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REARRANGEMENT OF O-ARENESULFONYL PHENYLHYDROXYLAMINES

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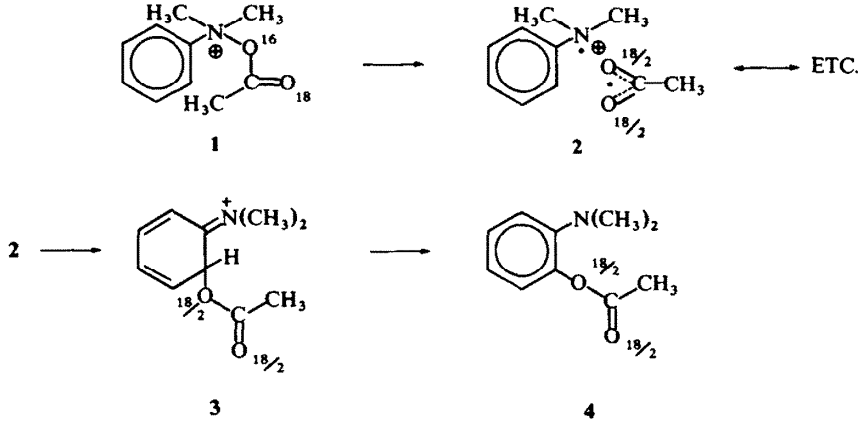
Abstract—When treated with arenesulfonyl chlorides, phenylhydroxylamines rearrange to *o*-arenesulfonyloxyaniline derivatives. The rearrangement of N-benzoyl-phenylhydroxylamine, under the influence of *p*-nitrobenzenesulfonyl chloride, was studied in detail. The *ortho*:*para* ratio is greater than 50. The oxygen introduced into the aniline ring comes exclusively from the sulfonyl group on the sulfonyl chloride, as shown by O^{18} labeling. This demands a concerted, cyclic mechanism for the rearrangement of the intermediate N-benzoyl-N-(*p*-nitrobenzenesulfonyloxy) aniline.

INTRODUCTION

ACYLOXY derivatives of amines undergo a wide variety of molecular rearrangements. One class of these is the Lossen rearrangements of acyloxy carbonamides[3] and sulfonamides.[4] A second class is formed by the rearrangements of O-acyl amine oxides. Acylation of phenyldimethylamine N-oxide leads to *ortho* acylated phenyldimethylamine[5] in an intramolecular rearrangement of the intermediate acyloxy derivative. Oae[6] found that the two oxygens in the migrating group become equivalent and proposed a radical pair mechanism:



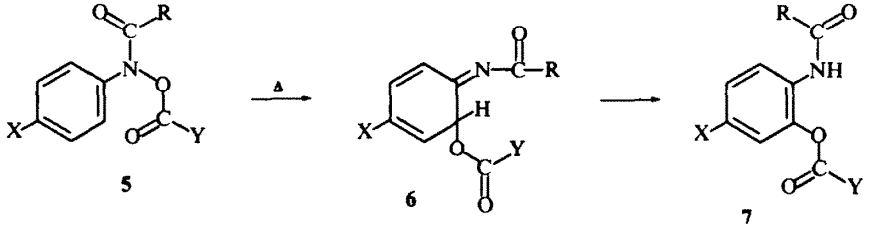
Rearrangement is also observed upon O-acylation of N-oxides in which the nitrogen forms part of a hetero-aromatic system.[7]

Oae studied the reaction of O^{18} labeled acetic anhydride with 2-, 3-, and 4-picoline-N-oxides and observed an interesting spectrum of mechanisms. The 2-picoline-N-oxide rearranges—with migration of the acetoxy group both to the Me carbon and the

3- and 5-positions of the ring—to give pyridine derivatives in which the oxygens from the N-oxide and the acetyl functions are completely mixed. The rearrangement is, however, intramolecular and Oae assumes a radical pair mechanism,[8] while other authors prefer an ion-pair intermediate.[9]

This controversy, however, is not of critical importance to the reaction we wish to report below. What is of interest is Oae's observation that the degree of intramolecularity changes with relatively small changes of structure. In the case of 4-picoline-N-oxide, there is some exchange with external acetic anhydride,[10] and with 3-picoline-N-oxide,[11] this exchange is complete, the reaction is now intermolecular.

