$C_6H_{11}]^+$, 100), 457 ([M - $C_6H_{11}$ - $Ph_3P]^+$, 39). Anal. Calcd for $C_{43}H_{41}O_3F_3P_2SPt$: C, 54.26; H, 4.34. Found: C, 54.40; H, 4.36.

Carbon monoxide was bubbled through the mother liquors for 2 h, leading to a white precipitate. Workup as above afforded 313 mg (50%) of carbonyl product **4b** as white microcrystals.

**Single-Crystal X-ray Diffraction Analysis of 5b.** Colorless single crystals of **5b** were obtained as thin plates by diffusion crystallization from $CH_2Cl_2/Et_2O$. X-ray data were collected on a CAD4 automated diffractometer as summarized in Table I. The structure was solved by treating the phenyl rings of the $Ph_3P$ as rigid bodies and by other standard heavy-atom techniques using the UCLA Crystallographic Package.

**NMR Observation of $\eta^3$-Allyl Complex 5c Formation.** Complex **1** (11.3 mg, 1.51 × $10^{-2}$ mmol) was placed in a thin-wall 5-mm NMR tube equipped with a rubber septum. Previously degassed $C_6D_6$ (0.6 mL) was added via syringe along with toluene (1.1 mg, 1.2 × $10^{-2}$ mmol) as an internal standard ($\delta$ 2.1 ppm). A $^1H$ NMR spectrum was obtained at room temperature, and then 3,3-dimethyl-2-butenyl triflate was added via syringe. The tube was inverted five times to mix the reagents, and then the reaction was monitored by $^1H$ NMR. The arrayed spectra were recorded with preacquisition delays of 0, 212, 212, 212, 512, 512, 512, 512, 1112, 1112, 1112, 1112, 1712, 1712, 1712 s, and the acquisition time for each spectrum was 48 s.

**Reaction of 6 with $Et_3N$.** Complex **6** (13.3 mg, 1.40 × $10^{-2}$ mmol) was placed in a thin-wall 5-mm NMR tube and charged with 0.45 mL of THF-$d_8$. The tube was sealed with a rubber septum and $Et_3N$ (3.9 μL, $d$ 0.726 g/mL, 2.8 × $10^{-2}$ mmol) was then added via syringe. The mixture was heated in a 65 °C oil bath for 6 h, leading to a yellow heterogeneous solution. The $^1H$ NMR showed the clean production of 2,3-dimethyl-1,3-butadiene (**16**).

**Reaction of 5b with $Et_3N$ in the Absence of $Ph_3P$.** Complex **5b** (12.8 mg, 1.35 × $10^{-2}$ mmol) was weighed into a thin-wall 5-mm NMR tube and 0.50 mL of THF-$d_8$ was added via syringe. The tube was sealed with a rubber septum and $Et_3N$ (2.0 μL, $d$ 0.726 g/mL, 1.5 × $10^{-2}$ mmol) was added via syringe. The septum was wrapped with liberal amounts of parafilm, and the mixture was heated at about 50 °C in an oil bath for 4 h. The clear solution turned orange within 5-10 min. At the end of the reaction, a precipitate was present. The $^1H$ NMR spectrum of the heterogeneous mixture showed the formation of 2-methyl-1,3-pentadiene (**17**) and trace impurities with resonances between 6.5 and 6.8 ppm.

**Reaction of 5b with $Et_3N$ in the Presence of $Ph_3P$.** The reaction was performed according to the above procedure with **5b** (13.1 mg, 1.38 × $10^{-2}$ mmol), $Et_3N$ (2.1 μL, $d$ 0.726 g/mL, 1.5 × $10^{-2}$ mmol), and $Ph_3P$ (4.0 mg, 1.5 × $10^{-2}$ mmol) in 0.50 mL of THF-$d_8$. The $^1H$ NMR spectrum of the heterogeneous mixture revealed the clean formation of **17**.

**Isomerization Reaction of 2-Methyl-1,3-pentadiene (17) and 4-Methyl-1,3-pentadiene (18) in the Presence of $Et_3N$ and $Ph_3P$.** $Ph_3P$ (6.3 mg, 2.4 × $10^{-2}$ mmol) was placed in a thin-wall 5-mm NMR tube. THF-$d_8$ (0.50 mL) was then added and the tube was sealed with a rubber septum. $Et_3N$ (3.3 μL, $d$ 0.726 g/mL, 2.4 × $10^{-2}$ mmol) was added via syringe followed by the pure diene **17** (2.6 μL, $d$ 0.718 g/mL, 2.4 × $10^{-2}$ mmol). The septum was then wrapped with liberal amounts of parafilm. The solution was placed in a 60 °C oil bath for 24 h. The 75/25 mixture of **17** and **18** was also subjected to the same conditions. No isomerization of the pure diene or the mixture dienes had occurred according to $^1H$ NMR spectroscopy.

**Isomerization Reaction of 2-Methyl-1,3-pentadiene (17) and 4-Methyl-1,3-pentadiene (18) in the Presence of $(Ph_3P)_2Pt(C_2H_4)$ (1), $Ph_3P$, and $Et_3N$.** Platinum ethylene complex **1** (11.8 mg, 2.4 × $10^{-2}$ mmol) and $Ph_3P$ (6.3 mg, 2.4 × $10^{-2}$ mmol) were weighed into a thin-wall 5-mm NMR tube. THF-$d_8$ (0.50 mL) was added and the tube was sealed with a rubber septum. $Et_3N$ (3.3 μL, $d$ 0.726 g/mL, 2.4 × $10^{-2}$ mmol) was added via syringe followed by the pure diene **17** (2.6 μL, $d$ 0.718 g/mL, 2.4 × $10^{-2}$ mmol). The septum was wrapped with liberal amounts of parafilm. The resulting yellow solution was then heated in a 60 °C oil bath for 24 h. The 75/25 mixture of **17**/**18** was also subjected to the same conditions. The $^1H$ NMR spectra of both solutions were obtained. No isomerization of dienes was observed.

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**Supplementary Material Available:** Details of the single-crystal X-ray structure of **5b** (32 pages); observed and calculated structure factors for **5b** (19 pages). Ordering information is given on any current masthead page.

# Thianthrene 5-Oxide as a Mechanistic Probe for Assessing the Electronic Character of Oxygen-Transfer Agents

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**Abstract:** Thianthrene 5-oxide (SSO) was employed to assess the electronic nature of oxygen-transfer reagents: Those oxidants that attack preferentially the sulfide "S" site to give the bis(sulfoxide) SOSO are electrophilic in their reactivity; those that predominantly react at the sulfoxide "SO" site to give the sulfone $SSO_2$ are nucleophilic. The $X_{SO}$ parameter was introduced, defined as the mole fraction of $SSO_2$ product (SO attack), for which strongly electrophilic oxygen-transfer agents (typically acidified hydroperoxides and hypochlorite) take near-zero values and strongly nucleophilic ones (typically basified hydroperoxides and superoxide) near-unity. On the $X_{SO}$ scale, ozone and peroxy acids are as expected electrophilic oxidants and dioxiranes are significantly more nucleophilic but more electrophilic than carbonyl oxides. The latter exhibit pronounced nucleophilic reactivity toward SSO, which is in agreement with their observed reactivity. Free radicals, e.g., $t$-BuOO•, display very high electrophilicity in their oxygen-transfer propensity by reacting essentially exclusively at the S site. Control experiments have established that such radicals do not act through electron transfer to afford the $SSO^{\bullet+}$ radical cation, although the latter, generated either by photosensitized or chemical oxidation, behaves toward dioxygen strongly electrophilic. While the SSO probe provides a realistic measure of the electronic nature of oxygen-transfer agents, caution should be excercised when preferential complexation of the reagent at the S or SO site of SSO takes place or when electron transfer is involved with SSO to produce the $SSO^{\bullet+}$ or $SSO^{\bullet-}$ radical ions. Also, during the in situ generation of transient oxidants, several species of different electronic character might act simultaneously and the composite $X_{SO}$ value erroneously express the reactivity of the oxidant in question. In such suspicious cases, control experiments are obligatory to acquire meaningful $X_{SO}$ data with SSO.

