Arylsulfonoxylation of Aromatic Compounds. V. An Oxygen-18 Tracer Study of the p-Nitrophenylsulfonoxylation of Arenes[1]

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p-Nitrobenzenesulfonyl peroxide labeled with oxygen-18 in the sulfonyl oxygens was used to arylsulfonoxylate *p*-xylene and benzene to produce aryl *p*-nitrobenzenesulfonates in which the labeling of the phenolic oxygens was determined by mass spectral studies of the esters themselves or their hydrolysis products. From substitutions previously established to be kinetically clean first order with respect to arene (*p*-xylene in ethyl acetate solution and benzene in methylene chloride) the phenolic oxygens of the arylsulfonates arose exclusively from the peroxidic oxygens of the peroxide. Arylsulfonoxylation of benzene in ethyl acetate solution, which has previously been kinetically established to proceed 35% by a competing zero-order process, now from labeling experiments is found to give 41% of product incorporating sulfonyl oxygen of the peroxide as phenolic oxygen of the ester. In neat benzene, *p*-nitrophenylsulfonoxylation produces an ester arising 30.3% from the sulfonyl oxygens of the reagent. Possible mechanisms for these reactions are discussed.

The reaction of aromatic compounds with substituted benzenesulfonyl peroxides to give the corresponding aryl nitrobenzenesulfonates has been classified as an electrophilic substitution[2-7] on the basis of partial rate factors for the nitrophenylsulfonoxylationof monosubstituted benzenes, esr measurements of the reacting solutions, and the lack of side-chain hydrogen abstraction from alkylbenzenes.

Kinetic studies[4,5] have revealed that benzene derivatives behave identically upon arylsulfonoxylation in that a clean first-order rate dependence on arene concentration is observed in both ethyl acetate and methylene chloride as solvents. The arylsulfonoxylation of benzene itself, in contrast, exhibits a first-order dependence with respect to the aromatic only in methylene chloride; in ethyl acetate a partial (0.66–0.70) order is obtained. This fractional order results from a competition to the familiar first-order reaction by a reaction zero order with respect to benzene.[4]

Three possible mechanisms involving the introduction of electropositive oxygen into the nucleus of an aromatic substrate and one for a radical substitution are given in Chart I. Which of these four mechanisms is operative might be established by nitrophenylsulfonoxylatingarenes with a peroxide labeled with oxygen-18 in one of each pair of sulfonyl oxygens and determining the amount of incorporation of the oxygen-18 label in the phenolic oxygen of the resultant ester. If the reaction proceeds through **1**, the phenolic oxygen of **5** will contain no oxygen-18. If the mechanism involves **2**, the percentage of oxygen-18 in the phenolic oxygen of **5** should be one-half that of a labeled sulfonyl oxygen of the peroxide. If the ion pair **3** or radical **4** is the