A third class of rearrangements contains those of O-acylated arylhydroxylamines. Horner found that heating N-acyloxybenzanilides results in migration of the acyloxy group from the nitrogen to the *ortho* position of the ring of the aniline moiety. The reaction rate is the higher the stronger the acid corresponding to the migrating acyloxy group. A OMe group in *para* position on the aniline function greatly accelerated the reaction.[12]



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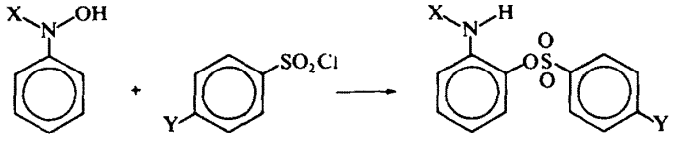
The compound prepared from N-acetylphenylhydroxylamine and dichloroacetyl chloride (R = Me; X = H; Y = $CHCl_2$) and labeled at the dichloroacetyl-carbonyl with O^{18} was studied by Cox.[13] He obtained both the *ortho* and the *para* dichloroacetyloxyacetanilides, and the phenol oxygen of the hydrolysis contained half the O^{18} label. Thus, the two oxygens of the migrating group become equivalent in the process. Together with Horner's data, this points to an ion-pair, or to an even more dissociated, intermediate. The formation of copious amounts of para rearrangement products reminds one of the Bamberger rearrangement of arylhydroxylamines under the influence of acid.[14] On the other hand, phenylhydroxylamine-O-sulfonic acid rearranges to *o*-aminophenol with the formation of, at the most, traces of *p*-aminophenol.[15] Boyland proposed a cyclic ionic mechanism for this rearrangement to the *ortho* position.

We have studied the rearrangement of some derivatives of phenylhydroxylamine under the influence of arenesulfonyl chlorides. Ortho sulfonyloxyaniline derivatives are formed, as discussed below.

RESULTS AND DISCUSSION

Phenylhydroxylamine (**8**) was treated with equimolar quantities of triethylamine begracht wird.[8] Beide Verfahren sind jedoch allein* nicht absolut sicher struktur- was isolated in 23% of the theoretical yield. When N-carbethoxy-phenylhydroxylamine (**9**) was treated with *p*-nitrobenzenesulfonyl chloride and triethylamine in refluxing ether, a 73% yield of N-(2,*p*-nitrobenzene-sulfonoxyphenyl) urethan (**12**) was isolated in crystalline form. Treatment of N-benzoyl-phenylhydroxylamine (**10**)

with *p*-nitrobenzenesulfonyl chloride in ether at 0°, in the presence of triethylamine, gave a 71% yield of crystalline 2-(*p*-nitrobenzenesulfonoxy) benzanilide (**13**). The structure of **11** was established by comparison with an authentic sample, that of **12** by its conversion to benzoxazolone (**14**) by heating with aqueous sodium bicarbonate solution, and that of **13** by its hydrolysis to 2-hydroxybenzanilide, which was compared with an authentic sample. All the products had the proper IR and NMR spectra, and the new compounds **12** and **13** had correct elemental analyses.



9 X = CO_2Et; Y = NO_2
10 X = COC_6H_5; Y = NO_2
8 X = H; Y = CH_3

12 X = CO_2Et; Y = NO_2
13 X = COPh; Y = NO_2
11 X = H; Y = Me

The substantial yields of **12** and **13**, and the apparent absence of the corresponding *para* disubstituted products suggested an intramolecular—and perhaps concerted—mechanism. System **10** was chosen for closer investigation. To determine the extent to which *para* rearrangement product was formed, the reaction mixture from **10** was partially hydrolized to the hydroxybenzanilides and analyzed by gas chromatography. A 1·4% yield of *p*-hydroxybenzanilide was found. The *o*-hydroxybenzanilide cyclized partially to 2-phenylbenzoxazole under the VPC conditions, and its amount could not be determined accurately. Assuming that the 71% yield of isolated, crystalline **13** corresponds to a 80% yield of **13** actually formed, the ratio of *para* to *ortho*

TABLE 1.