Oxygen-transfer reactions are of wide interest in peroxide chemistry[1] due to their importance in biological oxidations as well as in industrial applications. For example, in the recent past, model studies have been made to understand the mechanism of oxygen

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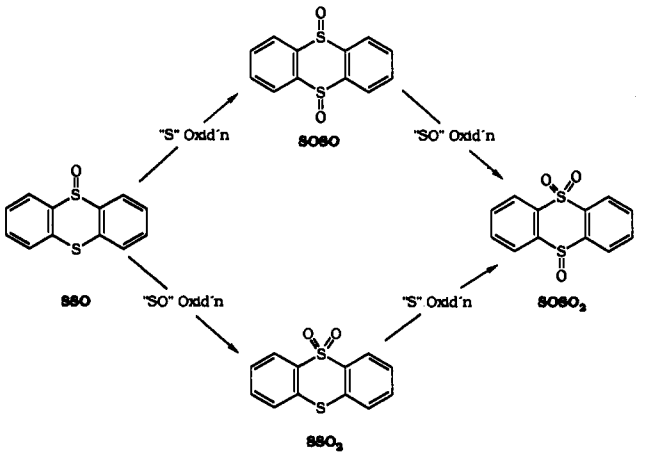
transfer of flavin monooxygenase enzymes,[3] carbonyl oxides, or Criegee's zwitterion in the ozonolysis of alkenes[4] or by the photooxygenation of diazo compounds,[5] hydroperoxides generated by singlet oxygenation of alkenes,[6] dioxiranes,[7] dialkylperoxonium ions,[8] and many others. Of particular value have been spectroscopic studies in combination with the matrix isolation technique, which have helped to assess the electronic structure of some of these reactive species, especially carbonyl oxides and dioxiranes.[9] Despite intensive work on oxygen-transfer reactions,[10,11] no definitive and consistent view exists to date on the electronic nature of these oxygen-transfer reagents, particularly what concerns the nucleophilic and electrophilic reactivity toward a given substrate such as olefinic, aromatic, and heteroatom-containing molecules (amines, phosphines, sulfides).

A few years ago we have reported thianthrene 5-oxide (SSO) as a useful mechanistic tool to assess the electronic character of a variety of oxidants.[12] Earlier studies using SSO include work by Oae[13] and by Matsui.[14] Several recent applications underscore the interest of the scientific community to employ our novel probe;[8,15] however, conflictive results have been reported in regard to the reliability of the acquired data. Thus, Murray[15a] questions the nucleophilic nature of dioxiranes in view of a negative $\rho$ value (−0.8) obtained in the oxidation of substituted aryl sulfides, which is unexpected of an electron-rich oxidant. Bloodworth[8] used SSO to assess the electronic nature of *gem*-dialkylperoxonium ions, which again revealed too high a nucleophilic reactivity for these presumed electrophilic oxidants, while Tomaselli[15b] implied radical-type activity (electron transfer) of several neutral and anionic metal peroxo complexes to rationalize their more electrophilic nature than determined by us with SSO.[12c] Yet for carbonyl oxides, Sander[15c] has shown that infrared frequencies and MINDO/3 calculations correlate well with our data determined with the SSO probe. Furthermore, Ortiz de Montellano[15d] used successfully the SSO probe to assess the electronic nature of biological oxidants.

In this paper, we present the complete details of our previous work[12] by defining the concept of the nucleophilicity parameters $X_{SO}$ for oxygen-transfer agents, the experimental method, and its application to a wide range of common oxidants. Besides typical stable nucleophilic and electrophilic oxidants, also intermediary species, particularly radical-type oxygen-transfer agents were included in this study. The usefulness of the SSO probe and its validity and limitations as a mechanistic tool to assess the electronic character of oxidizing reagents will be discussed. It is shown that the $X_{SO}$ parameter reflects reliably the electron demand of an oxidant, provided that no complexation occurs with the sulfur sites in SSO, no electron transfer takes place between the oxygen atom donor and acceptor, and no multicomponent oxidizing systems are used.

**Scheme I**



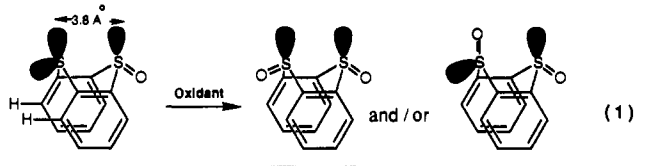

## Thianthrene 5-Oxide as Mechanistic Probe

The oxidation of organic substrates by oxygen-transfer agents has been extensively studied. Viewed from the perspective of the oxidant, such oxidations may proceed by either an electrophilic or a nucleophilic pathway.[16] As already proclaimed above, so far no clear-cut chemical method has been devised to assess the electronic character of oxygen-transfer agents; no detailed comparison of the relative oxygen-transferring ability of a variety of oxidants to set up a common scale is available. In this context, thianthrene 5-oxide (SSO) may serve as a suitable oxygen atom acceptor in view of its following unique features.

(a) SSO has both a sulfide and a sulfoxide site; the former, being electron-rich, is expected to undergo facile electrophilic oxidation, whereas the latter should preferably be oxidized by a nucleophilic oxidant. Intramolecular competition between the two sites offers the advantage of assessing the relative rates of oxygen transfer of an oxidant by merely determining the amount of sulfide attack to afford the bis(sulfoxide) SOSO and sulfoxide attack to lead to the sulfone $SSO_2$ in one and the same molecule. A similar approach has been adopted by Oae[13] in his study of the oxygen transfer to 3-methyl-1,2-dithiane 1-oxide by $H_2O_2$ or $NaIO_4$ under acidic conditions or by *m*-CPBA.

(b) Unlike Oae's system,[13] the SOSO and $SSO_2$ products do not readily interconvert and hence there is no ambiguity regarding the electronic nature of the oxygen-transfer agent.

(c) SSO has a fixed geometry, the folded conformation shown in eq 1, with a well-defined distance of 3.8 Å between the two functional groups.[17] Thus, steric factors in the approach of the oxidant toward the sulfide and sulfoxide sites should be nearly constant.




(1)

(d) X-ray analysis[17] of SSO reveals the boat-type structure, and oxygen transfer to the sulfide site would give rise to cis and trans diastereoisomers, which should enable one to examine the stereochemical course of the oxygen transfer and hence elucidate

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**Table I.** $X_{SO}$ Values of Oxygen-Transfer Agents Assessed by the Thianthrene 5-Oxide (SSO) Probe

