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Probing for Electronic and Steric Effects in the Peracid Oxidation of Thianthrene 5-Oxide

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A systematic examination of the electronic and steric effects in the peracid oxidation of thianthrene 5-oxide (SSO) was undertaken and has revealed valuable information on the oxidative reactivity of the SSO mechanistic probe toward peroxidic oxidants. Thus, no significant steric effect was found on the bisulfoxide (SOSO)/sulfone (SSO_2) product ratio for aliphatic peracids with varying size of alkyl groups [R = Me, Et, *i*-Pr, *t*-Bu, (*n*-Bu)(Et)$CHCH_2$]. However, a significant electronic effect was observed for CH_3CO_3H and CF_3CO_3H, for which the X_{SO} values were 0.16 and 0.01, i.e., predominant oxidation of the sulfide functionality to the SOSO product by these oxidants. In addition, substituted perbenzoic acids displayed this trend. In contrast, the nucleophilic peracid anion led exclusively ($X_{SO} = 1.00$) to oxidation of the sulfoxide site to the SSO_2 product. The oxygen transfer appears to be orbital-controlled since the more electrophilic oxidant is clearly the more reactive as well as more chemoselective, i.e., preferred attack at the more nucleophilic sulfide site in SSO.

Introduction

During the last decade, the oxidation of thianthrene 5-oxide (SSO) has been used as a mechanistic probe to determine the electronic character of an oxidant (Scheme 1).[1−3] Thus, electrophilic oxidants preferentially attack thianthrene 5-oxide (SSO) at its sulfide sulfur to afford the thianthrene 5,10-dioxides (*trans*-SOSO and *cis*-SOSO), while nucleophilic ones oxidize SSO predominantly to the thianthrene 5,5-dioxide (SSO_2). An undesirable second oxidation (overoxidation) of all three dioxides leads to trioxide $SOSO_2$ (Scheme 1). The X_{SO} parameter was introduced as mole fraction of SSO_2 product,[1a] for which $X_{SO} = 1.00$ represents exclusive oxidation of the sulfoxide site and $X_{SO} = 0.00$ exclusive oxidation at the sulfide terminal. Prototype examples are the peroxy anion ($X_{SO} = 1.00$)[1b] and protonated hydrogen peroxide ($X_{SO} = 0.05$),[1b] which span essentially the full range of this selectivity parameter. Clearly, the peroxy anion must function as nucleophilic oxidant by attack at the electrophilic sulfoxide functionality, while protonated hydrogen peroxide serves as an electrophilic oxidant through oxygen transfer to the nucleophilic sulfide site.

In a recent publication[4] an alternative mechanistic rationale was forwarded for metal peroxo complexes in that "...*all* the oxidation reactions are electrophilic processes...", which argues that oxidation of the sulfoxide site in SSO entails electrophilic attack at the lone pair rather than nucleophilic addition to the sulfoxide functionality. As a consequence, attack at the sulfoxide site does not necessarily reflect the nucleophilicity of an oxygen donor (peroxide) but rather that of the oxygen acceptor (substrate), since clearly the sulfide terminal is more nucleophilic than the sulfoxide site in SSO and, thus, more prone toward attack by an electrophilic oxidant. This would imply that the SSO probe differentiates between the electrophilic character of the peroxidic oxidant without ascribing nucleophilic reactivity to it.

To explore whether this mechanistic rationale is general for oxidants and not specific for metal peroxo complexes, we decided to investigate nonmetal-type peroxidic oxidants, in particular organic peroxy acids. Their choice rests on the fact that peracids are established electrophilic oxidants and their mechanism of oxygen transfer is well understood[5] and not obscured by whether substrate−oxidant complexation operates. For the variation of the electrophilic character of the peracid oxidant, the aliphatic cases CH_3CO_3H *versus* CF_3CO_3H and a series of *para*-substituted perbenzoic acids were selected, for which the X_{SO} parameter should reflect the electronic nature of the oxidant. The steric properties were to be probed for a set of aliphatic peracids, namely methyl, ethyl, isopropyl, *tert*-butyl, and the neopentyl-type (*n*-Bu)(Et)$CHCH_2$ as alkyl groups, by assessing the *cis*−*trans* ratio of the bisulfoxide product SOSO. The results of this study and its mechanistic implications are reported herewith.

Results

The oxidation conditions, product compositions, and X_{SO} values with the new analytical protocol[1b] for the various peracids are given in Table 1, together with previously reported data for the two dioxiranes methyl(trifluoromethyl)dioxirane (TFD) and dimethyldioxirane (DMD) (Table 1, entries 15 and 16). The data in Table 1 clearly confirm that the trifluoroperacetic acid (Table 1, entry 1) is, as expected, the most electrophilic peracid

