Arylsulfonoxylation of Aromatic Compounds. VII. The *p*-Nitrophenylsulfonoxylation of Benzyl Alcohol, Benzaldehyde, and Acetophenone[1a-c]

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p-Nitrobenzenesulfonyl peroxide (I) oxidized benzaldehyde in ethyl acetate solution at 0° in the presence of *N,N*-diphenylpicrylhydrazyl to give benzoic acid (85%) with a $\Delta H^{\ddagger}$ of 22 ± 4 kcal mol^{-1}. No nuclear substitution in the aromatic aldehyde was detected. I (1.00) reacts with a mixture of benzene (113) and benzyl alcohol (20) in ethyl acetate to give *p*-nitrobenzenesulfonic acid (1.19), benzoic acid (0.187), phenyl *p*-nitrobenzenesulfonate (0.206), and isomeric hydroxymethylphenyl *p*-nitrobenzenesulfonates (0.378). The orientations of nuclear substitution (partial rate factors based upon the competitive nuclear reactivity of 10.5 for benzyl alcohol) are: ortho, 29.3% (9.2); meta, 9.9 (3.1); para, 60.8 (37.8). The overall kinetics give a $\Delta H^{\ddagger}$ of 15.4 kcal mol^{-1} and $\Delta S^{\ddagger}$ of −23 cal deg^{-1} mol^{-1}. I (1.00) reacts with a mixture of acetophenone (200) and benzene (12) to give isomeric *p*-nitrobenzenesulfonoxy acetophenones (0.16), phenyl *p*-nitrobenzenesulfonate (0.056), *p*-nitrobenzenesulfonic acid (1.16), phenacyl *p*-nitrobenzenesulfonate (0.10), benzoic acid (0.592), and traces of 1,3,5-triphenylbenzene and dypnone together with tars which yield methyl iodide (0.15) when treated with hydrogen iodide. The orientations of nuclear substitution [partial rate factors based upon the relative reactivity (0.15) for acetophenone] are: ortho, 35.9% (0.15); meta, 50.3 (0.22); para, 13.8 (0.12). The overall pseudo-first-order rate constants for the disappearance of the peroxide gave $\Delta H^{\ddagger}$ of 16.7 kcal mol^{-1} and $\Delta S^{\ddagger}$ of 21.8 cal deg^{-1} mol^{-1}. These results are all consistent with electrophilic ionic reactions.

In the preceding papers of this series it has been found that nitrobenzenesulfonyl peroxides are sufficiently stable for routine laboratory use[2] and that they react with both activated and deactivated aromatic nuclei[3] by a typical electrophilic aromatic substitution to yield aryl sulfonate esters.

$$(O_2NC_6H_4SO_3)_2 + C_6H_5X \longrightarrow O_2NC_6H_4SO_3C_6H_4X + O_2NC_6H_4SO_3H \quad (1)$$

Treatment of either styrene or stilbene with sulfonyl peroxides results in oxidative addition to the double bonds to yield disulfonates.[4] However, the side chains of alkylbenzenes are completely unaffected by sulfonyl peroxides while the nuclei are undergoing arylsulfonoxylation.[1,5] Even the nucleus of anisole undergoes *m*-nitrobenzenesulfonoxylation without formation of any other type of oxidation product.[3] Although the arylsulfonyl peroxides are very reactive reagents for electrophilic substitution, they apparently have very limited power as general oxidizing agents.

In the present work it was planned to investigate the reactions of *p*-nitrobenzenesulfonyl peroxide (I) with benzyl alcohol, benzaldehyde, and acetophenone to determine whether nuclear substitution or oxidation of the reactive side chains would occur. The para peroxide was selected in preference to its isomers because preliminary experiments disclosed that some needed reference compounds derived from *o*- and *m*-nitrobenzenesulfonyl peroxides were oils, but the *p*-nitrobenzenesulfonyl analogs were easily purified crystalline solids.