| entry | reaction conditions[a] | total yield (%)[b] | product composition (%)[c] | | | $X_{SO}$[d] |
|---|---|---|---|---|---|---|
| | | | $SSO_2$ | SOSO | $SOSO_2$ | |
| 1 | $KO_2$, $C_6H_6$[e] | | 100 | <1.0 | <1.0 | 1.00 |
| 2 | $H_2O_2$, 1 N NaOH, $C_6H_6$ | | 100 | <1.0 | <1.0 | 1.00 |
| 3 | *t*-BuOOK, $C_6H_6$[e] | | 99.7 | 0.3 | <1.0 | 0.99 |
| 4 | *t*-BuC(Me)=$N_2$, $^1O_2$, $CH_2Cl_2$, −20 °C | | 93.9 | 3.2 | 2.9 | 0.96 |
| 5 | *t*-BuCH=$N_2$, $^1O_2$, $CH_2Cl_2$, −20 °C | | 91.4 | 3.6 | 5.0 | 0.92 |
| 6 | $Ph_2C$=$N_2$, $^1O_2$, $CH_2Cl_2$, 0 °C | 7.8 | 84.6 | 1.3 | 14.1 | 0.87[f] |
| 7 | isolated dioxirane, MeCOMe[g] | 33 | 84.9 | 15.1 | <1.0 | 0.85 |
| 8 | isolated dioxirane, $CH_2Cl_2$[g] | 16 | 77.2 | 22.8 | <1.0 | 0.77 |
| 9 | isolated dioxirane, in the spent solution of in situ dioxirane[g] | 36 | 58.8 | 10.4 | 30.8 | 0.68 |
| 10 | MeCOMe, Caroate, $CH_2Cl_2$, phosphate buffer, 0 °C[h] | 5 | 58.8 | 21.9 | 19.3 | 0.65 |
| | | 2.1 | 60.5 | 29.2 | 10.3 | 0.64 |
| 11 | isolated dioxirane, phosphate buffer, $CH_2Cl_2$ | 40 | 54.6 | 17.6 | 27.5 | 0.64 |
| 12 | *t*-BuCOMe, Caroate, $CH_2Cl_2$ phosphate buffer, 0 °C | 5.3 | 60.8 | 30.6 | 8.6 | 0.64 |
| 13 | *t*-BuCHO, Caroate, $CH_2Cl_2$, phosphate buffer, 0 °C[h] | 5 | 55.2 | 39.6 | 5.3 | 0.57 |
| 14 | Caroate, $CH_2Cl_2$, phosphate buffer, 0 °C | ca. 1.0 | 18.4 | 51.2 | 30.4 | 0.37 |
| 15 | *m*-CPBA, $CH_2Cl_2$ | 27 | 33.6 | 62.7 | 3.7 | 0.36 |
| 16 | $O_3$, $CH_2Cl_2$ | 3.1 | 22.7 | 75.8 | 1.5 | 0.24 |
| 17 | $H_2O_2$, 1 N HCl, ether | 3.3 | 9.3 | 89.0 | 1.7 | 0.10 |
| 18 | $H_2O_2$, $HClO_4$, $CH_2Cl_2$ | 17.8 | 1.8 | 93.8 | 4.4 | 0.06 |
| 19 | *t*-BuOOH, HCl(g), $CH_2Cl_2$ | | 3.8 | 96.2 | <1.0 | 0.04 |
| 20 | *t*-BuOCl, $CH_2Cl_2$ | | 2.1 | 97.9 | <1.0 | 0.02 |
| 21 | *t*-BuOOH, $HClO_4$, $CH_2Cl_2$ | | 0.7 | 99.3 | <1.0 | <0.01 |

[a] Performed, unless otherwise stated, at ca. 20 °C. [b] Percent conversion of SSO to $SSO_2$, SOSO, and $SOSO_2$; error less than 3%. [c] Relative yields (normalized to 100%) of $SSO_2$, SOSO, and $SOSO_2$ determined by HPLC on a silica gel column eluted with a 240:10:1 solvent mixture of petroleum ether (bp 50–70 °C), ethyl acetate, and methanol at a flow rate of 3 mL/min and *p*-nitrophenyl sulfone as internal standard; error less than 3%; <1% means that even at maximum HPLC sensitivity no product was detected. [d] Calculated according to eq 2; error less than 5% for at least two independent runs. [e] 18-Crown-6 was used as phase-transfer agent. [f] When the consumption of diazoalkane was allowed to vary from ca. 10 to 100%, the yield of $SOSO_2$ product increased from 12 to 21% but the $X_{SO}$ value was the same within ca. 5%; a control experiment revealed that $^1O_2$ did not oxidize SSO under comparable reaction conditions. [g] Isolated dioxirane as solution in acetone was prepared according to ref 21; in entry 9a, spent solution of in situ generated dioxirane (after 19 h at ca. 20 °C in $CH_2Cl_2/H_2O$) was used as medium and subsequently SSO and then isolated dioxirane in acetone were added. [h] Dioxirane was generated in situ by using Caroate in $CH_2Cl_2/H_2O$ at 0 °C in the presence of phosphate buffer.

the more subtle and intricate mechanistic details of the oxygen-transfer process.

In the previous papers,[12] we established that thianthrene 5-oxide constitutes a valuable probe to estimate the nucleophilic versus electrophilic nature of oxygen-transfer agents. We defined the general oxygen-transfer parameter $X_{SO}$ according to eq 2, in which the relative attack at the sulfoxide site is given in terms of the mole fraction of $SSO_2$ product. The $X_{SO}$ parameter spans the scale from zero to unity, $X_{SO} = 0.0$ representing complete electrophilic and $X_{SO} = 1.0$ complete nucleophilic character of the oxygen-transfer agent.

$$X_{SO} = \frac{n_{SO}}{n_{SO} + n_S} = \frac{(n_{SSO_2} + n_{SOSO_2})}{(n_{SOSO} + n_{SOSO_2}) + (n_{SSO_2} + n_{SOSO_2})} \quad (2)$$

$$n_{SO} = (n_{SSO_2} + n_{SOSO_2}) \qquad \text{total "SO" oxidation}$$

$$n_S = (n_{SOSO} + n_{SOSO_2}) \qquad \text{total "S" oxidation}$$

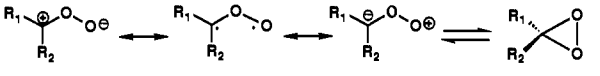
Since both the $SSO_2$ and SOSO products are in principle subject to further oxidation to the trioxide $SOSO_2$ (Scheme I), the $X_{SO}$ parameter must take such an "overoxidation" into account by simple bookkeeping of all oxygen-transfer steps involved in the formation of oxidized products, namely, $SSO_2$, SOSO, and $SOSO_2$. Thus, $SOSO_2$ may have derived from either an "S" oxidation of $SSO_2$ or an "SO" oxidation of SOSO (Scheme I); consequently, both pathways SSO → SOSO → $SOSO_2$ and SSO → $SSO_2$ → $SOSO_2$ contain both types of oxygen-transfer steps. For this reason, the amount of the "overoxidized" product $SOSO_2$ was added both to the S- and the SO-type attack. To minimize such corrections, the amount of overoxidized product $SOSO_2$ was kept as low as possible, in most of the cases under 10% of the total oxygen transfer. The absolute yields of SOSO, $SSO_2$, and $SOSO_2$ products were determined by quantitative HPLC analysis (for details, cf. Experimental Section), and the $X_{SO}$ values were calculated according to eq 2.

## Results

The chemical behavior of various oxygen-transfer agents, which have been diagnosed by the SSO probe, are presented in the tables. The oxygen-transfer parameter $X_{SO}$ ranges from completely electrophilic ($X_{SO} \approx 0.01$) to completely nucleophilic ($X_{SO} \approx 1.00$) values. For example, potassium superoxide, as expected, showed exclusively nucleophilic attack (Table I, entry 1; $X_{SO} = 1.00$), whereas hydrogen peroxide, which under basic conditions acted completely nucleophilically (Table I, entry 2; $X_{SO} = 1.00$), was found to attack essentially completely electrophilically (Table I, entries 17 and 18; $X_{SO} = 0.10$ and 0.06) under acidic conditions. Similar results were observed with *tert*-butyl hydroperoxide, in that potassium *tert*-butyl peroxide attacked the SO site of SSO to give rise to $X_{SO} = 0.99$ (Table I, entry 3), whereas under acidic conditions *tert*-butyl hydroperoxide was found to be strongly electrophilic in behavior (Table I, entries 19 and 21; $X_{SO} = 0.04$ and < 0.01). This is further supported by the fact that *tert*-butyl hypochlorite, an electrophilic oxidant, afforded mainly products from S-type attack (Table I, entry 20; $X_{SO} = 0.02$).

These model oxygen-transfer reactions establish that SSO is capable of differentiating between the nucleophilic and electrophilic nature of the oxidizing species. Further investigations were carried out with electrophilic oxidants such as *m*-CPBA and ozone, and as expected, they gave predominantly S-type attack (Table I, entries 15 and 16; $X_{SO} = 0.36$ and 0.24).

