removal of the solid residue the solvent was evaporated. When the oily mixture was treated with diethyl ether BI-DI **7Aa** was obtained in 20% yield.

1,2-Diphenyl-3-(*tert*-butylimino)-2-propen-1-one (13Aa). A mixture of 1 g of *tert*-butylhydroxylamine and 2.2 g of 1,2-diphenylpropane-1,3-dione in 50 mL of $CHCl_3$ was stirred in the presence of $MgSO_4$ for 24 h. After filtration and evaporation of the solvent **13Aa** was obtained as an oil in 61% yield: MS (EI), *m/e* (relative intensity) 277 (M^+, 4); IR (film) ν 2080 and 1650 cm^{-1}; ^1H NMR δ 1.2 (s, 9 H, $C(CH_3)_3$), 7.1-7.7 (m, 10 H, Ar); ^{13}C NMR 30.0 (q, J = 127 Hz, $C(CH_3)_3$), 62.5 (s, $C(CH_3)_3$), 107.9 (s, C-2), 126.1-141 (8 C, Ar), 168.0 (s, C-3), 193.0 (s, C-1).

***N*-*tert*-Butyl-2,3-diphenyl-3-oxopropanamide (16)** was formed from **13Aa** in refluxing aqueous ethanol: mp 178-180 °C; MS (EI), *m/e* (relative intensity) 295 (M^+, 4). Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 76.71; H, 7.41; N, 4.68.

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Supplementary Material Available: Listing of the ESR coupling constants of nitroxides **5** and **6**, of the characteristic NMR data of compounds **8**, **7**, and **12**, and of the values of $[R^\bullet]$, α, K, and ΔG for the equilibrium **8Aa** $\rightleftharpoons$ 2 **6Aa** at various temperatures (7 pages). Ordering information is given on any current masthead page.

Chemistry of Oxaziridines. 10.[1] Selective Catalytic Oxidation of Sulfides to Sulfoxides Using *N*-Sulfonyloxaziridines

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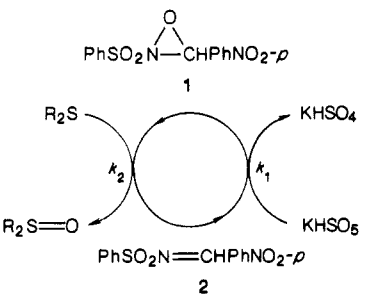
The chemoselective catalytic oxidation of aliphatic and aromatic sulfides to sulfoxides (90-95%) using a buffered potassium peroxymonosulfate (Oxone) generated *N*-sulfonyloxaziridine is described. This oxidizing system is rapid and relativily insensitive to the reaction parameters and the structure of the sulfide.

Sulfoxides are widely used synthons in organic synthesis and are commonly prepared by oxidation of sulfides.[2] The number of oxidizing reagents used for this purpose are many and varied because few, individually, have general or broad application.[2-9] Many of these oxidizing reagents are too reactive, resulting in significant overoxidation of sulfoxides to sulfones, particularly when the reagent is present in excess.[2b,3] With other reagents the chemoselectivity is poor, or they give undesirable side reactions such as cleavage of C-C and C-S bonds.[2b,3] Additional limitations include slow reaction rates, the necessity for careful control of the reaction parameters, instability, and expense.

Scheme I



A number of these limitations can be avoided by using *N*-sulfonyloxaziridines **1**, aprotic and neutral oxidizing reagents developed in our laboratories.[10,11] These reagents quantitatively and selectively oxidize most sulfides to

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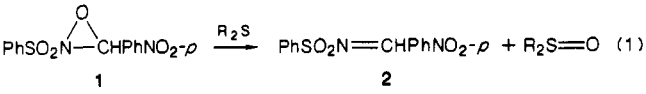
0022-3263/88/1953-5004$01.50/0

sulfoxides within a few minutes at room temperature.[12] Even in the presence of a large excess of 1, overoxidation of sulfoxides to sulfones is extremely slow.[12a] Zani and co-workers recently described the selective oxidation of thiones to sulfines using 1 (Ar = Ph).[13] *N*-Sulfonyloxaziridines 1 are highly chemoselective reagents that do not react with carbonyl groups, alcohols, or alkynes.[10] While these reagents stereoselectivity epoxidize alkenes, temperatures of 60 °C are generally required.[14] Zajac and co-workers recently reported that 1 (Ar = Ph) oxidizes sulfides 20 times faster than amines.[15]



