Formylation of Iodobenzene with PMHS in MeCN HMPA. Tetrakis(triphenylphosphine)palladium(0) (50 mg, 0.05 mmol) was placed in the reaction vessel which was then purged with nitrogen. Acetonitrile (20 mL), HMPA (2.5 mL), PMHS (2.0 mL), and iodobenzene (0.5 mL, 4.5 mmol) were introduced via a syringe through a rubber septum into the vessel. The reaction vessel was purged twice with carbon monoxide and then loaded with 50 psi of carbon monoxide at room temperature. The mixture was stirred at 80 °C for 20 h. After 20 h the reaction mixture was cooled to room temperature, ether (100 mL) was added, the mixture was filtered from solid polymer residue, and the volatile solvents were removed (rotoevaporator). The resulting yellow oil was dissolved in 30 mL of ether, washed with three portions of 30 mL of water, and dried with MgSO4 and the ether was removed under reduced pressure. n-Hexane (50 mL) was added and the formed precipitate was removed by filtration followed by evaporation of the n-hexane. Benzaldehyde (310 mg, 3 mmol) was isolated by Kugelrohr distillation. The pot residue consists of an oily material which had only one ¹H NMR signal at 0.15 ppm (Si-CH₃).

Formylation of Bromobenzene in MeCN/Me₂SO Solution. A mixture of 150 mg (0.15 mmol) of $Pd(PPh_3)_4$ and 2.65 g of tribenzylamine (9.2 mmol) was placed in the reaction vessel. After the mixture was purged with nitrogen, acetonitrile (10 mL), Me₂SO (10 mL), PMHS (20 mL), and bromobenzene (0.5 mL, 4.8 mmol) were introduced via a syringe through a rubber septum. Carbon monoxide (50 psi) was added at room temperature and the sealed reaction vessel was heated to 110 °C for 18 h. After workup as described before, 300 mg (2.8 mmol) of benzaldehyde were sep-

Formylation of Bromobenzene with Sodium Formate as the Hydrogen Donor. A mixture of 50 mg (0.05 mmol) of Pd(PPh₃)₄ and 400 mg (6 mmol) of sodium formate was placed in the reaction vessel. After the mixture was purged with nitrogen, acetonitrile (4 mL), dimethyl sulfoxide (4 mL), and bromobenzene (0.1 mL, 0.95 mmol) were added via a syringe through a rubber septum. Carbon monoxide (50 psi) was introduced at room temperature and the sealed reaction vessel was heated to 125 °C. After 18 h the reaction mixture was cooled to room temperature, methanol (30 mL) was added, and benzaldehyde (63.7 mg, 0.60 mmol) was determined by HPLC in the crude filtered methanol solution.

Registry No. HMPA, 680-31-9; PMHS, 9004-73-3; C₆H₅I, 591-50-4; 4-BrC₆H₄I, 589-87-7; C₆H₅Br, 108-86-1; 4-ClC₆H₄Br, 106-39-8; 2-CH₃C₆H₄I, 615-37-2; 2-CH₃C₆H₄Br, 95-46-5; 4-CH₃C₆H₄Br, 106-38-7; 2-CH₃OC₆H₄Br, 578-57-4; 4-CH₃OC₆H₄Br, 104-92-7; C₆H₅CH₂Br, 100-39-0; 4-NCC₆H₄Br, 623-00-7; C₆H₅Cl, 108-90-7; C₆H₅CHO, 100-52-7; 4-BrC₆H₄CHO, 1122-91-4; 4- $ClC_{6}H_{4}CHO$, 104-88-1; 2- $CH_{3}C_{6}H_{4}CHO$, 529-20-4; CH₃C₆H₄CHO, 104-87-0; 2-CH₃OC₆H₄CHO, 135-02-4; 4-CH₃OC₆H₄CHO, 123-11-5; C₆H₅CH₂CHO, 122-78-1; 4-NCC₆H₄CHO, 105-07-7; Pd(PPh₃)₄, 14221-01-3; Pd(OAc)₂, 3375-31-3; PhCH₂PdCl(PPh₃)₂, 22784-59-4; PdCl₂(PPh₃)₂, 13965-03-2; (Co(CO)₃PPh₃)₂, 10170-27-1; (C₆H₅CH₂)₃N, 620-40-6; Ca(OH)₂, 1305-62-0; CO, 630-08-0; H₃CN(Oct)₂, 4455-26-9; 1bromonaphthalene, 90-11-9; 2-bromothiophene, 1003-09-4; 1naphthaldehyde, 66-77-3; 2-thiophenecarboxaldehyde, 98-03-3; pyridine, 110-86-1; sodium formate, 141-53-7.

