_{13}H_{11}NO_5S$. [b] 34% *ortho*, 66% *para*; material lost in transference. [c] 36% *ortho*, 64% *para*.

Decomposition of *m*-Nitrobenzenesulfonyl Peroxide in Benzene–Chlorobenzene.—*m*-Nitrobenzenesulfonyl peroxide (0.404 g.) was decomposed in a mixture of benzene (19.5 g.) and chlorobenzene (80 g.). The crude ester mixture (isolated as previously described) was adsorbed on a column (10 g.) of alumina (Peter Spence, Type M) and eluted with 100 ml. of benzene. The eluent was evaporated to dryness and the residue was analyzed for chlorine and sulfur with the results shown in Table VII.

TABLE VII

REACTION OF *m*-NITROBENZENESULFONYL PEROXIDE WITH BENZENE–CHLOROBENZENE

Quantity measured	Run 1	Run 2
Peroxide (mmole)	1.00	1.00
Benzene (mmoles)	249	249
Chlorobenzene (mmoles)	713	713
Weight ester (g.)	0.225	0.242
Cl in ester (%)	7.79[a]	7.89[b]
Chloro ester in ester mixture (%)	70.2	71.0
S in ester (%)	11.05[c]	11.23[d]
Partial rate factor, *ortho*[e]	0.51	0.54
Partial rate factor, *para*[e]	3.7	3.8

[a] Average of 7.94 and 7.64. [b] Average of 8.02 and 7.76. [c] Average of 11.15 and 10.94. [d] Average of 11.15 and 11.31. [e] Calculated from per cent Cl and using 22:78 for the *ortho*:*para* ratio of substitution in chlorobenzene.

The partial rate factors for chlorobenzene shown were calculated from the chlorine analysis assuming that this fraction was composed exclusively of the sulfonate esters. The sulfur analysis was somewhat too high to correspond to the proposed ester composition. Since the sulfur analyses of the reference isomers (see Table I) were sometimes similarly high, the deviations are probably not significant and the partial rate factors are fairly reliable. If one assumes, however, that the high sulfur values are due to *m*-nitrobenzenesulfonic acid as an impurity, the following partial rate factors are calculated: *ortho*, 0.93; *para*, 6.6. Troubles were encountered in determining partial rate factors by gas chromatography of the phenols but rough figures of *ortho* (0.3) and *para* (1.8) were obtained.

Decomposition of *m*-Nitrobenzenesulfonyl Peroxide in Toluene–Chlorobenzene.—By a procedure identical with that for the benzene–chlorobenzene determination, the decomposition of *m*-nitrobenzenesulfonyl peroxide (0.404 g.) in a mixture of

TABLE VIII

REACTION OF *m*-NITROBENZENESULFONYL PEROXIDE WITH TOLUENE–CHLOROBENZENE

Quantity measured	Run 1	Run 2
Peroxide (mmole)	1.00	1.00
Toluene (mmoles)	200	200
Chlorobenzene (mmoles)	2000	2000
Weight ester (g.)	0.204	0.192
Cl in ester (%)	3.70[a]	3.66[b]
S in ester (%)	11.45[c]	11.64[d]
Partial rate factor, *ortho*	17	17
Partial rate factor, *para*	63	64

[a] Average of 3.88 and 3.51. [b] Average of 3.56 and 3.76. [c] Average of 11.52 and 11.39. [d] Average of 11.75 and 11.53.

toluene (18.4 g.) and chlorobenzene (225 g.) led to the results listed in Table VIII.

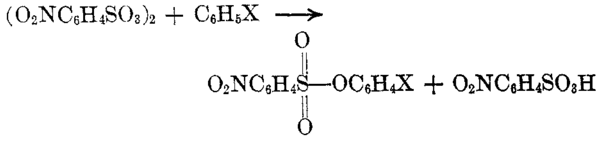
The reported rate factors for toluene are calculated from the chlorine analysis only. The sulfur values are again too high, and if they are assumed to arise from *m*-nitrobenzenesulfonic acid as an impurity, the partial rate factors for toluene are: *ortho*, 19.6; *para*, 72.9. Troubles were again encountered using gas chromatographic analysis of the phenols, but the crude partial rate factors thus determined were *ortho*, 10; *para*, 43.