The above results convinced us that the SSO probe is a reliable measure of the electronic nature of oxygen-transfer agents, and efforts were expended to differentiate between carbonyl oxides and their cyclic valence isomeric dioxiranes (eq 3). Carbonyl




(3)

oxides were generated in situ by photooxygenation of diazoalkanes[5,18] in the presence of SSO; the $X_{SO}$ values are reported in Table I (entries 4–6; $X_{SO} = 0.96$–0.87). With similar substitution pattern, the corresponding dioxiranes, generated in situ by the oxidation of respective ketones or aldehyde with potassium monoperoxysulfate,[19] were found to be appreciably more elec-

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**Table II.** $X_{SO}$ Values of Radical-Type Oxygen-Transfer Agents Assessed by the Thianthrene 5-Oxide (SSO) Probe

| entry | reaction conditions[a] | total yield (%)[b] | product composition (%)[c] | | | $X_{SO}$[d] |
|---|---|---|---|---|---|---|
| | | | $SSO_2$ | SOSO | $SOSO_2$ | |
| 1 | *t*-BuOOH, $Pb(OAc)_4$[e] (1:2)[f] | 1.6 | 52.1 | 41.1 | 6.8 | 0.55 |
| 2 | *t*-BuOOH, $Pb(AOc)_4$[g] (1:2)[f] | 1.9 | 49.4 | 43.4 | 7.2 | 0.53 |
| 3 | *t*-BuOOH, $Pb(OAc)_4$, galvinoxyl[h,i] (1:2)[f] | <1.0 | <1.0 | <1.0 | <1.0 | |
| 4 | *t*-BuOOH, $Pb(OAc)_4$ (2:1)[f] | 1.8 | 17.4 | 79.4 | 2.2 | 0.20 |
| 5 | *t*-BuOOH[h] | <1.0 | <1.0 | <1.0 | <1.0 | |
| 6 | $Pb(OAc)_4$[h] | <1.0 | <1.0 | <1.0 | <1.0 | |
| 7 | *t*-BuOOH, $O_3$ | 7.9 | 2.0 | 97.8 | 0.2 | 0.02 |
| 8 | *t*-BuOOH, $O_3$, galvinoxyl[h] | <1.0 | <1.0 | <1.0 | <1.0 | |
| 9 | $O_3$ | 3.1 | 22.7 | 75.8 | 1.5 | 0.24 |
| 10 | anthracene ozonide, benzene, 60 °C | 5.2 | 85.9 | 11.0 | 3.1 | 0.86 |
| 11 | anthracene ozonide, galvinoxyl,[i] benzene, 60 °C | 4.9 | 87.3 | 12.7 | <1.0 | 0.87 |
| 12 | *t*-BuOO-*t*-Bu, *t*-BuOOH, *hν*, benzene, 40 °C[k] | ca. 1 | 20.1 | 79.9 | <1.0 | 0.20 |
| 13 | PhCOPh, *t*-BuOOH, *hν*, 10 °C[h,l] | <1 | <1.0 | <1.0 | <1.0 | |
| 14 | DCA, $CH_3CN$, $O_2$, *hν*[l] | | 20.5 | 70.4 | 9.1 | 0.27 |
| 15 | $Ar_3N^{+}\cdot SbCl_6^{-}$[m], $O_2$, 0 °C | | 12.4 | 87.6 | <1.0 | 0.12 |
| 16 | $O_2$, *hν*, 40 °C[l] | | 77.9 | 22.1 | <1.0 | 0.78 |

[a] Performed, unless otherwise stated, in dichloromethane at −78 °C followed by warming to room temperature (20 °C) before HPLC analysis. [b] Same as for Table I. [c] Same as for Table I. [d] Same as for Table I. [e] SSO was administered after the addition of *t*-BuOOH at −78 °C. [f] Two equivalents of $Pb(OAc)_4$ was used. [g] SSO was present from the start before adding *t*-BuOOH. [h] At maximum HPLC sensitivity, no products were detected. [i] In the presence of radical scavenger galvinoxyl (cf. ref 23). [j] Two equivalents of *t*-BuOOH was used. [k] Irradiated in benzene by using a Rayonet Photochemical Reactor at 300 Å. [l] Irradiated in benzene at 334–364 nm by using an argon ion laser light source (Coherent Innova 100); no $^1O_2$ was produced under these conditions. [m] Ar = 2,4-dibromophenyl; in the absence of $O_2$, no oxygen transfer was observed.

trophilic (Table I, entries 7–13; $X_{SO}$ = 0.83–0.57) than their acyclic carbonyl oxide counterparts. However, on the $X_{SO}$ scale, as one would expect (vide infra), dioxiranes were found to be more nucleophilic than *m*-CPBA (Table I, entry 15; $X_{SO}$ = 0.36).

Recently, dimethyldioxirane has been isolated,[20] which permitted determining its $X_{SO}$ value in the absence of other oxidants, e.g., $KHSO_5$, and also test medium effects. The results (Table I) clearly indicate that the $X_{SO}$ parameter for dimethyldioxirane is appreciably influenced by the nature of the medium.[21] For example, dimethyldioxirane was found to act somewhat more nucleophilically in acetone (Table I, entry 7; $X_{SO}$ = 0.85) than in $CH_2Cl_2$ (Table I, entry 8; $X_{SO}$ = 0.77). Nevertheless, when the isolated dioxirane was added to a spent solution of the in situ generated dioxirane, within the experimental error the $X_{SO}$ value was that of freshly in situ generated dioxirane (Table I, entry 9 versus 10; $X_{SO}$ = 0.68 vs 0.65). Even better agreement in the $X_{SO}$ values was observed when the same biphasic medium, viz., phosphate buffer and $CH_2Cl_2$, was used for isolated (Table I, entry 11; $X_{SO}$ = 0.64) and in situ generated dioxirane (Table I, entry 10; $X_{SO}$ = 0.65). Control experiments were carried out under identical experimental conditions, but without acetone; it was found that oxygen transfer from $KHSO_5$ directly to SSO was almost negligible and significantly more electrophilic (Table I, entry 14; $X_{SO}$ = 0.37) than the in situ generated dimethyldioxirane (Table I, entry 10; $X_{SO}$ = 0.65).

The question arises whether the SSO probe is also valid to assess the electronic character of radical-type oxidants. The possibility of electron transfer to afford the radical cation $SSO^{\bullet+}$ would falsify the true nature of the oxygen-transfer reactivity. For this purpose, we examined the oxygen-transfer reactions of several peroxy radicals and radical cationic intermediates to assess the validity and limitations of our probe. The results are collected in Table II. For comparison, we chose first to investigate the oxidation of SSO by the *tert*-butylperoxy radical, which was generated by the decomposition of di-*tert*-butyl trioxide at −30 °C. The latter was in turn prepared through the oxidation of *tert*-butyl hydroperoxide by using lead tetraacetate at −78 °C;[22] the $X_{SO}$ value was found to be 0.55 (Table II, entry 1). The presence of SSO in the reaction mixture before adding *t*-BuOOH to $Pb(OAc)_4$ at −78 °C did not make any significant difference in the $X_{SO}$ value (Table II, entry 2; $X_{SO}$ = 0.53). The presence of the radical scavenger galvinoxyl[23] in either of the above experiments (Table II, entries 1 and 2) led to complete inhibition of these oxygen-transfer reactions (Table II, entry 3). In both of these cases, 2 equiv of $Pb(OAc)_4$ was employed to generate di-*tert*-butyl trioxide. In contrast, when instead 2 equiv of *t*-BuOOH was used under otherwise identical conditions, the highly electrophilic nature of the *tert*-butylperoxy radical was revealed (Table II, entry 4; $X_{SO}$ = 0.20). Control experiments showed that neither *t*-BuOOH nor $Pb(OAc)_4$ alone were capable of oxidizing SSO under the above given experimental conditions (Table II, entries 5 and 6).