Chart I

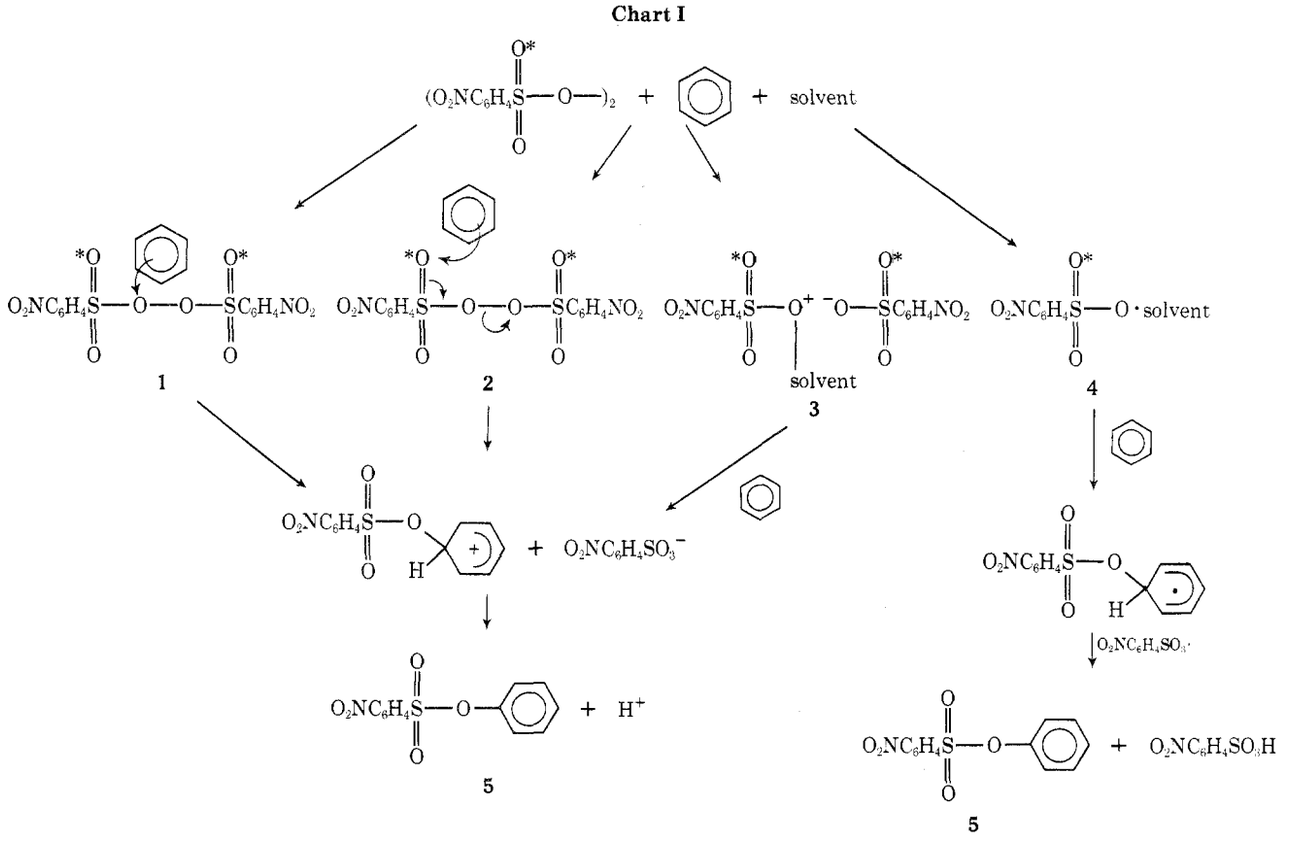


Table I
Mass Spectral Data and Isotope Ratios for the Reagents and Products

Expt	Comp	Registry no.	Ion	Number of scans	(M + 2)/M	% oxygen-18 excess[a]
1[b]	*p*-Xylyl *p*-nitrobenzenesulfonate	51821-10-4	$O_2NC_6H_4SO_3C_8H_7^+$	15[i]	0.1075[c]	4.02
1[b]	*p*-Xylyl *p*-nitrobenzenesulfonate		$O_2NC_6H_4SO_2^+$	16[i]	0.0984[d]	4.13
2	*p*-Nitrobenzenesulfonyl chloride	98-74-8	$O_2NC_6H_4SO_2^-$	10[i]	0.0907[f]	3.97
2[e]	Phenyl trimethylsilyl ether	1529-17-5	$C_6H_5SO_3Si(CH_3)_3^+$	11[i]	0.0455[g]	−0.003
3	*p*-Nitrobenzenesulfonyl chloride		$O_2NC_6H_4SO_2Cl^+$	2[k]	0.4380[d]	5.58
3[b]	Phenyl trimethylsilyl ether		$C_6H_5OSi(CH_3)_3^-$	8[i]	0.0552[g]	1.13
4[b]	Phenyl *p*-nitrobenzenesulfonate	32337-46-5	$O_2NC_6H_4SO_3C_6H_5^-$	8[i]	0.1274[h]	6.02
4[b]	Phenyl *p*-nitrobenzenesulfonate		$O_2NC_6H_4SO_2^-$	8[i]	0.1051[d]	4.77
5[i]	Phenyl *p*-nitrobenzenesulfonate		$O_2NC_6H_4SO_3C_6H_5^+$	13[j]	0.1236[h]	5.68
5[i]	Phenyl *p*-nitrobenzenesulfonate		$O_2NC_6H_4SO_2^+$	13[i]	0.1056[d]	4.82