Oxidative Deamination of Amines by Arylsulfonyl Peroxides¹

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Oxidation of primary and secondary amines with arylsulfonyl peroxides 1a,b was examined. Optimal results were obtained by using m-(trifluoromethyl)benzenesulfonyl peroxide, 1b, as the oxidant and potassium hydroxide as the promoting base in ethyl acetate at -78 °C. Under these conditions, yields of carbonyl products were generally higher than other methods for both amine types. The stability of the intermediate imine is of great importance in determining the success of the conversion.

It was previously reported that amines could be oxidatively deaminated to carbonyl products with arylsulfonyl This synthetic transformation, oxidative peroxides.² deamination,³ has been the subject of numerous studies using a variety of oxidizing agents,⁴ peroxides,⁵ and synthetic sequences.⁶⁻¹² These methods are subject to limitations of amine type and/or problems of overoxidation. Probably the best procedure for primary amines is the biomimetic method of Rapoport,¹⁰ while for secondary amines, the most successful method is the superoxide-

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promoted elimination of the N-chloramine derivative.^{6c} We have established that the reaction between amines and arylsulfonyl peroxides is a two-step process involving the formation and subsequent elimination of an N-aryl-

sulfonoxy intermediate (eq 1).¹³ Since each step of eq 1

 $RCH_{2}NHR' + (ArSO_{2}O)_{2} \xrightarrow{fost} RCH_{2}NR' + ArSO_{3}H$ $1a. Ar = 4 - NO_{2}C_{6}H_{4}$ $1b. Ar = 3 - CF_{3}C_{6}H_{4}$ $OSO_{2}Ar$ i $RCH_{2}NR' \xrightarrow{:9} RCH = NR' + ArSO_{3}^{-}BH^{+}$ (1) i $H^{+}, H_{2}O$ RCHO

proceeds rapidly and in high yield under appropriate conditions, we felt that it might be possible to develop this reaction synthetically for oxidative deamination.

As shown in eq 1, 2 equiv of arylsulfonic acid are produced in the oxidation which must be neutralized. Thus 3 equiv of amine are required; one is oxidized and two are converted to the ammonium salt. If these extra amine equivalents are not included, protonation of the unreacted amine renders it inert toward the peroxide, and the reaction does not proceed to completion. Thus yields of imine product, with respect to the amine, are limited by the stoichiometry. One way to improve the conversion is to use some other base to scavenge the acid as it is formed. Since arylsulfonyl peroxides themselves are degraded by soluble bases, it is necessary to use an insoluble (heterogeneous) base to scavenge the acid without decomposing the peroxide oxidant. A few examples reported earlier² used powdered potassium hydroxide in ethyl acetate for this purpose, but we wished to make a more complete survey of the influence of base, solvent, and the amine structure on the yield of oxidative deamination and thus determine the general synthetic utility of the process.

Results

Solvent. Initial screening was done by using p-nitrobenzenesulfonyl peroxide, 1a, pNBSP, as the oxidant, benzylamine, 2, and dibenzylamine, 3, as model primary and secondary amines, and powdered potassium hydroxide as the heterogeneous base. The highest yields were obtained in ethyl acetate (63% for 2, 75% for 3) while methylene chloride gave lower yields (22%, and 63%, respectively). No oxidative deamination was found in ether due to the insolubility of pNBSP in ether at -78 °C. Methanol was unsatisfactory since the solubility of potassium hydroxide even at -78 °C lead to decomposition of the peroxide.