Alternatively, the *tert*-butylperoxy radical was generated by the decomposition of di-*tert*-butyl trioxide, which was prepared in situ by the ozonolysis of *t*-BuOOH[24] in $CH_2Cl_2$ at −78 °C (Table II, entry 7; $X_{SO}$ = 0.02). Clearly, the oxygen transfer to SSO by this method was much more electrophilic than in the $Pb(OAc)_4$ oxidation of *t*-BuOOH (Table II, entries 1 and 4). Again in the presence of galvinoxyl, the oxygen-transfer reaction was inhibited (Table II, entry 8). Ozonolysis of SSO under the above experimental conditions afforded $X_{SO}$ = 0.24 (Table II, entry 9), which established that ozone is not electrophilic enough to be primarily responsible as an oxygen-transfer agent in this process.

To test whether the trioxide was directly oxidizing SSO rather than the peroxy radicals, the anthracene ozonide was prepared[25] and allowed to react with SSO at ca. 60 °C in benzene (Table II, entry 10; $X_{SO}$ = 0.86). The high $X_{SO}$ value clearly suggests that the electron-rich anthracene ozonide is a very nucleophilic oxidant that does not act through radical-type species. This was further supported by a control experiment, in which the presence of galvinoxyl gave the same $X_{SO}$ value (Table II, entry 11; $X_{SO}$ = 0.87).

Due to the large difference in the $X_{SO}$ value for *tert*-butylperoxy radicals obtained from different sources [$Pb(OAc)_4$ oxidation or ozonolysis of *tert*-butyl hydroperoxide], we decided to generate them by irradiation of a mixture of di-*tert*-butyl peroxide and *tert*-butyl hydroperoxide[26] in benzene (Table II, entry 12; $X_{SO}$ = 0.20). Interestingly, this $X_{SO}$ value was the same as that found in the 2:1 *t*-BuOOH/$Pb(OAc)_4$ oxidation of SSO (Table II, entry 4; $X_{SO}$ = 0.20). An attempt to generate *tert*-butylperoxy radicals by using benzophenone-sensitized irradiation of *t*-BuOOH in benzene (Table II, entry 13) failed, because under these conditions

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(20) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847.
(21) Adam, W.; Chan, Y.-Y.; Cremer, D.; Gauss, J.; Scheutzow, D.; Schindler, M. *J. Org. Chem.* **1987**, *52*, 2800.
(22) Bartlett, P. D.; Günther, P. *J. Am. Chem. Soc.* **1966**, *88*, 3288.
(23) Kharasch, M. S.; Joshi, B. S. *J. Org. Chem.* **1957**, *22*, 1437.
(24) Bartlett, P. D.; Lahav, M. *Isr. J. Chem.* **1972**, *10*, 101.
(25) Ito, Y.; Matsuura, A.; Matsuura, T. *Tetrahedron Lett.* **1984**, *25*, 1491.
(26) Silbert, L. S. In *Organic Peroxides*; Swern, D., Ed.; Wiley Interscience: New York, 1971; Vol. 2, p 725.

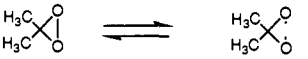
no oxygen transfer was observed.

Finally, to ascertain the possibility of whether the radical cation $SSO^{\bullet+}$ was formed by electron transfer of SSO with the intermediary peroxy radicals, so that $SSO^{\bullet+}$ rather than SSO was being oxygenated, we decided to generate $SSO^{\bullet+}$ independently by photochemical and chemical electron transfer. Thus, the 9,10-dicyanoanthracene (DCA) sensitized irradiation of SSO in the presence of dioxygen gave $X_{SO} = 0.27$ (Table II, entry 14), while the reaction of the tris(2,4-dibromophenyl)aminium hexachloroantimonate (Magic Green)[27] and dioxygen led to $X_{SO} = 0.12$ (Table II, entry 15). A control experiment showed that the photooxygenation of SSO by dioxygen under the irradiation conditions of the DCA photosensitization (Table II, entry 14) resulted in a relatively high SO-type attack (Table II, entry 16; $X_{SO} = 0.78$), although rather ineffectively.

## Discussion

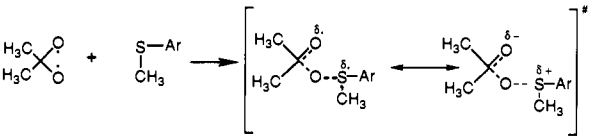
The results in Table I convincingly illustrate that the $X_{SO}$ parameter reflects in a realistic manner the reactivity of oxygen-transfer agents. For example, typical nucleophilic oxidants such as peroxy anions ($ROO^{\bullet-}$) or the superoxide ion ($O_2^{\bullet-}$) have $X_{SO}$ values near unity, while typical electrophilic oxidants such as acidified hydroperoxides ($ROOH_2$) or hypochlorites (ROCl) have $X_{SO}$ values near zero, thereby spanning the entire $X_{SO}$ scale. Of course, the actual $X_{SO}$ values are not to be taken as a quantitative measure of nucleophilic versus electrophilic reactivity but rather as a qualitative trend when comparing the selectivity of several oxygen-transfer agents. Moreover, although the experimental error amounts only to about 0.03 $X_{SO}$ units, differences in the $X_{SO}$ values of at least greater than ca. 0.1 for two oxidants adequately reflect the differences in their nucleophilic versus electrophilic nature. Thus, ozone ($X_{SO} = 0.24$) compared to *m*-CPBA ($X_{SO} = 0.36$), for which $\Delta X_{SO} \approx 0.12$, indeed expresses properly the fact that ozone is the more electrophilic oxidant. Alternatively, on the nucleophilic end of the $X_{SO}$ scale, the carbonyl oxide of pinacolone ($X_{SO} = 0.96$) compared to the corresponding dioxirane ($X_{SO} = 0.64$), for which $\Delta X_{SO} \approx 0.32$, acts clearly as a more nucleophilic oxygen-transfer agent. Qualitatively speaking, these chemical reactivity trends are quite reasonable because dioxiranes epoxidize electron-poor olefins, e.g., chalcones,[28] more efficiently than *m*-CPBA; thus, dioxiranes are more nucleophilic than peroxy acids in their oxidizing propensity. On the other hand, while dioxiranes readily oxidize pyridine,[7] carbonyl oxides do not,[29] which confirms that dioxiranes are more electrophilic than carbonyl oxides.

Why then does dimethyldioxirane give for the oxidation of thioanisoles to the corresponding sulfoxides a negative reaction constant ($\rho = -0.8$),[15a] which clearly signals that positive charge builds up at the sulfide reaction center in the transition state of this oxygen transfer? For an oxidant with significant nucleophilic character, as the value $X_{SO} = 0.77$ for the isolated dimethyldioxirane in $CH_2Cl_2$ implies, one would expect build-up of negative charge ($\rho > 0$) at the sulfide site. However, the discrepancy between the $X_{SO}$ and $\rho$ results is not necessarily conflictive from the mechanistic point of view. The $X_{SO}$ parameter reflects that when dioxirane has a choice between oxygen transfer to the SO site (electron-poorer) versus S site (electron-richer), it predominantly chooses the former, thereby revealing itself as an electron-richer or more nucleophilic oxidant than peroxy acids. When the competition exercised by SSO is not imposed on the dioxirane, electronic charge will be accumulated in the transition state of the oxygen-transfer reaction in such a way that it is most effectively stabilized through mesomeric effects. Since dioxiranes are ambiphilic, i.e., they oxidize electron-rich as well as electron-poor substrates, and in view of the fact that the oxygen-oxygen bond is very weak (ca. 10–15 kcal/mol),[7] we suspect that the actual oxidizing agent is the dioxyl diradical (eq 4). Such a radical-type species would nicely portray the ambiphilic nature of dioxiranes.



