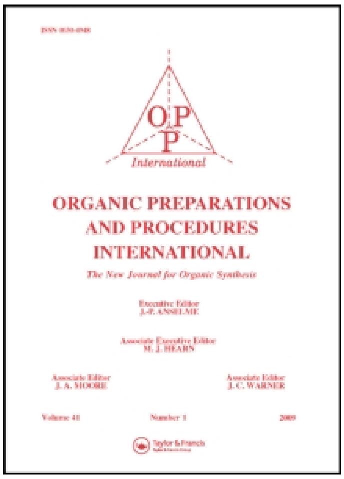

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THE OXIDATION OF ELECTRON DONORS WITH SULFONYL PEROXIDES

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A. π-Electron Donors

B. n-Electron Donors

THE OXIDATION OF ELECTRON DONORS WITH SULFONYL PEROXIDES

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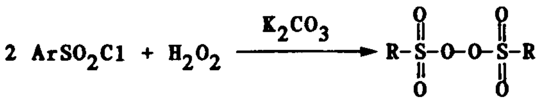
INTRODUCTION

While sulfonyl peroxides were first reported in 1903,[1] it has only been relatively recently that their chemistry has been investigated to any extent. In general, these materials act as two-electron oxidants for a variety of electron-donor organic functional groups. They function as pseudohalogens, and the sulfonoxy group behaves as an electrophile. The excellent nucleofugal character of the attached sulfonoxy group can thus be used to advantage in subsequent transformations of the initially formed products.

I. PREPARATION

Sulfonyl peroxides (1) are conveniently prepared by one of two methods depending on the nature of the R group attached to the sulfonyl function. When R is an aromatic group, the bis-(aryl)sulfonyl peroxide is most easily prepared by the base-promoted condensation of hydrogen peroxide with the requisite arylsulfonyl chloride (Eq. 1). A variety of substituted arylsul-



$$2\ ArSO_2Cl + H_2O_2 \xrightarrow{K_2CO_3} R-\overset{O}{\underset{O}{S}}-O-O-\overset{O}{\underset{O}{S}}-R \qquad (1)$$

1

fonyl peroxides have been prepared by one of two variants of this method; the substituents include p-NO_2, m-NO_2, o-NO_2, m-CF_3, 3,5-$(CF_3)_2$, p-Br and H.[2,3] The p-chloro and p-methyl derivatives have also been reported.[4,5] When the R group is not aromatic, the sulfonyl peroxides are best prepared by electrolysis of the corresponding sulfonic acids; methanesulfonyl peroxide[6] and trifluoromethanesulfonyl peroxide[7] have both been prepared in this manner.

II. PROPERTIES

The electron-withdrawing power of the sulfonyl group makes sulfonyl peroxides relatively stable compounds. The majority can be recrystallized and stored in the freezer for extended periods of time without significant decomposition. Furthermore, because of the low percentage of active oxygen (4-5%), their decomposition is not violent but merely exothermic. Arylsulfonyl peroxides with electron-withdrawing substituents such as p-NO_2 and m-CF_3 are the most stable and have been used most often in our work. The least stable analogs have weak electron-withdrawing or electron-donating groups attached to the sulfonyl function, e. g. $-C_6H_5$, $-CH_3$; both of these peroxides can, however, be prepared and used safely.

The decomposition of arylsulfonyl peroxides in chloroform yields two equivalents of the arylsulfonic acid resulting from homolysis of the oxygen-oxygen bond and hydrogen abstraction. Kinetic studies of this reaction have been used to estimate the -O-O- bond strength at ~ 24.5 kcal/mole, a value which indicates a fairly labile peroxide bond;[8,9] by the way of comparison, the O-O in benzoyl peroxide is ~ 30 kcal/mol.[10] This reaction has been found to be the method of choice for the preparation of anhydrous samples of arylsulfonic acids. The sulfonyl peroxide is prepared, purified and allowed to decompose in chloroform in the presence of oxygen; evaporation of the solvent and of the by-product phosgene leaves the pure sulfonic acid.