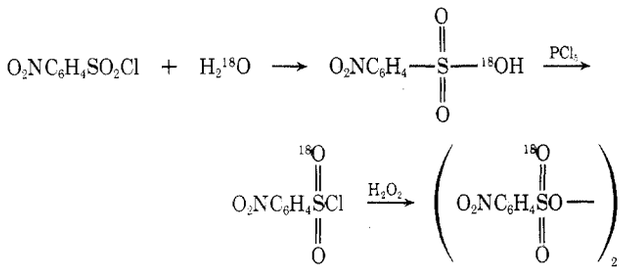
[a] Calculated for excess oxygen-18 in one oxygen only. [b] Reaction run in ethyl acetate solution. [c] Statistical value 0.0651 without labeling. [d] Statistical value 0.0550. [e] Reaction run in methylene chloride. [f] Statistical value 0.3789. [g] Statistical value 0.0438. [h] Statistical value 0.0634. [i] Reaction run in neat benzene. [j] Reference 9. [k] Reference 10.

proper intermediate, the phenolic oxygen of **5** should have one-third of the oxygen-18 concentration originally present in the peroxide's labeled sulfonyl oxygen.

In the present work labeling experiments were planned to clarify the mechanisms of the sulfonoxylation first order with respect to arenes and also the reaction in ethyl acetate zero order with respect to benzene.

Results and Discussion

Labeling of the Peroxide. Hydrolysis of *p*-nitrobenzenesulfonyl chloride with water enriched in oxygen-18 and treatment of the resultant acid with phosphorus pentachloride regenerated the sulfonyl chloride with one of its two oxygens labeled with oxygen-18. The acid chloride was converted to the peroxide as described in the literature.[3]



The labeling of the peroxide was measured by one of two methods in the present work. In some cases, after an arene had been arylsulfonoxylated, the resulting aryl *p*-nitrobenzenesulfonate was subjected directly to mass spectral analysis and the amount of oxygen-18 label present (as determined from the parent peak) was taken to be identical with the labeling of the peroxide. Alternatively, the oxygen-18 enrichment of the precursor sulfonyl chloride was measured by mass spectrometry and assumed to persist in the sulfonyl oxygens of the peroxide. This assumption was later proved correct when some reaction products were isolated which proved that scrambling of the oxygen-18 label in the peroxide had not occurred. Confirmation has also recently been reported by Yokoyama, *et al.*,[8] who treated the analogous labeled *m*-nitrobenzenesulfonyl peroxide with triphenylphosphine and found none of the oxygen-18 label in the triphenylphosphine oxide produced.

Substitution of *p*-Xylene in Ethyl Acetate Solution. Kinetic studies[4,5] of the arylsulfonoxylations of several benzene derivatives in ethyl acetate solution have demonstrated the substitutions to be first order with respect to the aromatic substrates. From the aromatics already proved to react by clean first-order kinetics,[4] *p*-xylene was selected for study in the present work because it yields only one monosubstitution product.

Oxygen-18 labeled *p*-nitrobenzenesulfonyl peroxide was added to *p*-xylene in ethyl acetate and the resultant 2,5-dimethylphenyl *p*-nitrobenzenesulfonate was isolated and subjected to mass spectral analysis.[9] From the parent peak, the labeling in one of the oxygens (necessarily corresponding to one of the sulfonyl oxygens of the peroxide) was 4.02% above natural abundance (Table I, expt 1). From the peak corresponding to the *p*-nitrobenzenesulfonyl ion ($O_2NC_6H_4SO_2^+$), the labeling of one of the sulfonyl oxygens was 4.13% above natural abundance. Therefore, within the limits of experimental error the sulfonyl label was unchanged and the phenoxy oxygen of the ester arose exclusively from the peroxy oxygens of the peroxide (intermediate **1**).