Compound	Atom-% Excess Oxygen-18[a]	
	Series A	Series B
p-Nitrobenzenesulfonyl chloride	0·443	0·485
o-(*p*-nitrobenzensulfonoxy) benzanilide (**13**)	0·345[b]	0·357[b]
o-hydroxybenzanilide	0·442	0·494[c]

[a] Calculated from the mass spectrometric data by the method of Denney (Ref. 19). The values given are atom-% oxygen-18 in excess of natural abundance *per molecule*. Not every oxygen atom in each compound is equally enriched. To obtain the enrichment in the labelled positions, these figures are to be divided by the ratio of the number of labelled atoms to the total number of oxygen atoms in the molecule. The number and identity of the labelled atoms in each substance must be ascertained independently.

[b] The values should be accurate to about 10% relative error. However, with compound **13**, which contains six oxygen atoms, the great disparity in the peak heights of masses 44 and 46 makes the determination of their ratio less exact.

[c] With the kind assistance of John Frõines, Yale University, New Haven, Connecticut.

products is 1:57. This is very different from the Bamberger rearrangement, which gives mainly *para* disubstituted products. Our results rather resemble those of Boyland and Nery.[15] To inquire further into the nature of the rearrangement process, **10** was treated with *p*-nitrobenzenesulfonyl chloride in which both sulfonyl oxygens were enriched with O^{18}. The *p*-nitrobenzenesulfonyl chloride-O^{18} was prepared by the method given by Oae[16] for the tosyl chloride. The level of the O^{18} label was determined in the sulfonyl chloride, the primary reaction product **13**, and the *o*-hydroxybenzanilide obtained by mild hydrolis of **13**. The results of two independent runs are shown in Table 1. Determination of O^{18} levels was by mass spectrometric analysis of the carbon dioxide produced by the Unterzaucher method[17,18] and calculated from the ratios of masses 44 and 46 by Denney's procedure.[19] The data in Table 1 show that all O^{18} label is retained in the primary product **13** (however diluted by the two oxygens brought in by **10**). Hydrolysis (with removal of 4 of the 6 oxygens) gives a product with the same O^{18} abundance as the starting *p*-nitrobenzenesulfonyl chloride, i.e. exactly one of the two labeled oxygens of the sulfonyl chloride is found in the *o*-hydroxybenzanilide. Since exchange of O^{16} for O^{18} in the carbonyl group is virtually impossible, this means that all the oxygen in the *ortho* position comes from the sulfonyl group, and none of it comes from the N-hydroxy group of **10**, (Fig. 1).

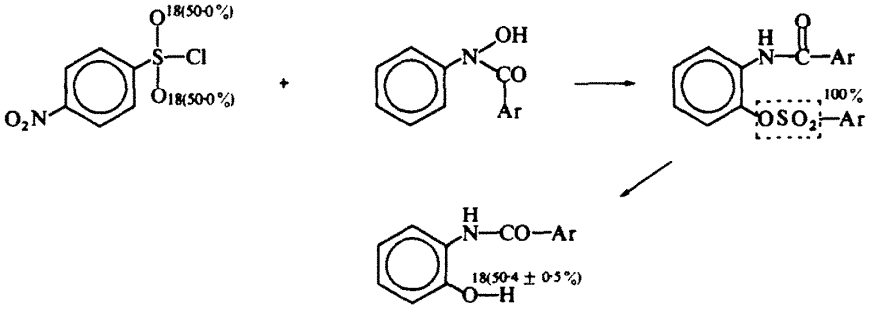
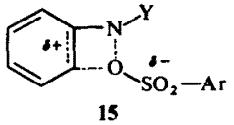


FIG. 1.