When electron-donors are present in solution, however, sulfonyl peroxides behave as electrophiles and can thus be described as pseudohalogens. The initially formed product is a cationic, sulfonoxy-donor adduct that undergoes further conversion to product (Eq. 2).

$$ArSO_2OOSO_2Ar + D: \longrightarrow ArSO_2O\text{-}D + ArSO_3^- \qquad (2)$$

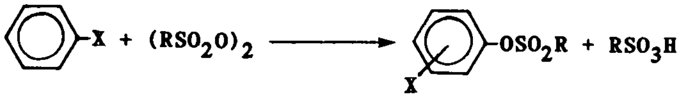
There are several features of this reaction that should be noted. When electron-donors are present, homolysis of the peroxide bond is not observed. Secondly, the donor undergoes a two-electron oxidation and electron pair donation is accompanied by cleavage of the peroxide bond, i.e. nucleophilic displacement on the O-O bond. Thirdly, no data have been obtained which suggest that single electron transfer from the donor to the peroxide is operative.[11] Finally, an electrophilic oxygen is the active agent and becomes attached to the donor as part of a powerful electron-withdrawing nucleofuge. These features render sulfonyl peroxides quite distinct from other electrophiles such as halogens and different from other electrophilic oxygenating agents such as peracids.

III. REACTIONS WITH ELECTRON DONORS

A. π-Electron Donors

1. Aromatic π-Donors

The characterization of sulfonyl peroxides as two-electron, oxygen-centered electrophiles was first obtained from work with aromatic



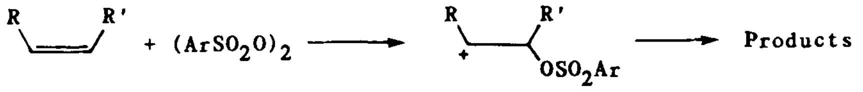
(3)

compounds. Aromatic substitution proceeds effectively to yield the corresponding O-arylsulfonate esters (Eq. 3). Although both alkyl[5] and arylsulfonyl peroxides[2,3,8,12-19] have been studied, the majority of work has employed the latter.

A variety of physical organic probes indicates that addition to the aromatic ring is a typical electrophilic aromatic substitution. Since the arenesulfonoxy group can be cleaved reductively with sodium naphthalide, this reaction constitutes an efficient route to substituted phenols.[20] A mixture of isomers is obtained, but sulfonyl peroxides are sufficiently selective that a single isomer predominates. Substrates with electron-donating substituents give 60-80% yields of the *para* product while those with electron-withdrawing substituents give 70-80% yields of the *meta* product.[3,12,14,16-18]

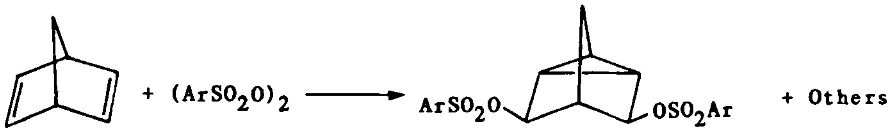
2. *Simple Olefins*

The π-bond of simple olefins is readily attacked by arylsulfonyl peroxides, but the product mixture is often complex. This is due to the fact that the intermediate cation produced from electrophilic addition has the arylsulfonoxy group attached *alpha* to the cationic center. Although the arylsulfonoxy group could undergo a bridging interaction with the adjacent cationic center through the ester or sulfonyl oxygens, no such interaction has been detected.[23] Instead, the powerful inductive effect of the arylsulfonoxy group[21] destabilizes the cation to the extent that a variety of eliminations and/or rearrangements occur rapidly, thus leading to several products (Eq. 4). The addition of arylsulfonyl peroxides to nor-



(4)

bornadiene and norbornene gives mixtures from which products of both addition and elimination could be separated (Eqs. 5 and 6).[22] Stilbene undergoes simple 1,2-addition because of its lack of available options,[4,23] while cyclohexene gives an inseparable mixture of products.[24]