Substitution of Benzene in Methylene Chloride. The substitution of benzene in methylene chloride solution has also been proved to be clean first order with respect to the arene.[4] The substitution of benzene in this solvent with *p*-nitrobenzenesulfonyl peroxide labeled with oxygen-18 (3.97% above natural abundance in one of the sulfonyl oxygens from the mass spectrum of the precursor sulfonyl chloride) produced a phenyl sulfonate which after isolation was cleaved with sodium–naphthalene and the resultant phenol was converted to the trimethylsilyl ether. Mass spectral analysis of this ether showed that its oxygen had zero enrichment of oxygen-18 (−0.003%, Table I, expt 2), which corresponds to its formation also *via* intermediate **1**. Arylsulfonoxylation of an aromatic *via* a process first order with respect to arene therefore exclusively involves incorporation of the peroxidic oxygens as phenolic oxygens of the product ester.

The complete absence of oxygen-18 in the phenolic oxygen of the ester is also proof that in the conversion of the labeled sulfonyl chloride to the corresponding peroxide, no scrambling of the labeled oxygen occurred.

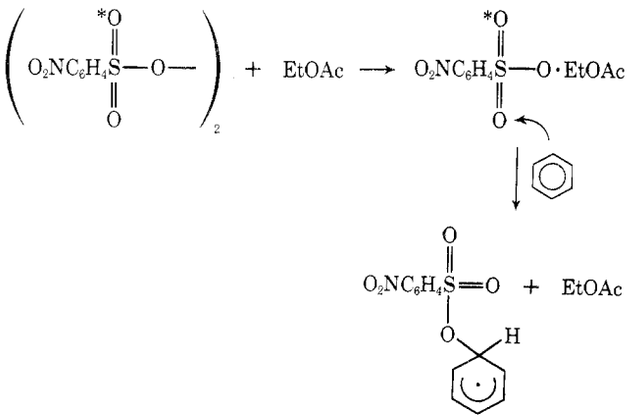
Substitution of Benzene in Ethyl Acetate. *p*-Nitrobenzenesulfonyl peroxide labeled in one-half of the sulfonyl oxygens (5.58%[10] above natural abundance of oxygen-18 in each of the labeled oxygens by measurement of the precursor sulfonyl chloride, Table I, expt 3) was added to benzene in ethyl acetate solution. The phenyl *p*-nitrobenzenesulfonate was cleaved by sodium–naphthalene,[11] the resultant phenol was converted to the trimethylsilyl ether, and the ether's oxygen-18 content (1.13% above natural abundance) was determined.[9] These analytical values, taking into account that the labeled and unlabeled sulfonyl oxygens are equivalent, correspond to 40.5% of the phenolic oxygens arising from sulfonyl oxygens, 59.5% from the peroxidic oxygens. In an alternate experiment (Table I, expt 4), the labeling of the peroxide was determined from the parent ion of the phenyl *p*-nitrobenzenesulfonate pro-

duced (6.02% oxygen-18 above natural abundance in one of the sulfonyl oxygens) and the labeling of the sulfonyl oxygens of the ester from *p*-nitrobenzenesulfonyl ion (4.77% oxygen-18 above natural abundance). From this alternate experiment, 41.6% of the phenolic oxygens arose from sulfonyl oxygens. The two procedures therefore check quite well with an average value of 41.0 ± 0.6%.

This partial labeling of the phenolic oxygen is not surprising because kinetic studies[4] have already shown that in ethyl acetate the reaction first order with respect to benzene (which should yield exclusive peroxidic oxygen incorporation in the phenol) competes with a reaction zero order with respect to aromatic. The present labeling experiment proves that the zero-order process also results in arylsulfonoxylation and must involve either exclusive sulfonyl oxygen attack or a symmetrical intermediate leading to a scrambling of oxygens prior to formation of the phenol. The rate constants reported for the k_0 and k_1 processes, unfortunately, are of limited accuracy because they must be derived from plots of experimentally determined pseudo-first-order rate constants. Correcting these reported rate constants[4] at 20° to room temperature (22°) and adjusting for the concentration of benzene (1.18 *M*) used in the present work gives the following rates: k_0, 3.2×10^{-5} mol l.$^{-1}$ sec^{-1}; k_1, 5.9×10^{-5} mol l.$^{-1}$ sec^{-1}. From these corrected values the zero-order process should account for 35% of the reaction. The kinetic (35%) and labeling (41%) values are reasonably close under the circumstances, and correspond only to exclusive attack on the sulfonyl oxygen (intermediate **2**).