Results and Discussion

Reaction of I with Benzyl Alcohol. Although the competitive reaction of I with a mixture of benzyl alcohol and benzene in ethyl acetate (eq 2) gave some oxidation of the

$$\underset{(1.00)}{I} + \underset{(20.0)}{C_6H_5CH_2OH} + \underset{(113.0)}{C_6H_6} \xrightarrow[\text{acetate}]{\text{ethyl}} \underset{(0.187)}{C_6H_5COOH} + \underset{(1.19)}{p\text{-}O_2NC_6H_4SO_3H} + \underset{(0.206)}{p\text{-}O_2NC_6H_4SO_3C_6H_5} + \underset{(0.378)}{p\text{-}O_2NC_6H_4SO_3C_6H_4CH_2OH} \quad (2)$$

Table I
Relative Reactivities (from Competitive Determinations), Orientations, and Partial Rate Factors for the *p*-Nitrophenylsulfonoxylation of Benzyl Alcohol and Acetophenone in Ethyl Acetate at 25°

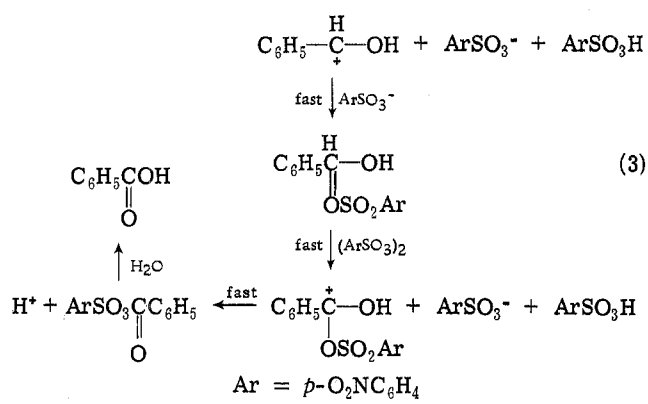
Quantity measured	Benzyl alcohol	Acetophenone
k_{Ar}/k_B	10.5	0.15
% ortho (partial rate factor)	29.3 (9.2)	35.9 (0.15)
% meta (partial rate factor)	9.9 (3.1)	50.3 (0.22)
% para (partial rate factor)	60.8 (37.8)	13.8 (0.12)

alcohol substituent (0.187 mol of benzoic acid per mole of peroxide), an overall 59% yield of nuclear substitution of the two aromatics included a 38% yield of arylsulfonoxylation of the alcohol. This is apparently the first reported successful nuclear substitution of benzyl alcohol and emphasizes the low oxidizing power but high electrophilic reactivity of the sulfonyl peroxides. The orientations of substitution and the partial rate factors (Table I) based upon the competitive relative reactivity to benzene (10.5) bear reasonable resemblance to the relative reactivity (6.48) and the orientations (partial rate factors) for the typically electrophilic nitration of benzyl methyl ether—ortho, 28.6 (9.97); meta, 18.1 (1.32); para, 53.3 (16.3)—even though the nitration apparently proceeds via the protonated ether.[6] The methylene group of benzyl alcohol is obviously activating and ortho–para directing toward arylsulfonoxylation but the inductive effect of the hydroxyl group modifies these effects.

The oxidation of the alcohol group, as expected, stoichiometrically consumed 2 mol of the sulfonyl peroxide per mole of benzoic acid produced (95.7% of the oxidizing power of the peroxide accounted for, but only an 88.7% recovery of the peroxide fragments). An ionic mechanism for the oxidation is probable because the addition of *N,N*-diphenylpicrylhydrazyl to the reaction mixture does not change the yield of benzoic acid.

Kinetic measurements of the disappearance of the peroxide in the reaction mixture (Table II) proved the overall reaction with benzyl alcohol to be clean first order with respect to the peroxide and first order (1.07) with respect to

the alcohol. The rate of reaction with the alcohol is more rapid than with benzaldehyde and yet no aldehyde can be detected in the benzyl alcohol sulfonoxylation products. Therefore benzaldehyde cannot be an intermediate in the oxidation of the alcohol because it should accumulate in measurable quantities. A possible mechanism consistent with these data involves hydride abstraction (eq 3) as a

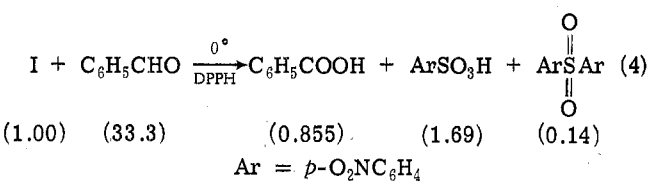


(3)