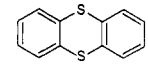
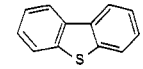
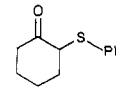
N-Sulfonyloxaziridines 1 are stable and readily prepared by biphasic oxidation of sulfonimines 2 with *m*-chloroperbenzoic acid (*m*-CPBA) and a phase-transfer catalyst.[16] Clearly, a catalytic oxidizing system, based on the demonstrated chemoselectivity of 1, would be of considerable value. Not only would such a system enhance the synthetic utility of these reagents but could result in simple methodology for the selective oxidation of aliphatic and aromatic sulfides to sulfoxides, avoiding many of the limitations observed with other oxidizing systems.[2-9]

Oxidation of sulfides to sulfoxides by 1 followed by reoxidation of the sulfonimine 2 to the oxaziridine 1 would establish a catalytic system (eq 1). *m*-CPBA cannot be used for this purpose because it oxidizes sulfides to sulfones under the reaction conditions. Furthermore, the rate of oxidation of 2 to 1 by this peracid is slow, i.e., 1–2 h, and *m*-CPBA is an expensive reagent.

Recently we described the application of buffered potassium peroxymonosulfate (Oxone) in the synthesis of *N*-sulfonyloxaziridines 1.[1] Oxidation of 2 to 1 was complete and quantitative within 15 min and a phase-transfer catalyst was not necessary. Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) is an inexpensive and stable oxidizing reagent that is commercially available. Although Oxone is reported to oxidize sulfides to mixtures of sulfoxides and sulfones,[17] we reasoned that in basic media, where the peroxymonosulfate anion is largely present, electrophilic oxidation of sulfides to sulfoxides would not occur (Table I, see entries 1 and 2). On the other hand, the peroxymonosulfate anion is necessary for the conversion of 2 to 1 (eq 1). The Oxone–oxaziridine catalytic system for the selective oxidation of aliphatic and aromatic sulfides is shown in Scheme I.

The catalytic oxidation of sulfides was carried out under biphasic conditions by placing the sulfide (typically 3 mmol) and sulfonimine 2 catalyst (0.6 mmol) in methylene chloride (turnover 5). The solution is buffered to ca. pH 8.5 by addition of an aqueous solution of potassium carbonate followed by addition of 4.5 equiv of Oxone (13.5 mmol of potassium peroxymonosulfate). Oxidation of sulfides to sulfoxides is generally complete within 10–30 min as determined by TLC. The reaction is quenched immediately on completion by addition of sodium metabisulfite which has the added advantage of removing the sulfonimine 2 catalyst. However, with larger scale oxidations it is necessary to separate the sulfoxides from the catalyst by distillation, extraction into *n*-pentane, or chromatography. The sulfoxides were isolated by preparative TLC on silica gel and identified by comparison of their spectral properties with values recorded in the literature (Table I).

Table I. Selective Catalytic Oxidation of Sulfides to Sulfoxides Using Buffered Oxone and 0.2 Equivalents of $PhSO_2N{=}CHPhNO_2$-*p* in CH_2Cl_2 at 25 °C