For the zero-order mechanism to proceed *via* an intermediate in which three oxygens equilibrate (**3** or **4**) and give the observed 1.13% oxygen-18 label, it would be necessary for the zero-order reaction to produce 61% of the ester product. The reported k values admittedly have some limitations in accuracy, but not of such magnitude to permit the zero-order rate to be 1.5 times as great instead of one-half as great as the first-order process. Only exclusive sulfonyl oxygen attack for the zero-order process is therefore compatible with the data.

A solvolytic dissociation of the peroxide (probably homolytic **4** and not heterolytic **3** from the entropy of activation) has been suggested for the reaction zero order with respect to benzene[4] because it is solvent dependent. If solvation of the peroxidic oxygen promotes the homolytic dissociation, then the solvating molecule(s) might sterically prevent approach of the benzene to this peroxidic oxygen site, leading to exclusive attack on the sulfonyl oxygens.



A reaction of the labeled peroxide with an ethyl acetate solution of benzene was undertaken in the presence of galvinoxyl. It was expected that the zero-order process (if homolytic) would be inhibited and only the first-order reaction would occur with a complete absence of incorporation of oxygen-18 in the phenolic oxygen of the resultant ester. Unfortunately, the peroxide reacted primarily with the galvinoxyl (probably *via* nuclear substitution) and too little phenyl *p*-nitrobenzenesulfonate was produced to permit isolation and sufficient purification for a mass spectral analysis.

***p*-Nitrophenylsulfonoxylation of Neat Benzene.** If the observed zero-order reaction with benzene in ethyl acetate is the result of a solvolytic dissociation of the peroxide, in neat benzene a clean first-order reaction yielding exclusive attack on peroxidic oxygen might be expected. A kinetic dependence in the neat solvent cannot be established, but a labeling experiment should be elucidating.

The reaction of the labeled peroxide with neat benzene has now been used to produce phenyl *p*-nitrobenzenesulfonate (5.68% oxygen-18 above natural abundance in one oxygen from the parent ion peak of the mass spectrum of the ester, Table I, expt 5). The *p*-nitrobenzenesulfonyl ion peak (4.82% oxygen-18 above natural abundance in one sulfonyl oxygen) in the mass spectrum showed that 30.3% of the phenolic oxygen arose from sulfonyl oxygen attack. Similarly the reaction of labeled *m*-nitrobenzenesulfonyl peroxide in neat benzene has recently[8] been reported to produce phenyl *m*-nitrobenzenesulfonate with 35–36% of the phenolic oxygen arising from sulfonyl oxygens. These low percentages do not correspond to any single intermediate and must arise from competing reactions.

These data are difficult to interpret. It is known, however, that coordination of the peroxide with the aromatic precedes electrophilic substitution[5] and that with some polynuclear hydrocarbons at normal concentrations in ethyl acetate[7] arylsulfonoxylation is second order with respect to arene. In neat benzene it is conceivable that the transition state might involve two or more arene molecules coordinated to different oxygen atoms. Such a transition state could produce the partial scrambling of the oxygen-18 label because any one of the coordinated arene molecules might produce the aryl ester product.

Experimental Section

Boiling points and melting points are uncorrected.

Materials. The $H_2{}^{18}O$, about 10 atom % enriched, was obtained from Yeda R. and D. Co. or Thompson and Packard, Inc., and used directly. Hexamethyldisilazane (Peninsular ChemResearch Inc.) and *p*-nitrobenzenesulfonyl chloride (Eastman Kodak) were used as received. Benzene (Matheson Coleman and Bell, spectroquality) was fractionally distilled and ethyl acetate (J. T. Baker, analyzed reagent) was purified[12] before use.