The labeling experiment rules out a number of mechanisms: (1) The observed rearrangement cannot be the result of the N-hydroxy group migrating to the *ortho* position and then being sulfonylated; it must be the rearrangement of the N-sulfonyloxy compound, as tacitly assumed above. (2) Both an ion-pair and a radical-pair mechanism are ruled out. Such mechanisms would lead to scrambling of the label within the sulfonyloxy group. Compound **13** would, with such scrambling, have the label observed, but the hydrolysis product would have only $\frac{2}{3}$ of the observed label. (3) A 4-centered transition state, such as **15** is ruled out, because it would lead to *o*-hydroxybenzanilide without any label.



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Our data are best accommodated by a concerted mechanism in which step 1 either is irreversible, or in which k_2 is considerably greater than k_{-1}. If these conditions were not fulfilled, isotopic equilibration within the sulfonyloxy group would occur, since the O^{16} from the N-hydroxy function becomes a sulfonyl oxygen in the first step of the rearrangement. Fig. 2 summarizes this mechanism.

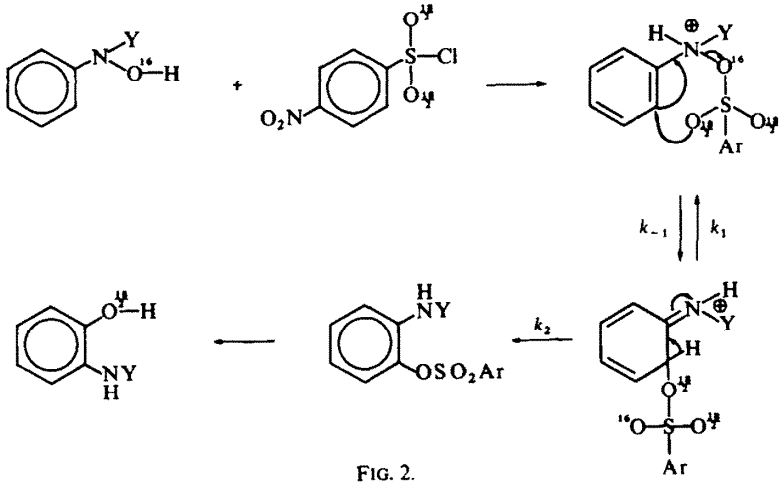
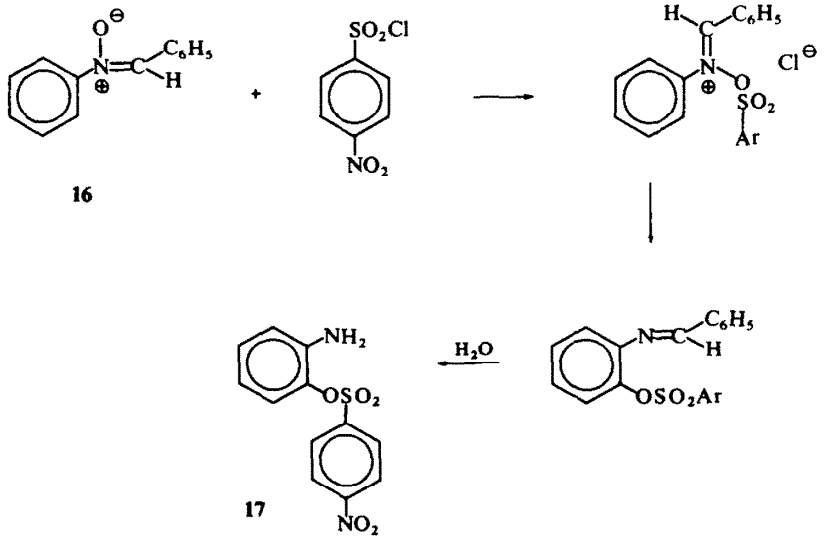


FIG. 2.

Attempting to force the rearrangement into a different course, and to produce para disubstituted product, 2,6-dimethylhydroxylamine was treated with *p*-nitrobenzenesulfonyl chloride. A black resin was produced, from which no pure compounds could be isolated.