entry	sulfide	equiv of Ozone[a]	*T*, (h)	% isolated yields sulfoxide/sulfone	ref
1	*p*-tolylSMe	1.5[b]	4	26/64	8
2		1.5[c]	5	reaction	
3		1.5	0.5	91/5	
4	PhSMe	1.5 ($CHCl_3$)	0.5	95/d	12a
5		1.5 (K_2CO_3)	0.25	95/d	
6	$PhSCH_2Ph$	1.5 ($CHCl_3$)	18	95/0	12a
7		3.0 ($CHCl_3$)	4	96/0	
8	PhSPh	1.5 ($CHCl_3$)	24	92/3	17b
9		4.5 ($CHCl_3$)	8	90/0	
10		4.5 (K_2CO_3)	0.5	90/0	
11	$PhSCH{=}CH_2$	1.5	24	90/d	18
12		4.5	8	88/d	
13		4.5 (K_2CO_3)	0.5	90/d	
14		4.5 (K_2CO_3)	1.5	76/15	
15	$PhSCH_2CH_2OH$	1.5	0.5	0/95	23
16	$PhSCH_2CH_2OH$	0.75	1	0/65 (23)[e]	
17	$PhSCH_2CH_2Cl$	1.5 (K_2CO_3)	0.5	92/0	24
18	$(n\text{-}C_4H_9)_2S$	1.5	0.5	95/0	12a
19		1.5 (K_2CO_3)	0.25	92/0	
20	$(s\text{-}C_4H_9)_2S$	1.5	0.5	95/0	25
21	$(t\text{-}C_4H_9)_2S$	1.5	0.5	95/0	26
22		1.5	0.5	0/94	27
23		1.5	1	8/63 (23)[e]	
24		1.5	18	90/0[f]	7
25		4.5	2	91/0	
26		1.5	18	30/0 (62)[d]	4
27		7.5	8	88/0	
28		4.5 (K_2CO_3)	0.5	89/0	
29		4.5	18	89/0	28
30		4.5 (K_2CO_3)	2	90/0	

[a] Buffer with 7.0 equiv of $KHCO_3$ or K_2CO_3 based on Oxone unless otherwise noted. [b] Buffer and sulfonimine absent. [c] Sulfonimine absent. [d] Approximately 3–4% sulfone was detected by GLC. [e] Recovered starting material. [f] Only the monosulfoxide was detected.

A typical example is illustrated by the catalytic oxidation of phenyl vinyl sulfide to phenyl vinyl sulfoxide in greater than 90% isolated yield within 30 min (entry 13). Less than 3–4% of the corresponding sulfone was detected by GLC. A larger scale oxidation of phenyl vinyl sulfide (26.8 mmol) gave this sulfoxide, after distillation, in 81–2% yield. Phenyl vinyl sulfoxide has previously been prepared in 68–70% yield by *m*-CPBA oxidation at −78 °C.[18]

The results summarized in the table illustrate that the *N*-sulfonyloxaziridine-based catalytic system (Scheme I) selectively oxidizes a variety of sulfides to sulfoxides in high chemical yield. The catalytic system is remarkably chemoselective, tolerating functionalities such as alkenes

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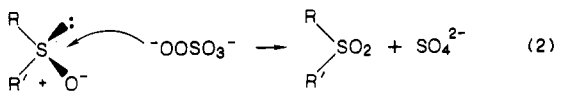
(entry 11–14), halides (entry 17), and carbonyl groups (entries 29–30). For the more nucleophilic sulfides oxidation was complete within 10–30 min, while the less nucleophilic diaryl sulfides required several hours.

Since the oxidation of sulfides to sulfoxides by 1 is usually complete within a few minutes, the rate-limiting reaction must be oxidation of the sulfonimine 2 to the oxaziridine 1; i.e. $k_1 \ll k_2$ (Scheme I). As previously described, increasing the pH of the buffer to 8.5 using K_2CO_3 increases the rate of formation of 1 which in turn increases the rate of sulfoxide production (entries 5, 10, 13–14, 17, 19, 28 and 30).