***p*-Nitrobenzenesulfonyl Chloride-*sulfonyl*-^{18}O.** Oxygen-18 enriched water (2.1 g, 0.117 mol), *p*-nitrobenzenesulfonyl chloride (22.3 g, 0.1 mol) and dry dioxane (2 g) were heated to 100° for 19 hr in an aerosol compatibility tube. The tube was then cooled, the evolved hydrogen chloride was allowed to escape, methylene chloride (30 ml) was added, and the precipitate (12.8 g, 63%) which formed was collected by filtration to yield crude *p*-nitrobenzenesulfonic acid which melted at 85–90° (lit.[13] mp 90°). To the crude acid was added phosphorus pentachloride (25.6 g, 0.122 mol) and dry dioxane (3 g). After the vigorous evolution of hydrogen chloride had ceased, the mixture was warmed on a steam bath for 10 min and then poured over crushed ice, and the product was extracted with three 50-ml portions of chloroform. The combined chloroform extracts, after drying with magnesium sulfate, were evaporated to dryness *in vacuo*. Addition of heptane (20 ml) to the residue produced crystalline *p*-nitrobenzenesulfonyl chloride (10.25 g, 73%) which melted at 73–75° (lit.[14] mp 77°). Reduction in volume of the heptane filtrate gave a second crop of crystals (0.2 g) which melted at 77°.

***p*-Nitrobenzenesulfonyl Peroxide-*sulfonyl*-^{18}O.** In a conventional synthesis,[3] hydrogen peroxide (30%, 18.2 g) was added at −20° to potassium carbonate (7.8 g) in 2:1 water–ethanol (180 ml) in a Waring blender cup. *p*-Nitrobenzenesulfonyl chloride-*sulfonyl*-^{18}O (10 g) in chloroform (20 ml) was added and the mixture

was agitated at full power for 1 min. The resulting precipitate was collected by filtration, washed with water, and dried by drawing air through it. The crude peroxide was dissolved in acetone (180 ml), the solution was filtered, and after reduction in volume to 90 ml the filtrate was cooled in Dry Ice. The *p*-nitrobenzenesulfonyl peroxide-*sulfonyl*-^{18}O (4.6 g, 46% yield) which precipitated, after collection on a filter and drying *in vacuo*, melted at 125° (lit.[2] mp 127°).

p-Nitrophenylsulfonoxylation of p-Xylene. *p*-Nitrobenzenesulfonyl peroxide-*sulfonyl*-^{18}O (0.202 g, 0.5 mmol) in ethyl acetate (50 ml) and *p*-xylene (5.3 g, 0.05 mol) was stirred at room temperature for 24 hr. The mixture was washed successively with 5% aqueous potassium hydroxide (25 ml), 5% hydrochloric acid (25 ml), and water (40 ml) and dried with magnesium sulfate, and the solvent was removed *in vacuo*. Recrystallization of the residue from 1:1 benzene–heptane gave *p*-xylyl *p*-nitrobenzenesulfonate (0.083 g, 54%) which had an infrared spectrum identical with that of an authentic sample. This ester was subjected to mass spectral analysis (Table I, expt 1).

p-Nitrophenylsulfonoxylation of Benzene in Methylene Chloride. A mixture of labeled peroxide (3.1 g) in benzene (9.3 g) and methylene chloride (89 ml) was stirred at room temperature for 85 hr. A procedure identical with that above gave phenyl *p*-nitrobenzenesulfonate, mp 114–116° (lit.[15] mp 114°). The infrared spectrum was identical with that of an authentic sample. A portion of this ester, by the procedure given below, was converted to the trimethylsilyl ether, which was subjected to mass spectral analysis (Table I, expt 2).

Reaction of p-Nitrobenzenesulfonyl Peroxide-*sulfonyl*-^{18}O with Benzene in Ethyl Acetate Solution. A solution of *p*-nitrobenzenesulfonyl peroxide-*sulfonyl*-^{18}O (2.6 g, 6.5 mmol) in ethyl acetate (75 ml) and benzene (7.8 g, 0.1 mol) was stirred at room temperature for 70 hr. By a procedure identical with that previously described, phenyl *p*-nitrobenzenesulfonate was isolated and subjected directly to mass spectral analysis (Table I, expt 4).