Base. Various heterogeneous bases were screened by using 1a as the oxidant and 2 and 3 in ethyl acetate at -78°C. One requirement for all of these bases is that vigorous stirring must be employed throughout the reaction. Our working hypothesis assumes that as the oxidation occurs in solution, the sulfonic acid formed immediately produces the ammonium salt. Proton transfer from the partially soluble ammonium salt to the solid base is required to regenerate the free amine and thus carry the reaction to completion. Vigorous stirring is necessary to facilitate this proton transfer. The results of this survey are presented in Table I. Since it was possible that base-induced per-

Table I. Effect of Bases on the Oxidative Deamination of Benzylamine and Dibenzylamine by pNBSP in Ethyl Acetate at -78 °C

entry	amine	peroxide, equiv	base (equiv)	yield, %
1	benzylamine	1.2	KOH (6)	63
2		1.67	KOH (6)	49
3		1.2	MgO (6)	30
4		1.67	MgO (6)	22
5		1.2	K_2CO_3 (10)	50
6		1.2	basic alumina (>6)	31
7		1.67	basic alumina (>6)	24
8		1.67	neutral alumina ^a	15
9	dibenzylamine	1.2	KOH (6)	75
10		1.67	KOH (6)	95
11		1.2	MgO (6)	71
12		1.67	MgO (6)	70
13		1.67	BaO (6)	42
14		1.67	BaO (10)	54
15		1.2	K_2CO_3 (10)	70

^a 1 g/mmol was employed.

oxide decomposition might compete with the oxidation, two peroxide stoichiometries were tested (1.2 and 1.67 equiv). Potassium hydroxide was found to be the superior base (entries 1 and 10). The basicity of the base seems to be an overriding factor, since the somewhat weaker oxyanion base potassium carbonate (entry 5) gave reduced yields. Magnesium oxide and barium oxide proved unsuitable. Somewhat surprisingly, activated alumina failed to give satisfactory yields. This reagent has been reported to be a superior catalyst for the dehydrotosylation of secondary tosylates to the corresponding alkenes.¹⁴

No soluble base was found suitable as sterically hindered bases such as 1,8-bis(dimethylamino)naphthalene¹⁵ and N,N-diisopropylethylamine reacted with the peroxide reagent. We suspect that electron-transfer processes might be involved for such electron-rich amines interacting with sulfonyl peroxides, but we have no proof of this. The highly hindered 4-methyl-2,6-di-*tert*-butylpyridine (pK_a = 5.1)¹⁶ did not decompose the peroxide but was insufficiently basic to deprotonate the ammonium salts of amines (pK_a = 9-11).

Peroxide. While the initial survey of reaction conditions was carried out with pNBSP, we also evaluated m-(trifluoromethyl)benzenesulfonyl peroxide, 1b, mTFBSP. In general, improved yields were found for 1b. This is probably due to the improved solubility of both 1b and its ammonium salts which facilitates proton transfer to the base (the reactivities of these peroxides are similar^{13b}).

A striking example of this is in the oxidation of dicyclohexylamine which forms unusually insoluble ammonium sulfonate salts. When an excess (3 equiv) of the amine is oxidized by 1b (in the presence of potassium hydroxide), cyclohexanone is produced in 96% yield. However, oxidation of 1 equiv with 1b gives only 54% yield, while 1a, whose derived ammonium salts are quite insoluble, gives only 20% yield.

Amine Oxidations

With the best reaction parameters established (1b, 6 equiv of powdered potassium hydroxide, ethyl acetate, -78 °C), a variety of primary and secondary amines were oxidized and the yields of the carbonyl product determined