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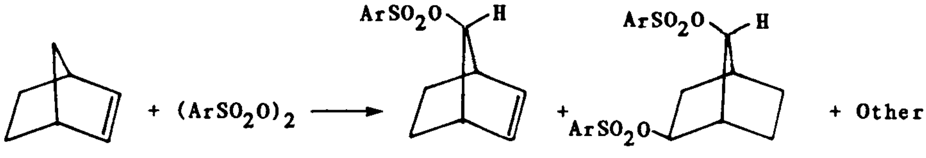
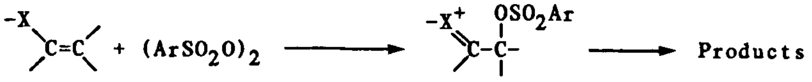


(6)

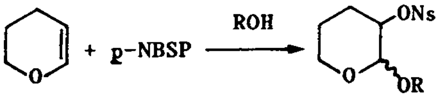
3. Electron-rich Olefins

Carbon-carbon double bonds which are substituted with oxygen or nitrogen (enols and enamines) are electron-rich by virtue of the resonance interaction of the π-bond with the lone pairs on the heteroatom. It is thus not surprising that these materials react rapidly with arylsulfonyl peroxides to yield simple product mixtures since the resulting cations are resonance stabilized (Eq. 7). For example, the reaction of the cyclic enol ethers dihydropyran, with p-nitrobenzenesulfonyl peroxide (pNBSP) in



(7)

the presence of alcohols gives high yields of the 2-alkoxytetrahydropyran p-nitrobenzenesulfonates 1 (Eq. 8);[25] a mixture of cis- and trans-isomers

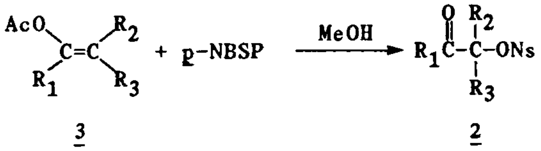


R = H (85%)
R = CH_3 (85%)
R = Et (77%)
R = CH_2CF_3 (15%)
R = i-Pr (80%)
R = Ac (91%)
R = t-Bu (91%)

(8)

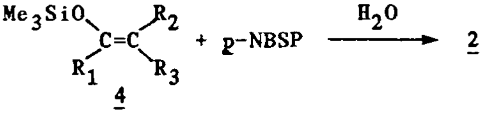
is obtained. The normally facile acid-catalyzed alkoxy exchange in the acetal function is inhibited by the inductive effect of the nosylate group and the ionization of the nosylate group is inhibited by the inductive effect of the acetal function. α-Sulfonoxyacetals are of interest because of their solvolytic behavior,[26] and can be used as an entry to further transformations in the pyran system.[27] This method could also be developed for intramolecular cyclizations by providing a hydroxyl group that can capture the intermediate oxonium ion intramolecularly.[28]

Enol esters[29] (3) and silylenol ethers[30] (4) also react readily with pNBSP. Unlike enol ethers which undergo 1,2-addition in the presence of nucleophiles, added nucleophiles attack the ester or silyl group to deliver α-p-nitrobenzenesulfonoxy ketones 2 in high yields (Eqs. 9 and 10). Enamines 5 react with pNBSP at -78° and give α-nosylketones after hydrolysis (Eq. 11).[30] It is likely that initial attack by the peroxide on the



(9)

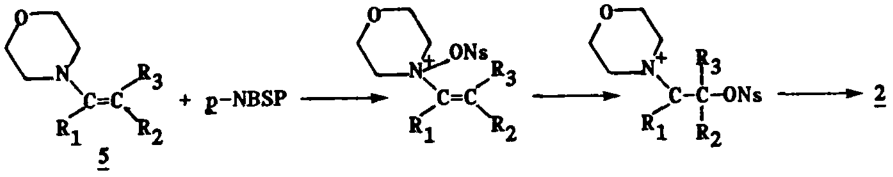
a) R_1 = Me, R_2 = R_3 = H (86%)
b) R_1 = Et, R_2 = H, R_3 = Me (95%)
c) R_1,R_2 = $(CH_2)_4$, R_3 = H (92%)
d) R_1 =Ph, R_2 = R_3 = H (90%)
e) R_1 = Ph, R_2 = Me, R_3 = H (95%)
f) R_1,R_2 = $-C_6H_4CH_2CH_2-$, R_3 = H (81%)