In a duplicate run this ester was cleaved to phenol, which was converted to the trimethylsilyl ether, which was then analyzed by mass spectrometry. Phenyl *p*-nitrobenzenesulfonate (0.73 g, 2.62 mmol) labeled with oxygen-18 and tetrahydrofuran (10 ml) were placed in a flask fitted with a rubber septum and purged with nitrogen for 5 min. Sodium–naphthalene in tetrahydrofuran[8] (0.6 *M*, 30 ml) was added *via* a syringe and after 3 min of stirring, water (0.5 ml) was added to quench the excess sodium–naphthalene. The mixture was filtered through a fritted glass funnel and the tetrahydrofuran was removed using a rotary evaporator. The residue was dissolved in ether (30 ml) and extracted with three 40-ml portions of 0.1 *M* KOH. The combined alkaline solutions were acidified with 3 *M* HCl and extracted with ether (three 50-ml portions). The combined ether extracts, after drying with magnesium sulfate, were evaporated *in vacuo*. To the residue was added hexamethyldisilazane (5 ml) and a trace of sand, and the mixture was refluxed for 3 hr. Vacuum distillation of the mixture gave a forerun of hexamethyldisilazane and a clear liquid (0.2 ml) whose infrared spectrum was identical with that of an authentic sample of phenyl trimethylsilyl ether. This liquid was subjected to mass spectral analysis (Table I, expt 3).

Reaction of p-Nitrobenzenesulfonyl Peroxide-*sulfonyl*-^{18}O with Benzene (Neat). *p*-Nitrobenzenesulfonyl peroxide-*sulfonyl*-^{18}O (1.0 g, 2.5 mmol) in benzene (50 g, 0.64 mol) was allowed to stand overnight at room temperature. By the procedure already described, phenyl *p*-nitrobenzenesulfonate was isolated and subjected to mass spectral analysis (Table I, expt 5).

Registry No.—*p*-Nitrobenzenesulfonylperoxide, 6209-72-9; *p*-xylene, 106-42-3; benzene, 71-43-2.

References and Notes

(1) (a) Supported in part by the U. S. Army Research Office (Durham) through Grant DA-ARO-(D)-31-124-G720 and by National Science Foundation Grant GP-19018. (b) Taken in part from the dissertation of R. V. Hoffman, submitted to the Graduate School of Case Western Reserve University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Dec 1969. (c) Presented in part at the International Symposium on the Chemistry of Organic Peroxides, Berlin, 1967.
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Reactivity of Aryl Nitrenes. Competition between Carbazole Formation and Internal Bond Reorganization in Biphenylnitrenes

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A series of three 3′,5′-disubstituted 2-azidobiphenyls (**1b–d**) has been prepared. The sensitivity of carbazole yield on photolysis to the presence of the nucleophilic trapping agent diethylamine (DEA) has been determined and compared with similar data for the unsubstituted compound **1a**. All four compounds exhibit formation of some 2-diethylamino-3-aryl-3*H*-azepine (**3a–d**) as well as the expected carbazole (**2a–d**) on photolysis in the presence of DEA. For electron-withdrawing substituents (CF_3, CO_2CH_3) the drop in carbazole yield is from ~80 to ~20–30% but for CH_3 and the unsubstituted compound the decrease is somewhat less. Deoxygenations of 2-nitrosobiphenyl and the 3′,5′-bis(trifluoromethyl) analog were studied to provide an alternative source of the presumed nitrene intermediates. These results appear to require revision of previous mechanisms for formation of carbazole from biphenylnitrene to include an azirine intermediate which can be diverted to azepine formation by DEA.

The chemistry of phenylnitrene is dominated by an internal bond reorganization which eventually leads to ring-expanded products in the presence of nucleophilic trapping agents, specifically secondary amines.[1] The initial reaction in this sequence is very rapid and flash-photolysis studies indicate that phenylnitrene has a half-life of 30 μsec or less.[1a] Intermolecular addition and insertion reactions are inefficient processes for phenylnitrene.[2,3] In contrast, arylnitrenes with adjacent sites of unsaturation cyclize with efficiency.[4] Biphenylnitrene, for example, gives carbazole in yields of around 80%.[5] The cause of the general inefficiency of intermolecular reactions of phenylnitrene may lie in the