(4)

The possibility of electron transfer to result in the $SSO^{\bullet+}$ radical cation and dioxirane radical anion pair is unlikely, because as the data in Table II show (entries 14 and 15), under genuine electron-transfer conditions, very low $X_{SO}$ values were obtained. Under these circumstances, for the oxidation of thioanisole by dioxirane mesomeric stabilization in the activated complex (eq 5) derives



(5)

from dipolar structures that place preferentially positive charge on the sulfur atom, especially when the aryl group bears electron-donating substituents. For such a reaction center, a negative $\rho$ value would apply[15a] without necessarily involving an electrophilic oxidant. As a complementary trend, for sufficiently electron poor substrates, one might obtain positive $\rho$ values in their oxidation by dioxirane. In other words, over a wide range of substituents on the aryl sulfide, a Hammett plot might exhibit parabolic-type curvature.

Nevertheless, as useful and convenient as the SSO probe may be for assessing the nucleophilic or electrophilic character of oxygen-transfer agents (cf. $X_{SO}$ values in Table I), it possesses some rather evident shortcomings. These should be clearly recognized and the necessary control experiments performed to avoid erroneous conclusions on the electronic nature of the oxidants. A rather apparent one concerns the possibility that several oxidants might simultaneously be engaged in the oxygen transfer, a situation that may arise during in situ generation of the oxidant, particularly in the case of transient or short-lived species. This constitutes a difficult situation, and one can only resort to the independent generation of such oxidants in as many different ways as possible and separately test the efficiency of the reagents employed for the generation of the transient oxidant under the utilized oxygen-transfer conditions. A number of such cases are given in Table II, e.g., the formation of *tert*-butylperoxy radicals by $Pb(OAc)_4$ oxidation of *tert*-butyl hydroperoxide (entries 1–6), by ozonolysis of *tert*-butyl hydroperoxides (entries 7–11), and by photochemical means (entries 12 and 13). The results are quite conflictive, but the value $X_{SO} \approx 0.02$ most realistically reflects the expected electrophilic nature of *t*-BuOO$^{\bullet}$ as oxidant.

In this context, some other limitations have been uncovered that need to be divulged here. For example, that the $Pb(OAc)_4$ oxidation of *t*-BuOOH involves free radicals was clearly established by the fact that in the presence of the radical scavenger galvinoxy no oxidation of SSO took place (Table II, entry 3). Yet, when the ratio of *t*-BuOOH to $Pb(OAc)_4$ was varied from 1:2 to 2:1, this caused significant changes ($\Delta X_{SO} \approx 0.33$) in the $X_{SO}$ values for this oxidizing system (Table II, entries 1 and 2 versus 4). We suspect that preferential complexation[30] of $Pb(OAc)_4$ at the S site intervenes with the oxygen transfer, so that predominant attack is obliged to take place at the SO terminal. Under these in situ conditions for generating *t*-BuOO$^{\bullet}$, their propensity of transferring oxygen atoms is much too nucleophilic. For comparison, by generating *t*-BuOO$^{\bullet}$ by the ozonolysis of *t*-BuOOH, which is devoid of such complexation, indeed the very electrophilic value $X_{SO} = 0.02$ (Table II, entry 7) was obtained. Therefore, even the quite low value $X_{SO} = 0.20$ for the *t*-BuOOH/$Pb(OAc)_4$ ratio of 2:1 (Table II, entry 4) indicates some degree of complexation, presumably by the $Pb(OAc)_2$ that is formed in the generation of *t*-BuOO$^{\bullet}$ radicals. $Pb(OAc)_2$ is a weaker Lewis acid than $Pb(OAc)_4$, and thus a lower degree of complexation with the S site in SSO is expected.[30]

The relatively high value $X_{SO} = 0.20$ obtained in the photochemical generation of *t*-BuOO$^{\bullet}$ radicals (Table II, entry 12) is

(27) (a) Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577. (b) Steckhan, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 638.
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(29) Griesbaum, K. *Chem. Commun.* **1966**, 920.
(30) *Gmelins Handbuch der anorganischen Chemie, Blei*, 8th ed.; Verlag Chemie: Weinheim, 1971; Part C4, p 1700.

difficult to reconcile, but such a complex mode of producing these transient species is expected to be subject to complications, e.g., photosensitized electron transfer. In such a process, the radical cation $SSO^{\bullet+}$ would be produced, which should behave very differently from SSO as oxygen atom acceptor. Consequently, electron-transfer processes between SSO and the oxidant, or arising from the conditions to generate the oxidant, constitute a further limitation of the SSO probe. Fortunately, the oxidation potential of SSO is quite high ($E_{ox}$ = 1.76 V; cf. Experimental Section), so that it would require rather strong redox-type oxidants for this purpose. Thus, $Pb(OAc)_4$ ($E_{ox}$ = 1.45 V[31]) is not capable of initiating efficient redox chemistry with SSO, a fact that is corroborated by a control experiment (Table II, entry 6). In fact, even *t*-BuOO$^{\bullet}$ radicals are ineffective in promoting electron transfer with SSO because their oxidation potential is too low ($E_{ox} \approx 1.5$ V).[32]

Nonetheless, we decided to generate the $SSO^{\bullet+}$ radical cation by authentic means and examine its oxidation by dioxygen. Photochemical oxidation by 9,10-dicyanoanthracene or DCA (Table II, entry 14) and chemical oxidation by tris(2,4-dibromophenyl)aminium hexachloroantimonate, i.e., Magic Green (Table II, entry 15), in the presence of $O_2$ were carried out. For the photosensitized electron transfer with DCA, an estimation of the free energy change ($\Delta G$) by means of the Rehm–Weller equation[33] indicated a large negative value and thus this process seemed likely to take place. The oxidation potential for Magic Green is $E_{ox}$ = 1.74/NHE V,[27] which is just high enough to effect chemical electron transfer from SSO, particularly since such redox processes are irreversible. Both the photosensitized and the chemical modes of one-electron oxidations afforded predominant electrophilic oxygen transfer to SSO; however, again a significant discrepancy in the $X_{SO}$ values, i.e., $\Delta X_{SO} \approx 0.15$, was observed. The lower value $X_{SO}$ = 0.12 for the chemical oxidant ($Ar_3N^{+\bullet}$ $SbCl_6^-$) is presumably the more reliable one, because for the photochemical oxidant (DCA, $h\nu$) it is known[34] that, in the presence of dioxygen, the superoxide ion is formed in situ. Concurrent oxidation of SSO with the latter by nucleophilic attack at the SO site (Table I, entry 1) would offset the electrophilic attack by dioxygen on the $SSO^{\bullet+}$ radical cation, and a composite $X_{SO}$ value would result that should be too high. Irrespective of these complications, the $SSO^{\bullet+}$ radical cation, as expected, reacts much more electrophilically toward dioxygen than SSO (Table II, entries 14 and 15). Thus, should an oxidant act by electron transfer to generate the $SSO^{\bullet+}$ radical cation, erroneous $X_{SO}$ values are to be expected.

In conclusion, with the help of the SSO probe, useful mechanistic data on oxygen-transfer processes can be obtained, which give insight into the electronic nature of an oxidant in terms of the $X_{SO}$ values. Low $X_{SO}$ values indicate an electrophilic oxidant, which attacks primarily the S site, while high $X_{SO}$ values signify a nuleophilic oxidant, which reacts predominantly at the SO site. Caution must be exercised when several oxidants are engaged simultaneously, a situation that is quite likely during the in situ generation of short-lived, intermediary oxygen-transfer agents. In such cases, control experiments are obligatory to diagnose the difficulties. Equally problematic are reagents that complex preferentially at the sulfide or the sulfoxide functionalities, thereby preventing the oxidant to reflect its true reactivity. Finally, erroneous $X_{SO}$ values are the consequence of electron-transfer processes with SSO, which lead to the radical ions $SSO^{\bullet+}$ or $SSO^{\bullet-}$ and thereby afford either too electrophilic or too nucleophilic reactivity on part of the oxidant. Nevertheless, cognisance of such complications when using the SSO method can provide valuable mechanistic data on the oxygen-transfer process under scrutiny.