(10)

a) (30%)
b) (69%)
c) (77%)
d) (76%)
e) (95%)
f) (95%)
g) R_1 = i-Pr, R_2,R_3 = Me (71%)
h) R_1,R_2,R_3 = 2-norbornyl (95%)
(see Eq. 9 for R_1, R_2, R_3)

enamine nitrogen followed by 1,3-rearrangement leads to an α-nosyliminium



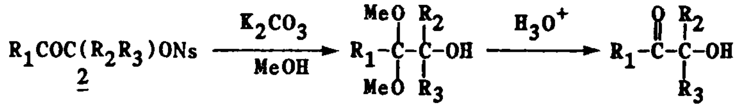
(11)

b) (81%) c) (82%) e) (88%) f) (60%) h) (52%)
(see Eqs. 9 and 10 for R_1, R_2, R_3)

ion as the first product which upon hydrolysis gives the nosyl ketone. Similar yields are obtained if m-trifluoromethylbenzenesulfonyl peroxide (mTFBSP) is used with any of the above substrates, but these products are oils as opposed to the normally crystalline nosylates.

There has been increasing interest in the chemistry of α-sulfonoxy ketones as precursors to α-keto carbocations,[31] as Favorski ring contraction substrates,[32] and as thiol-specific electrophiles.[33] Creary has also described some interesting base-catalyzed reactions of these compounds.[31] Previous preparations of α-sulfonoxy ketones are quite erratic[34] although Koser[35] recently described the preparation of α-tosyloxy ketones from ketones and [hydroxy(tosyloxy)iodo]benzene. This method gives good yields but is not regiospecific for non-symmetric ketones. The present method is clean, efficient, and regiospecific.

Since α-arylsulfonoxy ketones are structurally analogous to α-haloketones, it was expected that their chemistry would be similar. In fact, the chemistry of α-arylsulfonoxyketones is greatly simplified over that found for α-haloketones. Whereas α-haloketones can undergo attack at up to six sites with nucleophiles/bases,[36] α-sulfonoxyketones undergo two modes of reaction.[37] The principal reaction is nucleophilic addition to the carbonyl group followed by intramolecular displacement of the sulfonoxy group in the resulting tetrahedral intermediate. Highly efficient preparations of α-hydroxyketals and α-hydroxyketones and high yield conversion to α-aminoketones are shown in Eq. 12 and Eq. 13 respectively; when the base is non-nucleophilic, conversion to the α-sulfonoxy enolate is



$$\underset{\underline{2}}{R_1COC(R_2R_3)ONs} \xrightarrow[MeOH]{K_2CO_3} R_1-\overset{MeO}{\underset{MeO}{C}}-\overset{R_2}{\underset{R_3}{C}}-OH \xrightarrow{H_3O^+} R_1-\overset{O}{\overset{\|}{C}}-\overset{R_2}{\underset{R_3}{C}}-OH \qquad (12)$$

$$\underline{2} + R_2'NH \longrightarrow R_1-\overset{O}{\overset{\|}{C}}-\overset{R_2}{\underset{R_3}{C}}-NR_2' \qquad (13)$$

observed.[37] **As an α-substituent, the sulfonoxy group plays a much stronger role than a halogen in influencing the chemistry and α-sulfonoxy compounds have great potential as intermediates for the preparation of a variety of α-substituted carbonyl compounds.**

B. n-Electron Donors

1. Amine Donors. Preparation of O-Sulfonylhydroxylamines

The electron pair of amines provides an electron-rich site for attack by electrophiles. It was reasoned that if sulfonyl peroxides were used as the electrophiles, then normal two-electron oxidation would lead to an adduct with the sulfonoxy group attached to the amino nitrogen. It was indeed found that primary and secondary amines react readily at -78° with arylsulfonyl peroxides to give N-alkyl or N,N-dialkyl-O-arylsulfonylhydroxylamines (6) (Eq. 14).