Significantly, with only a few exceptions, overoxidation of sulfides to sulfones was not detected. This is true even for the diaryl sulfides (entries 8–10, 24–28), where overoxidation to sulfones is often difficult to stop with other oxidizing systems. Buffered Oxone does not oxidize sulfides to sulfoxides in the absence of 2, the oxaziridine precursor (entry 2), and the rate of sulfoxide to sulfone oxidation by 1 is extremely slow. Therefore, sulfone formation (entries 3–5, 11–14, 15–16, and 22–23) must result from nucleophilic oxidation of the polar sulfoxide by the peroxymonosulfate anion *after* sulfoxide formation by 1 (eq 2). Nucleophilic oxidation of sulfoxides to sulfones



(2)

has been described.[19] Both 2-hydroxyethyl phenyl sulfide and thiacyclobutane afford sulfoxides soluble in the aqueous phase, where nucleophilic oxidation is presumed to take place. Note that as the time of oxidation of phenyl vinyl sulfide is increased from 30 to 90 min, the yield of phenyl vinyl sulfone increases from 4% to 15%, respectively (entry 14).

The similarity and utility of *N*-sulfonyloxaziridines 1 as models for the oxygen-transfer reactions of the metal peroxides are further emphasized by the results presented here.[20] Many transition-metal-catalyzed oxidizing systems of synthetic and industrial importance are thought to involve the transient formation of metal peroxides which, like 1, have their active-site oxygen as part of a three-membered ring.[20,21] Our results provide additional support for a mechanism of oxygen-transfer from the metal peroxides involving an "external" S_N2-type mechanism rather than an "internal" coordinated pseudocyclic mechanism as advocated by Mimoun.[22] *N*-Sulfonyloxaziridines 1 transfer oxygen by a typical S_N2-type substitution mechanism.[20]

In summary, efficient new methodology for the chemoselective catalytic oxidation of aliphatic and aromatic sulfides to sulfoxides has been developed. This methodology avoids many of the limitations of other oxidizing systems in that it is selective, fast, and relatively insensitive to the reaction parameters and the structure of the sulfide. The only limitation appears to occur with less lipophilic sulfides which afford water-soluble sulfoxides that are oxidized to the sulfones. Studies are currently in progress aimed at increasing the catalytic efficiency of this system.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and were uncorrected. ^1H and ^{13}C NMR spectra were measured on a JOEL FX 90Q (90 MHz) NMR spectrometer and on a Bruker 250 (250 MHz) NMR spectrometer. Chemical shifts are reported relative to tetramethylsilane. IR spectra were recorded on a Perkin-Elmer 467 grating spectrometer. Analytical gas chromatographs were performed on a Varian 3700 gas chromatograph equipped with a FID detector and electronic integrators using a Supelco 30 M, 0.75-mm I.D., 1.0-μm film SBP-35 wide bore capillary column. Sulfides were purchased from Aldrich and Parish Chemical Companies. α-(Phenylthio)cyclohexanone was repared according to the procedure of Trost and co-workers.[28b]

Samples of Oxone exposed to moisture for extended periods of time give reduced reactivity in these oxidations. Oxone that titrates to 4.6–4.7% active oxygen ($KI-Na_2S_2O_3$) is recommended.

***N*-(*p*-Nitrobenzylidene)benzenesulfonamide (2).**[16] In a 1-L, single-necked, round-bottom flask equipped with a Dean–Stark separator, condenser, and argon inlet were placed 15.7 g (0.1 mol) of benzenesulfonamide, 15.1 g (0.1 mol) of 4-nitrobenzaldehyde, 25 g of 5-Å powdered molecular sieves, and 0.2 g of Amberlyst 15 ion-exchange resin in 500 mL of toluene. The reaction mixture was heated at reflux until all of the water has separated (typically 24 h), diluted with 200 mL of methylene chloride, and filtered. The residue was washed with an addition 200 mL of methylene chloride and the filtrates were combined. The solvent was removed on the rotatory evaporator to give a yellow solid which was washed with 200 mL of *n*-pentane to give 20.9 g (72%) of 2; mp 155–60 °C. Crystallization from ethyl acetate gave 17.4 g (60%) of yellow crystals of 2; mp 162–4 °C; NMR ($CDCl_3$) δ 7.2–7.35 (m, 1 H), 7.83–7.40 (m, 2 H), 7.83–8.23 (m, 4 H), 8.23–8.55 (m, 2 H), 9.10 (s, 1 H, N=CH).