(31) Häusler, K. G.; Geyer, R. *Z. Chem.* **1977**, *17*, 146.

(32) For the $HOO^{\bullet}$ radical, the $E_{ox}$ = −1.5 V; cf. Weast, R. C.; Astle, M. J. *Handbook of Chemistry and Physics*, 62nd ed.; CRC Press: Boca Raton, FL, 1981; p D-134.

(33) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(34) Erikson, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083.

## Experimental Section

Commercially available reagents were used without further purification. Thianthrene oxides, potassium *tert*-butyl peroxides, 18-crown-6, 2,6,3′,5′-tetra-*tert*-butyl-4′-phenoxy-4-methylene-2,5-cyclohexadien-1-one radical (galvinoxyl),[23] di-*tert*-butyl trioxide,[22] 1-*tert*-butyl-6,7,8,9-dibenzo-5-methyl-2,3,4-trioxabicyclo[3.2.2]nonane (transannular anthracene ozonide),[25] *tert*-butyldiazomethane, *tert*-butylmethyldiazomethane, diphenyldiazomethane, and dimethyldioxirane[21] were prepared according to the literature procedures. Solvents were evaporated on a rotary evaporator, usually at room temperature (RT) and 15 Torr, and drying of the reaction mixtures after aqueous workup was carried out over anhydrous magnesium sulfate. Peroxide tests were performed with potassium iodide in acetic acid to afford the characteristic brown iodine color.

$^1H$ NMR spectra were recorded on a Hitachi Perkin-Elmer R-24B (60 MHz); HPLC chromatograms were run on a Waters liquid chromatograph (pump 6000 A, UV detector Model 440, injector U 6K) or Kontron (pump 414, UV detector Uvikon 720 LC), and electronic integration was performed on an Anacomp 220 computer. The column used on both chromatographs was 250 mm × 4 mm LiChroSorb Si 60, 5 μm, with 40 mm × 4 mm LiChroSorb 5 CN, 5 μm, or 40 mm × 4 mm LiChroSorb Si 60, 5 μm, as precolumn. The UV detector was operated at a wavelength of 254 nm. For the quantitative analysis of the oxygen-transfer products, a 240:10:1 mixture of petroleum ether (50–70 °C), ethyl acetate, and methanol was used as eluent at a flow rate of 3.0 mL/min. Thianthrene 5,5-dioxide ($SSO_2$), thianthrene 5,10-dioxide (SOSO), and thianthrene 5,5,10-trioxide ($SOSO_2$) were calibrated against di-*p*-nitrophenyl sulfone as the internal standard. The thianthrene 5-oxide (SSO) used in the oxygen-transfer experiments was purified by column chromatography on basic alumina (activity grade II–III) by using a 95:5 mixture of petroleum ether and ethyl acetate as eluent. Other preparative chromatographic separations were performed on a Chromatotron with 4-mm layer plates of silica gel $PF_{254}$. Polarographic studies were carried out on a Par T-170 with Pt electrode and an Ag/AgCl counter electrode.

**General Procedure of Oxygen Transfer by Potassium Superoxide and Basified Potassium *tert*-Butyl Hydroperoxide and Hydrogen Peroxide.** To a solution of SSO in dry benzene ((2–8) × $10^{-2}$ M) was added the oxygen-transfer reagent in such an amount as to get a (2–4) × $10^{-2}$ M solution of the oxygen donor. This solution was stirred at ca. 20 °C. The reaction was carried out to ca. 20–30% conversion of SSO. The reaction mixture was washed with water, the organic phase separated, washed with 20% aqueous sodium bisulfite (10 mL) and water (2 × 10 mL), dried, and filtered, and the solution passed through a bed of silica gel (ca. 2 g) by eluting with 50 mL of methanol. The combined eluates were evaporated, and the residue was dissolved in $CH_2Cl_2$ (10 mL) and analyzed by HPLC.

**General Procedure of Oxygen Transfer by Carbonyl Oxides Generated in Situ through the Photooxygenation of Diazoalkanes.** A solution of the particular diazoalkane (1.0–7.0 mmol), SSO (0.1–0.7 mmol), and ca. 5–20 mg of tetraphenylporphine (TPP) in 10–30 mL of absolute $CH_2Cl_2$ at −20 to 0 °C was irradiated with a sodium lamp while passing a gentle stream of dry oxygen gas. After complete consumption of the diazoalkane (either by $^1H$ NMR monitoring or disappearance of the characteristic diazoalkane color), the reaction mixture was allowed to warm to RT (ca. 20 °C), the solvent removed by rotoevaporation (ca. 30 °C at 15 Torr), and the residue submitted to quantitative HPLC analysis.

**General Procedure of Oxygen Transfer by in Situ Generated Dioxiranes.** A solution of $KHSO_5$ (408 mg, 0.664 mmol) and EDTA (20 mg) in 10 mL of triply distilled water at ca. 0 °C was allowed to drop slowly to a biphasic mixture of phosphate buffer solution (20 mL, 0.6 M; pH ca. 7.5), aldehyde or ketone (11.3 mmol), 18-crown-6 (250 mg, 0.94 mmol), and SSO (180 mg, 0.775 mmol) in $CH_2Cl_2$ (30 mL). The reaction mixture was stirred for 19 h at RT (ca. 20 °C). The organic layer was separated and the aqueous layer extracted with $CH_2Cl_2$ (3 × 15 mL). The combined organic phases were dried ($MgSO_4$) and filtered, and the solvent was evaporated. The residue was dissolved in 10 mL of $CH_2Cl_2$ and analyzed by HPLC.

**General Procedure of Oxygen Transfer by Isolated Dimethyldioxirane.** To 4.60 mg (0.020 mmol) of SSO in 2.5 mL of acetone or $CH_2Cl_2$ was added 0.1 mL of a 0.092 M (0.0092 mmol) freshly distilled dioxirane solution in acetone, and the resulting mixture was allowed to stand at ca. 20 °C for 20 min. The acetone was removed by evaporation, and the residue was taken up in 1 mL of $CH_2Cl_2$, dried over $MgSO_4$, and analyzed by HPLC.

**Oxygen Transfer by *m*-Chloroperbenzoic Acid (*m*-CPBA).** A solution of SSO (232 mg, 1.00 mmol) and *m*-CPBA (80%, 216 mg, 1.00 mmol) in $CH_2Cl_2$ (10 mL) was stirred at ca. 20 °C for 8 h. The reaction mixture was neutralized by 10% aqueous $NaHCO_3$ (10 mL), the organic layer separated and dried, and the solvent evaporated under vacuum. The residue was dissolved in $CH_2Cl_2$ (10 mL) and analyzed by HPLC.

**Oxygen Transfer by Ozone.** A solution of SSO (180 mg, 0.775 mmol) in $CH_2Cl_2$ (20 mL) was ozonized at −78 °C for 0.5 h, and the excess ozone was removed by flushing with a slow stream of nitrogen gas until the blue ozone color had disappeared. The solvent was removed under vacuum and the residue dissolved in $CH_2Cl_2$ (10 mL) and analyzed by HPLC.

**Oxygen Transfer by Acidified Hydrogen Peroxide.** To a solution of SSO (232 mg, 1.00 mmol) and $H_2O_2$ (35%, 1.00 g, 10.0 mmol) in $CH_2Cl_2$ (10 mL) was added a catalytic amount of $HClO_4$ (50 μL) or 1 N HCl (1 mL), and the contents were stirred vigorously at ca. 20 °C for 8 h. The reaction mixture was neutralized by 10% aqueous $NaHCO_3$ (10 mL) and the organic layer separated, dried, and evaporated under vacuum. The residue was dissolved in $CH_2Cl_2$ (10 mL) and analyzed by HPLC.