Ar = p-$O_2NC_6H_4$

rate-determining step. The intermediate hydroxy sulfonate could be formed instead by a concerted reaction or a free-radical cage process involving a benzyl alcohol–sulfonyl peroxide coordinated species. From the pseudo-first-order rate constants at various temperatures (Table II), $\Delta H^{\ddagger}$ for the overall reactions was found to be 15.5 ± 0.5 kcal mol^{-1} and $\Delta S^{\ddagger}$ to be − 23 ± 1 cal deg^{-1} mol^{-1}. The $\Delta S^{\ddagger}$ is certainly characteristic of an ionic process, but, as it is calculated from an overall rate, it does not exclude a homolytic process for the side reaction of oxidation.

Reaction of I with Benzaldehyde. The decomposition of I in an ethyl acetate solution of a large excess of benzaldehyde with *N,N*-diphenylpicrylhydrazyl (DPPH) present (eq 4) gave no detectable amount of substitution in the ring

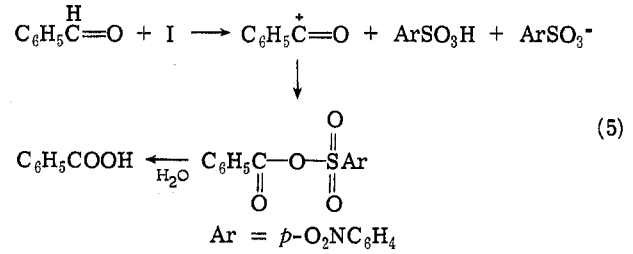


(4)

(1.00) (33.3) (0.855) (1.69) (0.14)

Ar = p-$O_2NC_6H_4$

of the aldehyde. In the absence of DPPH or at higher temperatures the yield of benzoic acid decreases to about 60% while the yields of tars and usually the sulfone increase. Degassing the solvent also increases the yield of benzoic acid. The oxidation of the aldehyde to benzoic acid thus appears to be an ionic process, probably proceeding via a



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Ar = p-$O_2NC_6H_4$

hydride abstraction (eq 5). There is a competing homolytic induced decomposition involving the peroxide which produces tars and the sulfone.

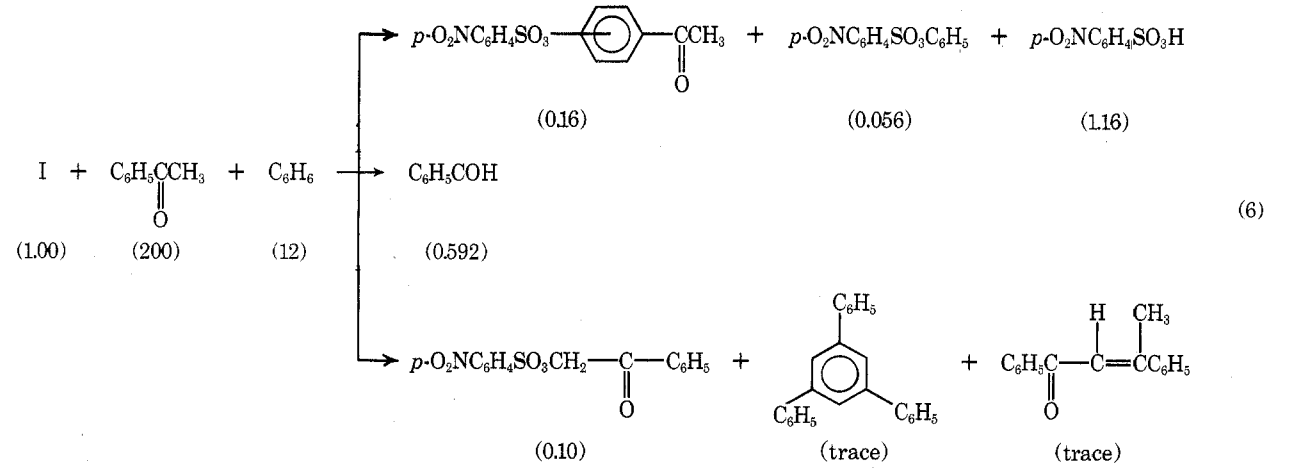
Kinetic studies were complicated by the inability to completely exclude oxygen from the system with its consequent formation of stable peroxides via the free-radical oxidation of the aldehyde. However, by taking duplicate aliquots of the reaction mixture and quenching the sulfonyl peroxide in one sample with anisole before titration, it was possible to correct for the stable carbon peroxides present. Anisole reacts very rapidly with sulfonyl peroxides at room temperature[3] but does not react with the carbon peroxides under these conditions. The difference in titration between the quenched and unquenched samples therefore corresponds to the residual sulfonyl peroxide. The sulfonyl peroxide was found to decompose by first-order kinetics with a $\Delta H^{\ddagger}$ of 22 ± 4 kcal/mol. The inaccuracy of this value precludes a calculation of $\Delta S^{\ddagger}$ of reasonable precision.