Treatment of α,N-Diphenylnitrone with *p*-nitrobenzenesulfonyl chloride gave a 20% yield of *o*-(*p*-nitrobenzenesulfonyl oxy) aniline (**17**), presumably by the following mechanism:



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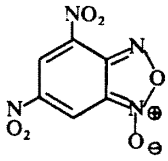
Truce[20] has reported a similar, but intramolecular, rearrangement.

Picrylhydroxylamine, when reacted with *p*-nitrobenzenesulfonyl chloride and sodium bicarbonate, gave an almost quantitative yield of 2,4-dinitrobenzofuroxan (**18**), presumably by O-acylation followed by nucleophilic displacement of *p*-nitrobenzenesulfonate ion from nitrogen by the oxygen of an adjacent nitro group. The same furoxan is produced when picrylazide is decomposed thermally in inert solvents.[21,22]



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EXPERIMENTAL

Instruments. IR spectra were taken on a Perkin–Elmer model 421 or a Beckman IR 8 spectrometer, UV spectra on a Cary 11 model s, and NMR spectra on a Varian A-60 instrument. VPC was carried out on an Aerograph 90 P3 gas chromatograph.

Reaction of phenylhydroxylamine with tosyl chloride. Phenylhydroxylamine (2·18 g; 0·02 mole) was dissolved in 200 ml ether. To the stirred, ice-cooled soln were added dropwise and at equal rates solutions of *p*-toluenesulfonyl chloride (3·82 g; 0·02 mole) in 150 ml $CHCl_3$ and Et_3N (2·02 g; 0·02 mole) in 100 ml ether. After a total reaction time of 2 hr, the soln was filtered and concentrated to give a viscous oil. This was extracted with large volumes of boiling hexane. The hexane soln yielded 1·21 g (23% of the theoretical quantity) prisms, m.p. 101–102° after recrystallization from $CHCl_3$–hexane. The IR and NMR spectra of this material were undistiguishable from those of authentic[23] 2-(tosyloxy) aniline. The IR spectrum (in KBr) showed bands at 3510, 3415, 1490, 1335, 1180 and 1170 cm^{-1}. The NMR spectrum showed CH_3 at 2·47 δ (3); NH_2 at 5·89 δ (broad) (2); phenyls at 6·65–8·20 δ (multiplet) (8). (Found: C, 59·59; H, 5·26; N, 5·07. Calc. for $C_{13}H_{13}NO_3S$: C, 59·41; H, 5·00; N, 5·34%.)

N-Carbethoxy-phenylhydroxylamine was prepared in 47% yield from phenylhydroxylamine and ethyl chloroformate in ether, and crystallized from hexane, m.p. 48·5–49·5°, reported 47–48°.[24] IR spectrum in CCl_4: 3150, 3010, 2980, 2930 and 1690 cm^{-1}. NMR spectrum in CCl_4: CH_3 at 1·15 δ (triplet, 3); CH_2 at 4·80 δ (quartet, 2); phenyl at 6·80–7·55 δ (multiplet, 5); OH at 8·95 δ (singlet, 1).

Reaction of N-carbethoxyphenylhydroxylamine with p-nitrobenzene-sulfonyl chloride. N-Carbethoxyphenylhydroxylamine (3·62 g; 0·021 mole) and Et_3N (2·02 g; 0·021 mole) were dissolved in 100 ml ether. To the boiling soln, *p*-nitrobenzenesulfonyl chloride (4·44 g; 0·020 mole) in 50 ml ether was added dropwise. After 1 hr, the soln was filtered and concentrated, leaving a yellow oil. Recrystallization from MeOH–water gave 2·66 g (73%) light yellow granules of **12**. After two recrystallizations from MeOH–water and CCl_4 the m.p. was 125·5–127°. (Found: C, 49·41; H, 3·86; N, 7·90. Calc. for $C_{15}H_{14}N_2O_7S$: C, 49·18; H, 3·83; N, 7·65%.) IR spectrum in CCl_4: 3445 (sharp); 1750, 1210, 1200 cm^{-1}. NMR spectrum in $CDCl_3$: CH_3 at 1·28 δ (triplet, 3); CH_2 at 4·13 δ (quartet, 2); phenyls and NH at 6·50 to 8·67 δ (multiplet, 9). These data are consistent with the structure of N-(*o*-(*p*-nitrobenzenesulfonoxyphenyl) urethan.