$$2\ R_1R_2NH + (ArSO_2O)_2 \longrightarrow \underset{\underline{6}}{R_1R_2NOSO_2Ar} + R_1R_2NH_2^+\ ArSO_3^- \qquad (14)$$

$$R_1 = \text{alkyl},\ R_2 = H;\quad R_1,R_2 = \text{alkyl}$$

Although products (6) from the reaction of amines and sulfonyl peroxides are not very stable materials and are most conveniently generated and used in situ, methods have been developed for their isolation and characterization.[38] Most work has employed pNBSP or mTFBSP as the peroxide partner, since these are the most electrophilic and the resulting adducts (6) are the most stable. Structurally these products are of interest since they have powerful leaving groups attached to nitrogen. While unsubstituted O-arylsulfonylhydroxylamines (R_1, R_2 = H) are well-known materials,[39] N-substituted analogs were heretofore rare. In spite of earlier attempts,[41] only two reports of their preparation were extant.[40] More recently, condensation methods have been used to prepare mesylate[42] and sulfate[43] derivatives of aromatic amines. The present route is by far the most direct, simple, and general.

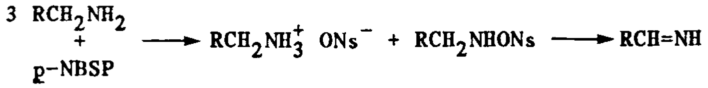
A significant effort has been devoted to understanding the initial interaction between the amine and peroxide. Since a variety of mechanisms can be considered including both one- or two-electron candidates, it was desirable to demonstrate the general two-electron character of sulfonyl peroxide oxidations. In summary, the evidence demonstrates convincingly that a two-electron pathway best accounts for the experimental results,[44] and the interaction between amines and sulfonyl peroxides is best depicted as a nucleophilic attack by the amine on the O-O bond which results in heterolytic cleavage of the peroxide bond.

Because the N-sulfonoxyamines (6) are the initial products of amine oxidations with sulfonyl peroxides, the chemistry of these O-sulfonoxyamines determines the ultimate products obtained in the oxidation. Attachment of the most effective arylsulfonoxy leaving groups to nitrogen was desirable in order to insure that subsequent reactions would proceed to products resulting from exclusive heterolytic rupture of the N-O bond.

Should this be the case, it would be possible to use a nitrogen atom as a cationic reaction center in the same ways that carbon has been used when it bears a good leaving group. Attempts to carry out this strategy in the past have been hampered by reliance on materials which have a halogen as the leaving group attached to nitrogen. While readily prepared, N-haloamines are capricious in their reactions since at least four different modes of N-X cleavage are possible and are often competitive.[45] It was expected that arylsulfonoxy leaving groups on nitrogen would undergo ionic cleavage exclusively and the bonded electrons of the N-O-bond would depart with the leaving group. Our expectations have been reduced to practice in three areas which are described below.

a. Oxidative Deamination

If an excess (3 equiv.) of an amine is oxidized with pNBSP or mTFBSP, acidic hydrolysis delivers a carbonyl product from oxidative deamination (Eq. 15).[46] Examination of the stoichiometry reveals that three equivalents of the amine are required; one is oxidized and two are converted to the ammonium salt. The O-sulfonylhydroxylamine intermediate undergoes base-promoted elimination,[44,47] to an imine which provides the carbonyl compound after hydrolysis. If a heterogeneous base is added to the mixture to scavenge the arylsulfonic acid formed in the oxidation, then a single equivalent of amine can be oxidized, and optimized yields with respect to the amine improve dramatically (40-90%).[48] While this procedure is one of the best general methods of oxidative deamination for both primary and secondary amines, it must be recognized that the weakness in any amine oxidation is that usually an imine is produced. The inherent



$$\begin{matrix}3\ RCH_2NH_2\\ +\\ p\text{-}NBSP\end{matrix} \longrightarrow RCH_2NH_3^+\ ONs^- + RCH_2NHONs \longrightarrow RCH{=}NH \qquad (15)$$