Discussion

Of all the arylsulfonyl peroxides synthesized in the present work only the nitro derivatives could be safely used as chemical reagents in routine laboratory work. Their stability arises from the electron-withdrawing inductive effect of the nitro group. This stabilizing effect was anticipated, for in peroxidic carbon systems[9] it has been found that factors leading to reduced electron density on peroxidic oxygens generally reduce the thermal lability of the compounds. The stability of the *m*-nitrobenzenesulfonyl peroxide proves that the effect of the nitro group in these compounds is inductive and not resonance in nature. The three isomeric nitrobenzenesulfonyl peroxides were equally safe to handle; the *meta* compound was selected as a reagent for aromatic substitution studies *only* because of its greater availability.

The decomposition of *m*-nitrobenzenesulfonyl peroxide in aromatic solvents (as evidenced by sulfonic acid formation) is so rapid that kinetic experiments have not yet been attempted. If traces of moisture are present, a precipitate forms within a few moments after placing the sulfonyl peroxide in an aromatic solvent. The addition of water was found to have no effect on the nature or quantities of products, however.

The reactions of aromatic substitution are comparable in material balance to the aromatic phenylations obtained with aroyl peroxides. The recovery of



$$(O_2NC_6H_4SO_3)_2 + C_6H_5X \longrightarrow O_2NC_6H_4\overset{O}{\underset{O}{S}}{-}OC_6H_4X + O_2NC_6H_4SO_3H \qquad (1)$$

the *m*-nitrobenzenesulfonic acid is reasonably quantitative, obeying the stoichiometry of eq. 1. The sulfonate esters are obtained in yields appreciably lower than theoretical. Thus, from the substitution reaction in benzene, the yield of phenyl *m*-nitrobenzenesulfonate (isolated as the pure ester, Table III, by column chromatography) was 73%. The discrepancy from a 100% yield may result from polysubstitution. No attempt has been made as yet to isolate any polyhydric phenol products.

The exclusive *ortho–para* substitution might be produced by either an electrophilic or homolytic process. From studies of molecular models and the fact that fluorobenzene has the lowest percentage of *ortho* substitution, steric hindrance is not significant in the present work. The substitution in toluene is similar to that obtained using methanesulfonyl peroxide (34% *ortho*, 6% *meta*, 60% *para*)[6] which Haszeldine, Heslop, and Lethbridge considered to proceed by a free-radical mechanism.

The partial rate factors in Tables VII and VIII are of limited accuracy, but their magnitude is certainly not that expected for a homolytic substitution. For homolytic phenylations, partial rate factors[10] for the *ortho* position vary from 1.8 to 6.8 (toluene, 1.4; chlorobenzene, 2.6), unless there is great steric hindrance, and for the *para* position from 1.2 to 6.6 (toluene, 1.4; chlorobenzene, 1.6). Although the partial rate factor for *m*-nitrophenylsulfonoxylation of the *para* position in chlorobenzene (3.8) fits this pattern fairly well, the low value for the *ortho* position (0.52) in chlorobenzene and the high partial rate factors for both the *ortho* (17) and *para* (63) positions of toluene are not those expected for a homolytic reaction. The benzenesulfonyloxy radical should be much more electrophilic, however, than the much-studied phenyl radicals, and this could conceivably lead to some deviation[11] from the familiar pattern.

The partial rate factors are most consistent, however, with an ionic electrophilic substitution. The ionic classification of the reaction is also substantiated by the inability to detect by e.s.r. any free radicals in a reacting solution of *m*-nitrobenzenesulfonyl peroxide in benzene.

This aromatic substitution reaction offers some promise as synthetic tool because the required nitrobenzenesulfonyl peroxides are readily available and safe to handle, the resultant esters easily hydrolyzed, and the phenols are isolated in good yield.

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(9) C. G. Swain, W. H. Stockmayer, and J. T. Clark, *J. Am. Chem. Soc.*, **72**, 5426 (1950).

(10) D. R. Augood and G. H. Williams, *Chem. Rev.*, **57**, 176 (1957).

(11) R. L. Dannley and M. Sternfeld, *J. Am. Chem. Soc.*, **76**, 4543 (1954).