Conversion of **12** *to benzoxazolone.* A soln of **12** (1·0 g; 0·027 mole) in a mixture of 10% EtOH and 90% water, containing a little $NaHCO_3$, was heated to reflux for 4 days, then cooled to give 0·137 g (39% yield) benzoxazolone, identified by comparison of its IR spectrum with that of an authentic sample, m.p. 138·4–139·8°, mixture m.p. undepressed.

Reaction of N-Benzoylphenylhydroxylamine with p-nitrobenzenesulfonyl chloride A soln of **10** (2·5 g; 0·012 mole) in 200 ml ether was kept at 0°. Solns of *p*-nitrobenzenesulfonyl chloride (2·69 g; 0·012 mole; in 50 ml $CHCl_3$ and Et_3N (1·25 g; 0·012 mole; in 50 ml ether) were added dropwise at equal rates. The mixture was kept at 0° for 2 more hr, filtered, then washed twice with 100 ml portions cold water, dried, and evaporated to dryness at reduced press. The ppt was stirred with 300 ml water for 1 hr, and the undissolved material

was dried and combined with the residue from the ether soln. Recrystallization from $CHCl_3$–hexane gave 3·4 g (71% yield) of **13**, m.p. 152–154°. (Found: C, 57·401; H, 3·50; N, 6·94. Calc. for $C_{19}H_{14}N_2O_6S$: C, 57·27; H, 3·51; N, 7·04.) IR spectrum (in KBr): 3410 (sharp), 1670, 1185 cm^{-1}. NMR spectrum (in DMSO-d_6) phenyls 7·15–8·40 δ (13), NH 9·88 δ (1).

Hydrolysis of 2-(p-*nitrobenzenesulfonoxy*) *benzanilide* (**13**). Stirring 2·0 g of **13** (0·005 mole) with 200 ml 1N NaOH in 50% dioxan–water (2 hr, 25°) gave a yellow soln, which was neutralized with AcOH, saturated with NaCl, and extracted with 3 times 150 ml dichloromethane. The dried dichloromethane soln was concentrated to 50 ml. Adding hexane to the boiling dichloromethane soln to the clouding point, cooling and finally refrigerating, gave 1·0 g (95% yield) *o*-hydroxybenzanilide, m.p. 167–169° after 2 recrystallizations from $CHCl_3$–hexane. Its IR spectrum was undistinguishable from that of an authentic sample.[25] IR spectrum (in KBr): 3410, 3050, 1640 cm^{-1}.

Search for the para-*isomer of* **13** *in the product mixture from* **10**. The reaction mixture from **10** was hydrolyzed as above, using a 1N NaOH in 50% water-dioxan. Exhaustive extraction of the hydrolysis soln gave a yield of 97%. Ten VPC columns were tried, at different temps. The best results were given by a 20% Silicone SF 96 on 50/60 mesh Anachrom ABS column of 400 cm length and 0·6 cm dia, at 215°. Under these conditions, some of the *o*-hydroxybenzanilide was converted to 2-phenylbenzoxazolone, but *p*-hydroxybenzanilide could be determined accurately. The detector response was calibrated by injecting weighed amounts of authentic *p*-compound. The VPC fraction (from the hydrolyzed mixture from the reaction of **10**) that corresponded in retention time to authentic *p*-hydroxybenzanilide was collected and identified by comparison of its IR spectrum with that of the authentic compound, and by its m.p. of 208°, yields of 1·4% of the *p*-compound were repeatably found.