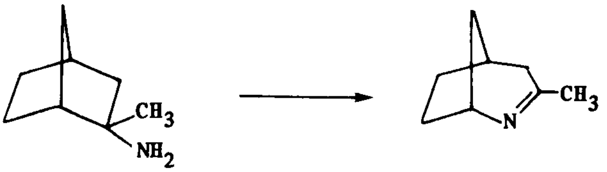
instability of imines is a serious obstacle in oxidative deamination, but the mild conditions of sulfonyl peroxide oxidations minimize this problem in comparison to most other procedures.[48]

b. Ionization

In the absence of base, O-arylsulfonylhydroxylamines (6) decompose with ionization of the N-O bond accompanied by carbon to nitrogen skeletal rearrangement (Eq. 16). This process is quite analogous to Wagner-Meerwein rearrangement in all-carbon compounds. The first examples were observed in

$$R_1R_2R_3CNHONs \longrightarrow R_1R_2C{=}NR_3 + R_1R_3C{=}NR_2 + R_2R_3C{=}NR_1 \qquad (16)$$

systems that were highly prone to rearrangement such as trityl (R_1,R_2,R_3 = Ar, R_3 = H).[49] It has since been found that a wide variety of groups migrate efficiently to nitrogen.[50] Thus amines are generally amenable to oxidative rearrangement with sulfonyl peroxides. Since a mixture of products is possible when R_1, R_2 and R_3 are dissimilar, factors which control the product distribution were examined. Although inherent migratory aptitudes of the rearranging groups are important, they are often of secondary importance compared to electronic features at the migration origin (tertiary > secondary >> primary) and stereoelectronic effects, which demand an antiperiplanar relationship between the migrating group and the leaving group.[50] If these factors are taken into account, nitrogen can be smoothly incorporated into rings as shown in Eqs. 17 and 18.



(17)

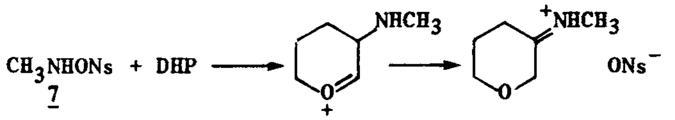
(18)

60-90%

Although the decomposition of the related tertiary cycloalkyl azides constitutes another method for achieving the same transformation, alkyl migration competes with ring expansion to afford mixtures.[51] The requirements for migration in N-sulfonoxyamines are sufficiently stringent that only ring expansion occurs. This methodology is presently being applied to the synthesis of azacyclic natural products in the solenopsin family.[52]

c. Aminations

A final reaction available to O-sulfonylhydroxylamines is replacement of the sulfonoxy group. Unsubstituted O-arylsulfonylhydroxylamines are well-known aminating agents;[9] however from a steric standpoint, substitution on nitrogen reduces the aminating ability and elimination and ionization (vide supra) predominate. Thus only under conditions where good, non-basic electron-donors are present and where ionization processes are slowed structurally, could the N-substituted compounds serve as aminating agents. In fact, compound 7 reacts rapidly with dihydropyran to give an iminium salt which presumably results from electrophilic addition to the double bond followed by hydride rearrangement in the intermediate oxonium ion (Eq.19).[53] While it is premature to speculate on the generality of the reaction, it may be possible to use sulfonyl peroxides to produce a variety of useful aminating agents from amines.



(19)

2. Hydrazines

Based on the excellent electron-donor properties of hydrazines and the facile elimination in N-arylsulfonoxy adducts, it was felt that sulfonyl peroxides might be excellent general oxidants for hydrazines. Thus the reaction of sulfonyl peroxides with several hydrazine derivatives such as arylhydrazines 8, monoacylhydrazines 9, and diacylhydrazines 10 have been studied. In all cases the pathway followed is analogous to that observed in amines, namely formation of an N-sulfonoxy adduct which undergoes elimination to yield to the -N=N- bond (Eq. 20).[54] The yields of product

$$\mathrm{RNHNHR'} \longrightarrow \mathrm{RNH\underset{\underset{ONs}{|}}{N}R'} \longrightarrow \mathrm{RN{=}NR'} \qquad (20)$$

are good. Two extra equivalents of hydrazine are needed to neutralize the two equivalents of sulfonic acid that are produced. If an excess of hydrazine is not used, protonation of the hydrazine renders it unreactive toward the peroxide and the reaction does not proceed to completion.