**Oxygen Transfer by Acidified *tert*-Butyl Hydroperoxide.** Through a mixture of SSO (110 mg, 0.50 mmol) and *tert*-butyl hydroperoxide (45.0 mg, 0.50 mmol) in $CH_2Cl_2$ (15 mL) was passed dry HCl gas for 2 min, or a catalytic amount of concentrated aqueous $HClO_4$ (50 μL) was added, and the contents were stirred vigorously for 24 h at ca. 20 °C in a closed flask. The reaction mixture was neutralized with 10% aqueous $NaHCO_3$ (10 mL) and the organic layer separated, dried ($MgSO_4$), and concentrated under vacuum. The residue was dissolved in $CH_2Cl_2$ (10 mL) and analyzed by HPLC.

**Oxygen Transfer by *tert*-Butyl Hypochlorite.** To a solution of SSO (116 mg, 0.50 mmol) in $CH_2Cl_2$ (10 mL) was added *t*-BuOCl (27.0 mg, 0.25 mmol), and the contents were stirred for 1 h at ca. 20 °C. The reaction mixture was neutralized by 10% aqueous $NaHCO_3$ (10 mL) and the organic layer separated, dried ($Na_2SO_4$), and evaporated under vacuum. The residue was dissolved in $CH_2Cl_2$ (10 mL) and analyzed by HPLC.

**Oxygen Transfer by *tert*-Butyl Hydroperoxide/Lead Tetraacetate.** To a solution of lead tetraacetate (1.48 g, 3.34 mmol) and SSO (180 mg, 0.775 mmol) in 30 mL of dry $CH_2Cl_2$ at −78 °C was added slowly a solution of *tert*-butyl hydroperoxide (290 mg, 3.22 mmol) in 10 mL of dry $CH_2Cl_2$ under a nitrogen gas atmosphere. After 0.5 h, the reaction was allowed to warm to ca. 20 °C during 2 h, stirred at this temperature for an additional 0.5 h, and then hydrolyzed with water. The organic layer was separated and washed with 0.5 N NaOH (20 mL) and water (20 mL), dried, and concentrated at reduced pressure. The residue was dissolved in $CH_2Cl_2$ (10 mL) and analyzed by HPLC. In a separate experiment under identical conditions, SSO was added after the addition of *tert*-butyl hydroperoxide but before the reaction mixture was warmed and processed as above.

A trapping experiment with galvinoxyl was performed by adding to a solution of 200 mg (0.45 mmol) of lead tetraacetate, 360 mg (0.156 mmol) of SSO, and 200 mg (0.474 mmol) of galvinoxyl in 20 mL of dry $CH_2Cl_2$, a solution of 42.0 mg (0.466 mmol) of *tert*-butyl hydroperoxide in 5 mL of dry $CH_2Cl_2$. The reaction mixture was processed as above.

**Oxygen Transfer by Ozonolysis of *tert*-Butyl Hydroperoxide.** A solution of *tert*-butyl hydroperoxide (0.2–0.1 M) in dry $CH_2Cl_2$ was ozonized at −78 °C until persistence of the blue color of ozone. The excess of ozone was flushed out by a slow stream of dry nitrogen gas for 0.5 h. To this solution was added at ca. −60 °C SSO (180 mg, 0.775 mmol) dissolved in 10 mL of dry $CH_2Cl_2$. The reaction mixture was warmed to RT (ca. 20 °C) during 2 h, washed with 2% aqueous $NaHCO_3$ (2 × 15 mL) and water (1 × 15 mL), dried, and filtered, the solvent removed by evaporation, and the residue dissolved in $CH_2Cl_2$ (10 mL) and analyzed by HPLC.

A trapping experiment with galvinoxyl was performed as described above by using 180 mg of (0.775 mmol) SSO, 0.302 mmol of ozonized *tert*-butyl hydroperoxide, and 10 mg (0.237 mmol) of galvinoxyl. After workup, the product mixture was submitted to HPLC analysis.

**Oxygen Transfer by 9-*tert*-Butyl-10-methylanthracene Ozonide.** A solution of anthracene ozonide (60.0 mg, 0.202 mmol) and SSO (177 mg, 0.762 mmol) in 10 mL of anhydrous benzene was heated to 60 °C for 18 h. The solvent was removed by evaporation and the residue dissolved in $CH_2Cl_2$ (10 mL) and analyzed by HPLC. A similar experiment was carried out in the presence of 212 mg (0.503 mmol) of galvinoxyl and processed as above.

**Oxygen Transfer by Photolysis of *tert*-Butyl Hydroperoxide and *tert*-Butyl Peroxide.** A solution of SSO (170 mg, 0.723 mmol), *tert*-butyl hydroperoxide (48.7 mg, 0.54 mmol), and *tert*-butyl peroxide (42.5 mg, 0.29 mmol) in 20 mL of dry benzene was irradiated at 300 nm in a Rayonet photoreactor for 2 h at 40 °C. The reaction mixture was washed with 20% aqueous sodium bisulfite (20 mL) and water (2 × 15 mL), dried, and filtered and the solvent removed by evaporation. The residue was dissolved in 10 mL of $CH_2Cl_2$ and analyzed by HPLC. A control experiment was carried out under identical conditions without peroxides.

**Oxygen Transfer by Benzophenone-Sensitized Photolysis with *tert*-Butyl Hydroperoxide.** To a solution of SSO (58.0 mg, 0.25 mmol) and benzophenone (45.0 mg, 0.25 mol) in benzene (10 mL) was added 45.0 mg (0.50 mmol) of *tert*-butyl hydroperoxide, and the solution was cooled to ca. 10 °C. The reaction mixture was irradiated with an argon ion laser light source (Coherent) at 333–364 nm for 1 h and then treated with 10% aqueous sodium sulfite (10 mL) to decompose the excess of *tert*-butyl hydroperoxide. The organic layer was separated and dried over $Na_2SO_4$ and the solvent removed by evaporation. The residue was dissolved in $CH_2Cl_2$ (10 mL) and analyzed by HPLC.

**Oxygen Transfer by 9,10-Dicyanoanthracene (DCA) Sensitization in the Presence of Dioxygen.** A solution of SSO (116 mg, 0.50 mmol) and DCA (11.5 mg, 0.050 mmol) in dry acetonitrile (15 mL) was irradiated in a Griffin–Warden tube for 1.5 h at ca. 10 °C and 333–364 nm by means of an argon ion laser light source (Coherent) under a 10-atm pressure of oxygen gas. The solvent was removed by evaporation and the residue dissolved in $CH_2Cl_2$ (10 mL) and analyzed by HPLC. A control experiment was run under the same conditions except in the absence of DCA and processed as described above.

**Oxygen Transfer by Tris(2,4-dibromophenyl)aminium Hexachloroantimonate (Magic Green) in the Presence of Dioxygen.** To a solution of SSO (90.0 mg, 0.037 mmol) in $CH_2Cl_2$ (20 mL) was added 422 mg (0.01 mmol) of Magic Green, the reaction mixture was cooled to ca. 0 °C, and dry oxygen gas was slowly allowed to pass through the solution. The brown precipitate was removed by filtration and the filtrate passed through a small column of silica gel (ca. 2–3 g) to eliminate any inorganic material by eluting with a 1:1 mixture of $CH_2Cl_2$/petroleum ether. The solvent was evaporated at reduced pressure and the residue dissolved in $CH_2Cl_2$ (10 mL) and analyzed by HPLC.

**Determination of the Oxidation Potential of SSO.** A solution of SSO (20.0 mg, 0.0861 mmol) and tetrabutylammonium tetrafluoroborate (200 mg, 0.607 mmol) in absolute acetonitrile (20 mL) was purged with a slow stream of dry nitrogen gas for ca. 10–15 min. The voltammogram was run at a scan rate of 200 mV $s^{-1}$ by using platinum and Ag/AgCl electrodes. A nearly irreversible oxidation of SSO took place with $E_{ox} \approx 1.76 \pm 0.02$ V (SCE).

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