Reaction of I with Acetophenone. The competitive reaction of I with a mixture of acetophenone and benzene in ethyl acetate solution (eq 6) obviously proceeds via three separate pathways: substitution of the aromatic nuclei (22%), substitution in the aceto group (10%), and oxidation of the aceto group to benzoic acid (59%).

From the relative yields of substitution in the nuclei of acetophenone and benzene and the orientations of substitution in acetophenone, the partial rate factors for the arylsulfonoxylation of the ketone were calculated (Table I). These partial rate factors are all less than unity with the meta value the largest of the three as expected for an electrophilic substitution.

The small yields of triphenylbenzene and dypnone are undoubtedly produced from acetophenone by condensations catalyzed by p-nitrobenzenesulfonic acid. These are typical aldol products and the competing addition of the sulfonyl peroxide to the olefinic bond of the aldol leads to phenacyl p-nitrobenzenesulfonate. Similar additions to the sulfonyl peroxides to olefins have been reported by Kergomard.[4,7]

The stoichiometry of the products provides enough oxidizing power by the peroxide to produce the benzoic acid only if the methyl group of the acetophenone persists as



(6)

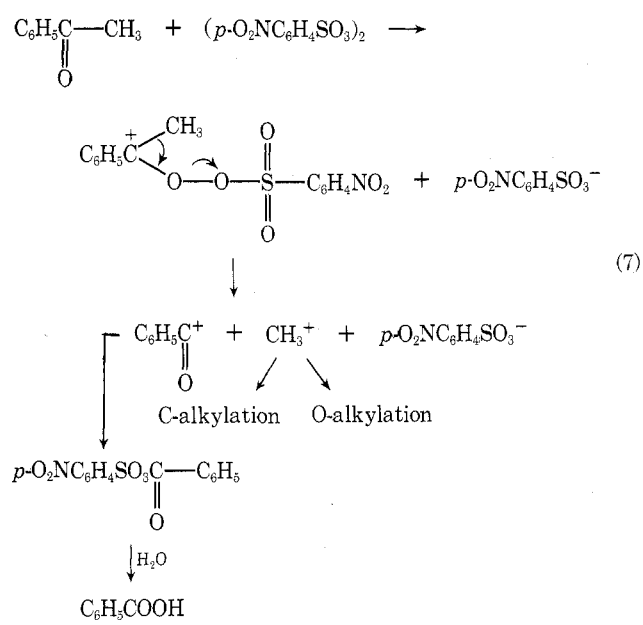
(1.00) (200) (12) (0.592) (0.16) (0.056) (1.16) (0.10) (trace) (trace)

Table II
Temperature and Aromatic Substrate Concentration Dependence of the Pseudo-First-Order Rate Constants for the Disappearance of *p*-Nitrobenzenesulfonyl Peroxide (0.01 *M*) in Ethyl Acetate Solutions of Aromatic Substrates

Aromatic	Concn aromatic, *M*	Temp, °C	$10^4 k$, $\times$ sec^{-1}
Benzyl alcohol[a]	0.75	9.95	2.86
Benzyl alcohol	0.75	3.95	1.625
Benzyl alcohol	0.565	−2.20	0.588
Benzyl alcohol	0.75	−2.20	0.759
Benzyl alcohol	1.00	−2.20	1.13
Benzyl alcohol	0.75	−7.35	0.476
Benzaldehyde[b]	0.75	20.0	1.98
Benzaldehyde	0.75	15.0	0.865
Benzaldehyde	0.75	10.0	0.502
Acetophenone[c]	0.75	35.15	1.71
Acetophenone	0.75	30.35	1.00
Acetophenone	0.75	25.40	0.681
Acetophenone	0.75	19.65	0.384