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Table II. Yields of Oxidative Deamination of Various Amines by mTFMB^o

		equiv of			
entry	amine	mTFBSP	product	yield,	%
1	benzylamine	1.2	C ₆ H ₅ CHO	77	_
2	-	1.67		50	
3	<i>n</i> -hexylamine	1.2	hexanal	34	
4		1.67		21	
5	<i>n</i> -octylamine	1.2	octanal	39	
6		1.67		21	
7	2-octylamine	1.2	2-octanone	42	
8		1.67		36	
9	cyclohexylamine	1.2	cyclohexanone	66	
10		1.67		52	
11	cyclopentylamine	1.2	cyclopentanone	10	
12		1.67		18	
13	α -methylbenzyl- amine	1.2	acetophenone	28	
14	dibenzylamine	1.2	benzaldehyde	98	
15		1.67		98	
16	di- <i>n</i> -hexylamine	1.2	hexanal	38	
17		1.67		77	
18	di- <i>n</i> -octylamine	1.2	octanal	26	
19		1.67		70	
20	dicyclohexylamine	1.2	cyclohexanone	54	
21		1.67		40	
22	<i>n</i> -methylbenzyl- amine	1.67	benzaldehyde	80	

 a Reactions were carried out with 1 equiv of amine and 6 equiv of potassium hydroxide in ethyl acetate at $-78~^\circ\mathrm{C}.$

after acid hydrolysis. The results are presented in Table II. For primary amines best yields were obtained with 1.1-1.2 equiv of oxidant while 1.6 equiv gave better results for secondary amines. When these conditions are used, oxidative deamination with 1b is comparable and often superior to other methods reported in the literature for the oxidation of primary and secondary amines.

It is also clear that a major stumbling block in oxidative deamination is the inherent instability of the imine product prior to its hydrolysis. Each step of eq 1 has been studied independently. Formation of the N-sulfonoxyamine adduct proceeds quantitatively^{1b} and kinetic studies reveal that the imine-forming elimination is also quantitative.^{13a,b} The fact that less-than-quantitative yields are obtained must be due to product loss before or during the workup. The most likely origin of such losses is condensation reactions of the imines. Imines are highly susceptible to trimerization and/or dimerization¹⁷ (eq 2) which lowers

$$R_{1} \xrightarrow{R_{2}} R_{1} \xrightarrow{R_{2}} R_{1} \xrightarrow{R_{2}} R_{1} \xrightarrow{R_{2}} R_{1} \xrightarrow{R_{2}} R_{1} R_{2} + (NHCR_{1}R_{2})_{n}$$
(2)
$$R_{1}R_{2}C = NH \xrightarrow{R_{2}} R_{1}R_{2} - NH$$

the yield of carbonyl product after hydrolysis. Primary aldimines and ketimines are notorious in this regard while N-substituted imines are much more resistant to condensation.

The data in Table II illustrate that the highest yields are obtained in those cases where the most stable imines are formed. Thus, secondary amines give higher yields than primary amines.

The importance of eq 2 in accounting for product loss is also shown by control reactions. Several imines 4 were prepared independently and found to be virtually unreactive toward mTFBSP at room temperature whereas methyleneaniline trimer, 5, reacted nearly instantaneously at -78 °C. Thus the sp²-hybridized nitrogen of imines is unreactive while sp³-hybridized nitrogen either in the CeHe

5

 $R_1R_2C = NR_3$

 4a, $R_1 = R_2 = CH_3$; $R_3 = n - C_4H_9$ N

 4b, $R_1 = R_2 = CH_3$; $R_3 = n - C_6H_{13}$ C_6H_5

 4c, $R_1 = H_1; R_2 = C_6H_5; R_3 = CH_2C_6H_5$ C_6H_5

 4d, $R_1 = H_1; R_2 = C_6H_5; R_3 = n - CH_2C_6H_4CH_3$ C_6H_5

parent amine or an imine trimer reacts rapidly with sulfonyl peroxides. Hence for primary amines, where condensation occurs readily, only a slight excess (1.1 equiv) of the peroxide is used to minimize further oxidation of the product trimer/oligomer. For secondary amines, where condensation is minimal, an excess of the peroxide (1.67 equiv) gives the highest yields. We suspect that these condensations play a major role in the rather low yields observed for many other oxidative deaminations.⁴⁻⁶