The oxidation of arylhydrazines (8) with mTFBSP (-78°) followed by stirring the reaction mixture in the presence of air gives the corresponding arenes (Eq. 21). The yields are based on the oxidant since

$$3\ \underset{\underline{8}}{\mathrm{ArNHNH_2}} + \underline{\mathrm{m}}\text{-}\mathrm{TFBSP} \longrightarrow \mathrm{ArH} + \mathrm{N_2} + 2\ \mathrm{ArNHNH_3^+}\ \mathrm{TFBSO^-} \qquad (21)$$

a) Ar = C_6H_5 (73%) b) Ar = $\underline{p}$-$CH_3C_6H_4$ (63%)
c) Ar = $\underline{p}$-ClC_6H_4 (47%) d) Ar = $C_6H_5CH_2$ (51%)

two extra equivalents of hydrazine are required to form the hydrazinium salt. A small amount of the arylazo compound was also detected in these oxidations and was isolated in the case of 8a (azobenzene, 5%). The requirement of air oxidation of the reaction mixture coupled with the formation of the azo compound are strong indications of an aryldiimide intermediate.[55] If an excess of peroxide is used (Eq. 22), further

$$4\ \underline{8a} + 2\ \underline{\mathrm{m}}\text{-}\mathrm{TFBSP} \longrightarrow \mathrm{PhN_2^+}\ \mathrm{ArSO_3^-} + 3\ \mathrm{PhNHNH_3^+}\ \mathrm{ArSO_3^-} \qquad (22)$$

oxidation to the diazonium takes place.[54] The course of the reaction is similar to those found for the oxidation of arylhydrazines by lead tetraacetate[56] and benzeneseleninic acid and anhydride.[57]

Monoacylhydrazines 9 are much less reactive than arylhydrazines 8. Nevertheless at 25° they undergo smooth oxidation by mTFBSP according to

$$4\ \underset{\underline{9}}{\mathrm{RCONHNH_2}} + m\text{-}\mathrm{TFBSP} \longrightarrow \mathrm{RCONHNHNCOR} + \mathrm{N_2} + 2\ \mathrm{RCONHNH_3^+}\ \mathrm{ArSO_3^-} \qquad (23)$$

a) R = C_6H_5 (68%) c) R = p-$CH_3OC_6H_4$ (40%)
b) R = m-ClC_6H_4 (58%) d) R = m-$CH_3C_6H_4$ (50%)
e) R = c-C_6H_{11} (32%)

Eq. 23. The acyldiimide formed in the oxidation is known to be a powerful acylating agent and reacts with the starting material to give the diacylhydrazine. This accounts for the extra equivalent (four total) required in Eq. 22. Yields are again based on the oxidant. Similar results were obtained for acylhydrazide oxidations with selenium oxidants,[57] lead tetraacetate[58] and halogens.[59]

Diacylhydrazines (10) react at room temperature with mTFBSP to give diacyldiimides as shown in Eq. 24. Of note here is the fact that the weaker basicity of diacylhydrazine minimizes its protonation, and only one equivalent of peroxide is required.

$$\underset{\underline{10}}{\mathrm{RCONHNHCOR}} + m\text{-}\mathrm{TFBSP} \longrightarrow \mathrm{RCON{=}NCOR} + \mathrm{ArSO_3H} \xrightarrow{\mathrm{MeOH}} 2\ \mathrm{RCO_2CH_3} \qquad (24)$$

a) R = C_6H_5 (86%) c) R = p-$CH_3C_6H_4$ (62%)
b) R = m-ClC_6H_4 (54%) d) R = m-$CH_3C_6H_4$ (81%)
e) R = c-C6H_{11} (78%)