[a] Registry no., 100-51-6. [b] Registry no., 100-52-7. [c] Registry no., 98-86-2.

methyl in the products. No methyl *p*-nitrobenzenesulfonate is formed. Partial proof of the fate of the methyl group was obtained by treating the reaction mixture with hydrogen iodide, resulting in a recovery of 25% of the lost methyl group as methyl iodide. These data are consistent with the loss of the methyl groups as carbonium ions (eq 7) which by



(7)

direct transfer either alkylate oxygen atoms to yield ether systems (which can be cleaved by hydrogen iodide) or alkylate unsaturated carbon atoms to produce structures inert to hydrogen iodide. The methyl carbonium ion may, of course, never have a discrete existence but be transferred directly to the species it alkylates. The pseudo-first-order rate constants (Table II) for the overall disappearance of the peroxide correspond to $\Delta H^{\ddagger}$ of 16.7 ± 0.5 kcal/mol^{-1} and $\Delta S^{\ddagger}$ of −21.8 ± 0.7 cal deg^{-1} mol^{-1}.

Hammett Plot. Most of the previous arylsulfonoxylation studies primarily have involved *m*-nitrobenzenesulfonyl peroxide. However, when isomeric nitrobenzenesulfonyl peroxides have been reacted with the same aromatic substrate, only very small differences in orientations and partial rate factors were observed with variation of the peroxide.[3,5] In a Hammett plot, the use of logarithmic values reduces these differences numerically even more. Previously unreported σ^+ parameters for the hydroxymethyl (*m*-, +0.11; *p*-, −0.12) and acetyl (*m*-, +0.36; *p*-, +0.41) substituents were obtained by extrapolation from the Hammett plot previously published[3] for the *m*-nitrophenylsulfonoxylation of benzene derivatives. The *m*-acyl σ^+ value (+0.36) is similar to the corresponding Hammett σ value (+0.376) as expected for a similar inductive influence.

Table III
Melting Points and Yields of Aryl *p*-Nitrobenzenesulfonates ($O_2NC_6H_4SO_3C_6H_4X$)

X	Registry no.	Mp, °C	Yield, %
o-Hydroxymethyl[a]	55660-61-2	84–86	31
m-Hydroxymethyl[a]	55937-77-4	90–91.5	58
p-Hydroxymethyl[a]	55937-77-4	120–122	53
o-Trimethylsiloxymethyl[a]	55660-63-4	75–76	79
m-Trimethylsiloxymethyl[a]	55660-64-5	42–43.5	81
p-Trimethylsiloxymethyl[a]	55660-65-6	52–53.5	84
o-Acetyl[a,b]	55660-66-7	117–119	37
m-Acetyl[a,b]	55660-67-8	100–101	39
p-Acetyl[a,b]	55660-68-9	105–105.5	81
p-Formyl[a]	55660-69-0	142–144	50

Analyses for the elements gave maximum deviations from the theoretical values as follows: all C values ±0.34; [a] all H values ±0.26;[a] all N values ±0.21.[b]

Experimental Section

Materials. Ethyl acetate, benzene, and *p*-nitrobenzenesulfonyl peroxide were prepared[2] or purified[5] by methods previously described. *Caution, p-nitrobenzenesulfonyl peroxide in high states of purity can flash fire if rubbed with a spatula.* Benzyl alcohol, acetophenone, and benzaldehyde were fractionally distilled before use. Recrystallization of the following materials from the given solvents gave *o*-hydroxybenzyl alcohol, mp 83–85° (lit.[8] mp 86°), from benzene–heptane; *m*-hydroxybenzyl alcohol, mp 70–72° (lit.[9] mp 72–73°), from benzene; *p*-hydroxybenzyl alcohol, mp 113–114° (lit.[10] mp 113–114°), from chloroform; *m*-hydroxyacetophenone, mp 95–97° (lit.[11] mp 95–96°), from benzene–heptane; and *p*-hydroxyacetophenone, mp 108–110° (lit.[12] mp 107°), from benzene–heptane. *o*-Hydroxyacetophenone was purified by the literature[13] method. Hexamethyldisilazane, *p*-nitrobenzenesulfonyl chloride, and *p*-hydroxybenzaldehyde were used as received.