General Procedure for the Catalytic Oxidation of Sulfides to Sulfoxides. In a 500-mL three-necked Morton flask equipped with an efficient mechanical stirrer and a 25-mL dropping funnel was placed 3 mmol of the appropriate sulfide and 0.18 g (0.6 mmol) of *N*-(*p*-nitrobenzylidene)benzenesulfonamide (2),[16] in 50 mL of methylene chloride. The solution was buffered to pH ca. 8.5 by addition of 4.8 or 14.49 g (34.5 or 103.5 mmol) of K_2CO_3 in 5 or 15 mL of water. To the rapidly stirring reaction mixture was added dropwise, over 10 min, 2.7 or 8.3 g (1.5 or 13.5 mmol, 3 or 9 equiv, of potassium peroxymonosulfate) of Oxone in 10 or 30 mL of water (see table). After the oxidation was complete, as determined by silica gel TLC, the reaction was immediately quenched by addition of 15 or 50 mL of a saturated solution of sodium metabisulfite in order to minimize overoxidation of some sulfoxides to sulfones. The reaction mixture was extracted with methylene chloride (2 × 50 mL) and the organic phase dried over anhydrous $MgSO_4$. After removal of the solvent with a rotary evaporator the sulfoxides were isolated by preparative TLC on silica gel, generally eluting with ethyl ether. With larger scale oxidations the sulfoxide was separated from the polar sulfonimine 2 by extraction into *n*-pentane and isolated by distillation, crystallization, or flash chromatography.

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE 8502076). We thank Dr. Frederick R. Longo (Drexel) for stimulating discussions.

Registry No. 1, 86428-23-1; 2, 36176-89-3; Me-*p*-C_6H_4SMe, 623-13-2; PhSMe, 100-68-5; $PhSCH_2Ph$, 831-91-4; PhSPh, 139-

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66-2; $PhSCH{=}CH_2$, 1822-73-7; $PhS(CH_2)_2OH$, 699-12-7; $PhS(CH_2)_2Cl$, 5535-49-9; $(n\text{-}C_4H_9)_2S$, 544-40-1; $(s\text{-}C_4H_9)_2S$, 626-26-6; $(t\text{-}C_4H_9)_2S$, 107-47-1; Me-*p*-$C_6H_4S(O)Me$, 934-72-5; Me-*p*-$C_6H_4SO_2Me$, 3185-99-7; PhS(O)Me, 1193-82-4; $PhSO_2Me$, 3112-85-4; $PhS(O)CH_2Ph$, 833-82-9; PhS(O)Ph, 945-51-7; $PhSO_2CH{=}CH_2$, 5535-48-8; $PhS(O)CH{=}CH_2$, 20451-53-0; $PhSO_2(CH_2)_2OH$, 20611-21-6; $PhS(O)(CH_2)_2Cl$, 27998-60-3; $(n\text{-}C_4H_9)_2S(O)$, 2168-93-6; $(s\text{-}C_4H_9)_2S(O)$, 13153-06-5; $(t\text{-}C_4H_9)_2S(O)$, 2211-92-9; benzenesulfonamide, 98-10-2; 4-nitrobenzaldehyde, 555-16-8; potassium peroxymonosulfate, 10361-76-9; thietane, 287-27-4; thianthrene, 92-85-3; dibenzothiophene, 132-65-0; thietane, 1-oxide, 13153-11-2; thietane, 1,1-dioxide, 5687-92-3; thianthrene 5,10-dioxide, 951-02-0; dibenzothiophene 5-oxide, 1013-23-6; dibenzothiophene 5,5-dioxide, 1016-05-3; 2-(phenylthio)cyclohexanone, 27920-40-7; 2-(phenylsulfinyl)cyclohexanone, 55705-17-4.