Preparation of p-*nitrobenzenesulfonyl* ("*Nosyl*") *chloride*-SO_2^{18}. Following Oae's method,[16] 2·0 g (0·013 mole) *p*-nitrothiophenol[26] (m.p. 74–75°) was suspended in 50 ml water of nominally 1·5 atom-% O^{18} content. A slow stream of purified Cl_2 was bubbled into the vigorously stirred suspension. After 12 hr, the buff colored solid was filtered off, washed with 50 ml water, and dried. The yield was 2·47 (85% of the theoretical), m.p. 78·5° after 2 recrystallizations from $CHCl_3$–hexane. Its IR spectrum was indistinguishable from that of authentic *p*-nitrobenzenesulfonyl chloride. Two samples were thus prepared. They analyzed for 0·443 and 0·485 atom-% excess O^{18}.

Reaction of **10** *with nosyl chloride*-SO_2^{18}. The two samples of O^{18}-labeled nosyl chloride were separately reacted with **10** as described, but at $\frac{1}{10}$ of the scale. The yield of **13** was 65%. Hydrolysis to *o*-hydroxybenzanilide was also carried out as described above. The O^{18} assays are listed in Table 1.

Reaction of 2,6-*dimethylphenylhydroxylamine with nosyl chloride* A soln of 1·5 g (0·011 mole) 2,6-dimethylphenylhydroxylamine[27] in 150 ether was treated with nosyl chloride and Et_3N as described above for phenylhydroxylamine. Only a black tarry residue could be obtained from the soln.

Reaction of α,N-*diphenylnitrone with nosyl chloride.* A soln of 1·97 g (0·01 mole) α,N-diphenylnitrone[28] in 50 ml dry, pure, THF was heated to reflux while a soln of 2·22 g (0·01 mole) nosyl chloride in 50 ml THF was added dropwise. After 6 hr boiling, the mixture was concentrated to 50 ml. TLC showed the presence of both starting materials and of a third component. The latter could be separated by chromatography on acid-washed alumina, which presumably provided the water required for the last (hydrolysis) step given in the text above. The product melted at 120–125° and had an IR spectrum indistinguishable from that of authentic 2-(*p*-nitrobenzenesulfonoxy) aniline

Preparation of 2-(p-*nitrobenzenesulfonoxy*) *aniline.* The compound was prepared like its toluenesulfonyloxy analog[23] from *o*-aminophenol and nosyl chloride. Recrystallization from $CHCl_3$–hexane afforded light yellow crystals, m.p. 128–130°, in 77% yield. (Found: C, 49·00; H, 3·54; N, 9·52. Calc. for $C_{12}H_{10}N_2O_5S$: C, 48·98; H, 3·40; N, 9·52%.) IR spectrum (in KBr): 3475, 3390 cm^{-1} (NH_2); 1520, 1480 (NO_2); 1190 cm^{-1} (SO_2). NMR spectrum (in THF-d_8): NH_2 at 4·55 δ (broad, 2); phenyls at 6·20 to 8·70 δ (complex, 8).

Reaction of picrylhydroxylamine with nosyl chloride. A soln of 2·8 g (0·012 mole) picrylhydroxylamine[29] in 250 ml dichloromethane was stirred vigorously at 0° while solns of nosyl chloride (2·60 g; 0·012 mole; in 50 ml dichloromethane) and $NaHCO_3$ (0·98 g; 0·012 mole; in 50 ml water) were added dropwise at approximately equal rates. The mixture was allowed to warm to room temp over a period of $\frac{1}{2}$ hr, filtered and separated. The queous phase was extracted twice with 50 ml portions dichloromethane, and the combined, dried, dichloromethane phases were evaporated at reduced press. The residue weighed somewhat more than corresponds to a theoretical yield of dinitrobenzofuroxan, and contained some unreacted picrylhydroxylamine. Recrystallization from benzene–hexane (1:1) gave yellow needles, and further recrystallization finally afforded a 32% yield of pure (m.p. 172–174°) 4,6-di-nitrobenzofuroxan.[22] IR

spectrum (in KBr): 3085 cm^{-1}, 1550, 1335 (NO_2); no absorption above 3100 cm^{-1}. (Found: C, 31·80; H, 0·90; N, 24·56. Calc. for $C_6H_2N_4O_6$: C, 31·86; H, 0·89; N, 24·77%.)

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