Isomeric Aryl *p*-Nitrobenzenesulfonates (Table III) were prepared by the literature[14] method. The hydroxymethyl derivatives were heated with hexamethyldisilazane to convert them to the trimethylsilyl ethers (Table III).

Arylsulfonoxylation of Benzene–Benzyl Alcohol. A solution of *p*-nitrobenzenesulfonyl peroxide[5] (0.203 g, 0.5 mmol) in benzyl alcohol (1.080 g, 10.0 mmol) and benzene (4.401 g, 56.4 mmol) was diluted to 75 ml with ethyl acetate and kept at −2.1° for 92 hr. The ethyl acetate solution was washed with ice water (100 ml), the water extract was neutralized to pH 5 with 1.0 *M* potassium hydroxide, reduced in volume to 20 ml in vacuo, and chilled to 0°, and *S*-benzylthiouronium chloride (0.19 g, 18 mmol) in water (20 ml) was added. The *S*-benzylthiouronium *p*-nitrobenzenesulfonate (0.1802 g) which precipitated, after collection and drying, melted at 200–202° (lit.[5] mp 203–204°). The ethyl acetate raffinate after washing with water was dried with magnesium sulfate and evaporated in vacuo at 0°. The residue was refluxed with hexamethyldisilazane (5 ml, 31 mmol) for 2 hr and *m*-tolyl *m*-nitrobenzenesulfonate was added as an internal standard. The mixture was analyzed (Table IV) by GLC for the isomeric *p*-nitrobenzenesulfonoxybenzyl trimethylsilyl ethers and phenyl *p*-nitrobenzenesulfonate using a column of 5% SE-30 on Chromosorb W (DMCS treated, acid washed). The mixture was also analyzed for trimethylsilyl benzoate by GLC on a similar 20% SE-30 column using naphthalene as an internal standard. When the sulfonoxylation was carried out at room temperature some transesterification with ethyl acetate occurred and some *p*-nitrobenzenesulfonoxybenzyl acetate (mp 89–91°) could be isolated by chromatography of the reaction mixture on silica using benzene to elute.

Table IV
Reaction of p-Nitrobenzenesulfonyl Peroxide with Benzyl Alcohol and Acetophenone

Compd or quantity	Benzyl alcohol[a]		Acetophenone[b]	
	Run 1	Run 2	Run 1	Run 2
Peroxide, mmol	0.5	0.5	0.5	0.5
Benzene, mmol	56.4	56.4	5.0	5.0
Benzene derivative, mmol	10.0	10.0	100	100
Ethyl acetate	to 75 ml	to 75 ml	to 75 ml	to 75 ml
Sulfonate esters, % yield	60.4	56.2	21.4	19.4
k_{ar}/k_B	10.9	10.0	0.141	0.151
p-Nitrobenzenesulfonic acid, mmol	0.575	0.610	0.725	0.714
Benzoic acid, mmol	0.093	0.094	0.300	0.292
Aryl sulfonates, mmol				
Phenyl	0.104	0.1015	0.028	0.027
o-Aryl	0.0575	0.0525	0.028	0.029
m-Aryl	0.0209	0.0167	0.0414	0.0386
p-Aryl	0.120	0.110	0.010	0.012
Isomer distribution, %				
Ortho	29.4	29.3	35.4	36.4
Meta	10.6	9.3	52.3	48.4
Para	60.0	61.6	12.4	15.2

[a] Temperature, −2.1°. [b] Temperature, 25°. Millimoles of phenacyl p-nitrobenzenesulfonate: 0.05, 0.05.

Arylsulfonoxylation of Benzene–Acetophenone. A solution of p-nitrobenzenesulfonyl peroxide (0.203 g, 0.5 mmol) in benzene (0.390 g, 6 mmol) and acetophenone (12.00 g, 100 mmol) diluted to 75 ml with ethyl acetate was kept at room temperature for 91 hr. The solution was then washed with water (70 ml), the raffinate was dried with magnesium sulfate, and the ethyl acetate was removed in vacuo at 0°. The volume was further reduced to about 7 ml by warming to 30° in vacuo to remove residual acetophenone. m-Tolyl m-nitrobenzenesulfonate was added to an aliquot as an internal standard and the isomeric acetylphenyl p-nitrobenzenesulfonates and phenyl p-nitrobenzenesulfonate were analyzed by GLC on the 5% SE-30 column previously described. To a second aliquot was added hexamethyldisilazane and after refluxing (1.5 hr) naphthalene was added as an internal standard and trimethylsilyl benzoate analyzed for by GLC as previously described. The water extract of the original reaction mixture was analyzed for p-nitrobenzene sulfonic acid via the thiouronium salt.