One limitation to the use of arylsulfonyl peroxides for oxidative deamination is for amines in which carbon-tonitrogen rearrangements occur readily. These amines are characterized as those in which the amine nitrogen is attached to a secondary carbon which also has a good migrating group (aryl) attached. For example, α -methylbenzylamine (28%) and benzhydrylamine (35%) give reduced yields of oxidative deamination due to competing skeletal rearrangement. Such rearrangement probably also contributes to the anomalously low yield of cyclopentanone from cyclopentylamine (entry 11, Table II). These rearrangements will be reported separately.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer as liquid films (liquids) or potassium bromide disks (solids); NMR spectra were taken on a JEOL PS-100 instrument; and mass spectra were taken on a Hitachi RMU-6 mass spectrometer. Gas chromatography was performed on either a Varian A-90-P-3 or a Varian 920 gas chromatograph. Carbonyl compounds were analyzed on column of QF-1 (6.2 mm \times 2 m, 5%, Anachrome 80–90 mesh support) and amines were analyzed on a column of carbowax 20M-2% KOH (6.2 mm \times 2.6 m, 10%, Anachrome 80-90 mesh). Detector response factors were calculated from known mixtures and applied to the raw peak area data. Amines used in this work were commercially available, were purified by distillation, and showed no extraneous components by gas chromatography. Solvents were reagent grade and were distilled before use. Sulfonyl peroxides $1a^{18}$ and $1b^{19}$ were prepared by literature methods. Imines 4a-dwere prepared by a standard procedure.²⁰ Methyleneaniline trimer was prepared by the method of Miller.²¹

Amine Oxidations. All oxidative deaminations were carried out similarly and a typical reaction is described. Powdered potassium hydroxide (0.51 g, 9 mmol, 6 equiv) was suspended in a solution of benzylamine (0.15 g, 1.5 mmol) in ethyl acetate (30 mL) under nitrogen at -78 °C. mTFBSP (0.81 g, 1.8 mmol, 1.2 equiv) was added in one portion and the mixture was stirred at -78 °C for 6-7 h. The solvent was removed by rotary evaporation without the application of heat and hydrochloric acid (2.5 N, 60 mL) was added to the pasty residue. The mixture was placed in an oil bath preheated to 150 °C and distilled until 40 mL was collected. The steam distillate was neutralized with saturated sodium bicarbonate and extracted with dichloromethane (3×10) mL). The organic extracts were dried $(MgSO_4)$, a suitable standard was added (anisole in this case), and the carbonyl products were analyzed by gas chromatography. The carbonyl products were identified by collection and comparison of their

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spectral properties with authentic samples.

Several solvents, bases, and stoichiometries for 1a and 1b were carried out with benzylamine and dibenzylamine by using the same general procedure. After the most suitable conditions were established, various primary and secondary amines were oxidized as described above and the results are collected in Table II. Precautions worthy of note are that, (a) the amines and reaction mixtures must be protected from carbon dioxide in the atmosphere to prevent carbamate salt formation and reduced yields and (b) rotary evaporation and then hydrolysis must be carried out as quickly as possible (without heating) to minimize condensation of the imine product.

In most cases the residue from the steam distillation was basified with potassium hydroxide, extracted with methylene chloride $(3 \times 10 \text{ mL})$, and analyzed for the starting amine by gas chromatography. Only small (3-5%) amounts of the amines were detected.

Reactions of Imines 4a-d with 1b. A solution of the imine (1.5 mmol) in ethyl acetate was treated with 1b (1.5 mmol), and the mixture was allowed to stand at room temperature. The active oxygen was monitored by iodometric titration. Loss of peroxide usually took longer than 20 h, and the products (after hydrolysis) were the carbonyl and amine components of the starting imine

(85-100%) and products from the decomposition of 1b, mostly m-(trifluoromethyl)benzenesulfonic acid (80-90%).

Reaction of 5 with 1b. Methyleneaniline trimer, 5, (1.5 mmol) was dissolved in ethyl acetate (30 mL), cooled to -78 °C, and treated with 1b (1.5 mmol). Loss of active oxygen was complete after several minutes and no volatile products were obtained after the usual workup.