The high acidity of the reaction mixture, however, promotes decomposition of the azodiacyl compound and it was found convenient to allow the diimide to react with added methanol and isolate the esters formed. The fact that some starting hydrazide was always recovered (15-20%), does not indicate inefficiency in the oxidation, but more likely results from the esterification of the diacyldiimide. In that process, the diimide produced

$$\begin{aligned} &\mathrm{RCON{=}NCOR + MeOH \longrightarrow 2\ RCO_2Me + [HN{=}NH]} \\ &\mathrm{RCON{=}NCOR + HN{=}NH \longrightarrow N_2 + RCONHNHCOR} \end{aligned} \qquad (25)$$

reduces some of the diacyldiimide to the hydrazine (Eq. 25). Control reactions with the diacyldiimide substantiate this rationale, as do literature precedents.[60]

These studies indicate that sulfonyl peroxides smoothly oxidize 1,2-disubstituted hydrazines to the corresponding azo compounds. The products obtained are similar to those obtained with other oxidants and reflect the reactivity of the azo function rather than influence of the oxidant.

A recurrent difficulty with sulfonyl peroxides is that two moles of an arylsulfonic acid are produced in these oxidations. This poses problems in that extra equivalents of basic substrates are needed to neutralize this acid. Where the substrates are not basic, the strong acid can degrade starting material and/or products. In certain cases a strong insoluble base can be used to scavenge the acid without destroying the peroxide; however, in these cases proton transfer is slow and sometimes the products do not survive the base. What is needed is a reasonably strong (pKa ≈ 12), non-nucleophilic, soluble base that can be added in stoichiometric amounts to the reaction mixture, to scavenge the acid without raising the basicity of the medium significantly. Traditional hindered bases such as Proton Sponge, diisopropylethylamine, and 2,2,6,6-tetramethylpiperidine all react readily with sulfonyl peroxides. On the other hand, the very hindered 2,6-di-*tert*-butylpyridine does not react with the peroxide, but is insufficiently basic (pKa ~ 4.2) to scavenge the acid competitively.

3. Phosphorus and Sulfur Compounds

Very little is known of the reactions of sulfonyl peroxides with n-electron donors other than amines. Based on their apparently general mode of reaction with electron donors, sulfonyl peroxides would be expected to serve as two-electron oxidants for many other types of compounds. The only information available in this regard is the report that triphenylphosphine is oxidized quantitatively to triphenylphosphine oxide by m-PNBSP.[8] Oxygen-18 labelling studies show that the phosphine attacks the peroxide

$$Ph_3P + ArSO_2^{*}O\text{-}OSO_2^{*}Ar \longrightarrow Ph_3PO + ArSO_2^{*}OSO_2^{*}Ar \qquad (26)$$

oxygens (Eq. 26). Although dimethyl sulfoxide rapidly decomposes sulfonyl peroxides, the products of these decompositions were not determined; these results are consistent with the concept of the sulfoxide acting as an n-electron donor to the peroxide. The oxidation of heteroatoms with sulfonyl peroxides is relatively uninvestigated, but seems quite promising in terms of interesting chemistry that might result.

C. Organometallic Donors

Electron rich σ-bonds found in organometallic compounds react with sulfonyl peroxides to give products of bond cleavage (Eq. 27).[61] The

$$R\text{-}M + (MeSO_3)_2 \longrightarrow MeSO_3\text{-}R + MeSO_3\text{-}M \qquad (27)$$

reaction of a series of alkyl- and arylmercury, -tin, and -lead compounds with methanesulfonyl peroxide was investigated. Carbon-mercury bonds are readily cleaved in high yields (85-95%) while carbon-tin bonds give lower yields (10-20%) of products. The decreased yields for tin and lead are due to diminished reactivity since the uncleaved starting material is recovered. In these cases, the decomposition of methanesulfonyl peroxide is competitive with its reaction with the organometallic. The use of a more stable and more electrophilic arylsulfonyl peroxide should improve these reactions markedly. Nevertheless the results of this preliminary study suggest that a very important new method for organometallic cleavage can be developed. Much work is needed to define the scope and utility of the method.

IV. CONCLUSIONS

Our experience with sulfonyl peroxides has shown them to be excellent reagents for the oxidation of a variety of functional types. They are easily prepared, handled and used. Furthermore, although they are peroxidic, they have proven to be very safe in the laboratory, in fact much safer than other routine reagents such as LAH or bromine, for example. With further development, a variety of new synthetic routes to difficult molecules may be discovered.

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