Isolation of the reaction products was accomplished from a large-scale (1.006 g of I) reaction mixture. After water extraction and removal of solvent and remaining acetophenone, the dark residue was chromatographed on silica gel using benzene for elution. The first fraction to elute yielded a white solid (94 mg, mp 129–130°) identified as phenacyl p-nitrobenzenesulfonate by its NMR spectrum: a methylene absorption at τ 5.12 (2 H) and two aromatic absorptions centered at τ 7.10 and 7.61 (9 H total). Anal. Calcd for $C_{14}H_{11}NO_6S$: C, 52.33; H, 3.39. Found: C, 52.33; H, 3.45. The second fraction to elute was a mixture of *cis*- and *trans*-dypnone identified by the mass spectrum (*m/e* 222) and the NMR and ir spectra. Subsequent fractions yielded phenyl p-nitrobenzenesulfonate [180 mg, mp 113–114° (lit.[16] mp 114°)] and a mixture of the isomeric acetylphenyl p-nitrobenzenesulfonates (0.268 mg) which gave three peaks via GLC with retention times identical with those of authentic isomers as well as an ir spectrum identical with that of a mixture of authentic samples.

Zeisel Cleavage of the Products of I with Acetophenone. A mixture of I (1.00 g, 2.5 mmol) and acetophenone (4.0 g, 33 mmol) was stirred at room temperature for 4 days under a nitrogen atmosphere. Hydrogen iodide (60 ml) was then added and the mixture was refluxed for 1 hr while the nitrogen stream was bubbled through toluene (3 ml) in a trap at −80°. The trap contents were analyzed for methyl iodide by GLC on a 150-ft SE-30 capillary column. A 2-ml sample of the toluene solution was treated with tri-n-propylamine to yield methyl tri-n-propylammonium iodide, mp 207–208° (lit.[17] mp 207–208°).

Reaction of I with Benzaldehyde. Freshly distilled benzaldehyde (2.65 g, 25 mmol) and DPPH (3 mmol) diluted to 75 ml total with ethyl acetate was added to I (0.203 g, 0.5 mmol) and the mixture was stirred at room temperature for 24 hr. The reaction mixture was extracted twice with 0.1 *M* potassium hydroxide (20 ml) and the alkaline extract, after acidification to pH 5 with hydrochloric acid, was extracted with three 30-ml portions of ether. These ether extracts were combined, dried, evaporated, and analyzed for benzoic acid by the procedure previously described. The acidified aqueous solution was analyzed for p-nitrobenzenesulfonic acid via the S-benzylthiouronium salt. The ethyl acetate raffinate was dried with magnesium sulfate and evaporated to dryness in vacuo, the gummy residue was triturated with heptane (three 30-ml portions), and benzene (30 ml) was added to the combined heptane extracts. Cooling produced a solid (22 mg) which after recrystallization from 1:2:2 acetone–benzene–heptane had mp 248–250° dec and an ir spectrum identical with that of an authentic sample[18] of bis(p-nitrophenyl) sulfone. It was then found that the sulfone could be quantitatively measured (14%) by GLC on a 5% SE-30 on Chromosorb W column using p-formylphenyl p-nitrobenzenesulfonate as a standard.

Under identical conditions, but either at 25° or in the absence of DPPH, the yield of benzoic acid decreases to ca. 60% and the tars increase.

Registry No.—I, 6209-72-9; hexamethyldisilazane, 999-97-3; S-benzylthiouronium chloride, 55660-70-3; p-nitrobenzenesulfonoxybenzylacetate, 55660-71-4; phenacyl p-nitrobenzenesulfonate, 55660-72-5; *cis*-dypnone, 54435-79-9; *trans*-dypnone, 22573-24-6; bis(p-nitrophenyl) sulfone, 1156-50-9.

References and Notes

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