Properties of a Tetracyanopentacenequinone and Its Tetracyanoquinodimethane Derivative

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A soluble tetracyanopentacenequinone was prepared. This quinone was converted to a TCNQ derivative by base-catalyzed reaction with malononitrile at high temperature. Variable-temperature NMR spectroscopy revealed a slow conformation change for the TCNQ derivative. Electrochemical reductions of the quinone and its TCNQ derivative were studied and UV–vis–NIR spectra of the neutrals, anion radicals, and dianions were recorded. The ions from the tetracyanopentacenequinone show very long wavelength NIR bands ascribed to strong perturbation of the quinone$^{\bullet-}$ by the cyano groups.

Tetracyanoquinodimethane (TCNQ) and its analogues have attracted continuing attention. Most fundamentally, this attention has resulted because these compounds are excellent electron acceptors. As such they form anion radicals, e.g., TCNQ$^{\bullet-}$, at very positive potentials and form charge-transfer complexes with many donors. The most famous of these is TTF–TCNQ, which was the first organic solid to show metallic conductivity. A number of derivatives have been synthesized in order to explore the conductivity. Of particular interest in the present context are several anthracene derivatives like **3**-CN,[1-3] which were prepared and studied to provide a TCNQ with an extended π-system.

Recent work from this laboratory has been directed toward the preparation of quinones with extended π-systems and also linear arrays of such polyacenequinones.[4,5] One point of particular interest has been the unusual near-infrared (NIR) absorption bands exhibited by the anion radicals of these compounds.[6] It was of interest to extend the scope of this work by preparing TCNQ derivatives of our unusual quinones. We report here on a five-ringed tetracyano quinone (**5**-O) and its TCNQ derivative (**5**-CN). This structure was selected as a synthetic goal out of considerations of solubility, synthetic accessibility, and redox potential. Thus, the aryl groups provide solubility and the four aromatic cyano groups keep the quinone reduction potential from being too negative. Our findings include unusual ^{1}H NMR results showing a conformational change in **5**-CN and UV–vis–NIR results on **5**-O, **5**-O$^{\bullet-}$, **5**-O^{2-}, **5**-CN, and **5**-CN^{2-}. It is shown that the strong interaction of the aromatic cyano groups with the quinone on **5**-O$^{\bullet-}$ leads to NIR bands not observed for pentacenequinone, **6**$^{\bullet-}$, which lacks the aromatic cyano groups.

Synthesis. Previous studies have demonstrated the utility of Diels–Alder addition to the bis diene **4**.[4] This precursor is of special utility because the *p-tert*-butylphenyl groups provide solubility even to rigid polyacenequinone derivatives 75 Å long.[5] In the present study, addition of fumaronitrile to **4** followed by aromatization gave **5**-O, which was identified spectrally.

The quinone **5**-O could not be converted to **5**-CN by using the published conditions[2] ($TiCl_4$, pyridine in chloroform), but a modicum of success was achieved by using 1,8-bis(dimethylamino)naphthalene as the base in the higher boiling solvent 1,1,2,2-tetrachloroethane. The product **5**-CN was purified by flash chromatography and gave satisfactory IR, NMR, UV, and high resolution mass spectra.

^{1}H NMR of 5-CN. This NMR spectrum is interesting because it reveals a slow conformational change. Comparison of the spectrum of **5**-CN with that of **5**-O and other derivatives allows a firm assignment of the peaks. Of interest are the aryl hydrogens of the attached *p-tert*-butylphenyl groups. The spectra of **5**-O and other derivatives show a pair of A–B doublets for the ortho and meta hydrogens. In contrast, **5**-CN in $CDCl_3$ shows four pairs of doublets.

This complexity is due to a slow conformational change, as shown by a variable-temperature ^{1}H NMR study. Toluene-d_8 was used as solvent to get a more suitable liquid range. This change in solvent changed the chemical shifts and coupling constants, but the spectrum at 0 °C was recognizably similar to that obtained at room temperature in $CDCl_3$. There were four sets of slightly broadened doublets in the range of 7.5–8.0 ppm. When the temperature was raised to 35 °C these peaks broadened further

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