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Registry No. 1a, 6209-72-9; 1b, 35673-10-0; 2, 100-46-9; 3, 103-49-1; 4a, 6700-95-4; 4b, 32838-32-7; 4c, 780-25-6; 4d, 41882-47-7; 5, 91-78-1; CH₃(CH₂)₅NH₂, 111-26-2; CH₃(CH₂)₇NH₂, 111-86-4; CH₃(CH₂)₅CH(NH₂)CH₃, 693-16-3; PhCH(CH₃)NH₂, 98-84-0; $[CH_3(CH_2)_5]_2NH$, 143-16-8; $[CH_3(CH_2)_7]_2NH$, 1120-48-5; PhCH₂NHCH₃, 103-67-3; PhCHO, 100-52-7; CH₃(CH₂)₄CHO, 66-25-1; CH₃(CH₂)₆CHO, 124-13-0; CH₃(CH₂)₅C(O)CH₃, 111-13-7; PhC(O)CH₃, 98-86-2; cyclohexylamine, 108-91-8; dicyclohexylamine, 101-83-7; cyclopentylamine, 1003-03-8; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3.

Oxidation of Hydrazine Derivatives with Arylsulfonyl Peroxides¹

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A new method for the generation of the azo function is reported. A series of hydrazine derivatives, which included alkyl- and arylhydrazines, monoacylhydrazides, and diacylhydrazides, was oxidized with m-(trifluoromethyl)benzenesulfonyl peroxide. Smooth conversion to the diimide was observed. The diimides then yielded products typical of normal degradation pathways.

Amines react nucleophilically with arylsulfonyl peroxides to give N-arylsulfonoxy derivatives which undergo facile elimination to imines.² It would be useful to extend this chemistry to the oxidation of hydrazine derivatives with arylsulfonyl peroxides. If an analogous two-step reaction pathway were followed for hydrazines, (eq 1), then a new method for generating the azo linkage would be realized. OS0-Ar

RNHNHR' +
$$(ArSO_2O)_2$$
 RNHNR' + $ArSO_3H$
1a. $Ar = m - CF_3C_6H_4$
1b. $Ar = p - NO_2C_6H_4$
1c. $Ar = m - NO_2C_6H_4$
OSO₂Ar
RNHNR' $\frac{:B}{:RN} = NR' + ArSO_3^- + BH^+$ (1)

A good number of preparative routes to azo compounds are available.³ The most widely applicable route, however, is the oxidation of hydrazine derivatives.⁴ A variety of oxidants can be used, but many of these reagents exhibit a lack of generality, structure sensitivity, overoxidation, or side reactions. Therefore there is a continuing search

Table I. Oxidation of Monosubstituted Hydrazines 2 with mTFBSP^a

hydrazine	product (% yield) ^b				
$C_6H_5NHNH_2$, 2a	C ₆ H ₆ (73)				
	$C_{6}H_{5}N = NC_{6}H_{5}$ (4.7)				
$p-CH_3C_6H_4NHNH_2$, 2b	$CH_{3}C_{6}H_{5}$ (63)				
$p-ClC_{6}H_{4}NHNH_{2}$, 2c	$ClC_{6}H_{5}$ (47)				
C ₆ H ₅ CH ₂ NHNH ₂ , 2d	$C_{6}H_{5}CH_{3}$ (51)				
	C.H.CHO (25)				

^aReactions were carried out in dichloromethane at -78 °C. ^b Yields based on the peroxide oxidant averaged from two or more experiments.

for new oxidants which may circumvent some of these problems.

Based on the good nucleophilicity of hydrazines and the mild conditions under which elimination in N-arylsulfonoxy compounds takes place, it was felt that sulfonyl peroxides might be excellent general oxidants for hydrazines. Several hydrazine derivatives, 2-4, were chosen for study and the results are reported herein.



Results and Discussion

Monosubstituted Hydrazines 2. Slow addition of a dichloromethane solution of m-(trifluoromethyl)benzenesulfonyl peroxide, 1a, mTFBSP, to a solution of the hydrazine 2a-d at -78 °C followed by exposure to air gave

⁽¹⁾ Taken in part from the Ph.D Thesis of A.K. submitted to the

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