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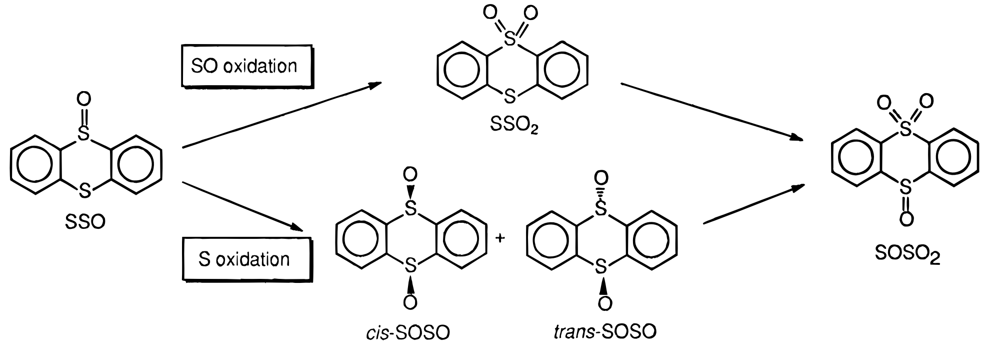
Scheme 1



$$X_{SO} = \frac{\text{SO oxidation}}{\text{total oxidation}} = \frac{SSO_2 + SOSO_2}{SSO_2 + SOSO + 2 \times SOSO_2}$$

Table 1. Oxidation[a] of Thianthrene 5-Oxide by Peroxidic Oxidants

					products[b] (%)				
						SOSO			
entry	oxidant	equiv of [O]	time[d] (min)	convn (%)	SSO_2	*cis*-	*trans*-	$SOSO_2$	X_{SO}[c]
1	F_3CCO_3H	0.30	0.5	30	0.6	75	23	1.6	0.02
2	F_3CCO_2H/UHP[e]	0.40	1 d	42	0.8	67	32	0	0.01
3	$MeCO_3H$	0.40	360	41	15	17	67	1.1	0.16
4	$(CH_3CO)_2O$/UHP[e]	0.50	5 d	8.6	9.1	38	47	5.9	0.14
5	CCl_3CN/H_2O_2[f]	10	1 d	9.2	9.4	22	69	0	0.09
6	*p*-$MeOC_4H_6CO_3H$	0.20	120	22	14	20	65	1.2	0.15
7	$C_6H_5CO_3H$	0.30	80	28	14	19	66	0.7	0.14
8	*m*-$ClC_6H_4CO_3H$	0.50	40	47	12	20	67	1.5	0.13
9	*p*-$NO_2C_6H_4CO_3H$	0.35	10	36	10	23	65	2.3	0.12
10	3,5-$(NO_2)_2C_6H_4CO_3H$	0.35	1	36	7.6	34	56	2.1	0.10
11	$EtCO_3H$	0.35	360	38	16	17	65	2.6	0.18
12	*i*-$PrCO_3H$	0.35	360	31	16	18	65	1.4	0.18
13	*t*-$BuCO_3H$	0.35	360	37	18	16	65	1.7	0.19
14	(*n*-Bu)(Et)$CHCH_2CO_3H$	0.35	360	30	16	17	66	1.3	0.18
15	TFD[g]	0.20		21	0.8	3.1	96	0.2	0.01
16	DMD[h]	0.50		52	6.8	3.1	90	0.1	0.07
17	*m*-CPBA/NaOH[i]	0.50	60	30	100	0	0	0	1.00

[a] CH_2Cl_2/25 °C unless noted otherwise. [b] HPLC analysis (RP-18, 64:34:2 MeOH/H_2O/MeCN), error ± 0.5% of the stated values, normalized on 100%. [c] X_{SO} is defined in Scheme 1; error ± 0.005 units. [d] The reaction times were determined by the peroxide test (KI/starch paper). [e] Urea hydrogen peroxide adduct (UHP). [f] 1:20 CH_2Cl_2/MeOH was used as solvent. [g] −78 °C. [h] −50 °C. [i] H_2O/CH_2Cl_2 as biphasic solvent system; *n*-Bu_4NOH as phase transfer catalyst.

examined herein. The fact that the CF_3CO_2H/UHP oxidant (Table 1, entry 2) possesses the same X_{SO} value (within the experimental error) suggests also that in this case CF_3CO_3H is the active oxygen transfer agent. When compared to peracetic acid (entry 3), it is evident that CF_3CO_3H is not only the more electrophilic and, thus, more reactive, it is also the more selective in that it almost exclusively oxidizes the sulfide site. Again, the same X_{SO} values (0.15 ± 0.01) for peracetic acid (Table 1, entry 3) and the acetic anhydride/UHP system (Table 1, entry 4) establishes that also in the latter CH_3CO_3H is the active oxidant.

Also, the trichloroacetonitrile-hydrogen peroxide combination (Table 1, entry 5) constitutes an electrophilic oxidant, for which presumably the peroxyiminocarboxylic acid intervenes, produced by addition of the H_2O_2 to the nitrile functionality. Usually alkaline hydrogen peroxide is employed for such oxidations,[6] as the intermediary peroxyiminocarboxylic acid serves as a mild epoxidizing agent. It should, however, be kept in mind that the CCl_3CN/H_2O_2 system is a rather ineffective oxidant, i.e., ca. 9.2% conversion of SSO in 24 h with 10 equiv of H_2O_2, presumably because the rate of peroxyiminocarboxylic acid formation is slow under these conditions.

For the substituted perbenzoic acids (Table 1, entries 6-10) a similar reactivity behavior as for the aliphatic derivatives is displayed, but the differentiation is much less pronounced, i.e., only 0.05 X_{SO} units, which is definitely outside the experimental error (±0.005 units). Thus, the *p*-methoxy derivative is the less electrophilic, less reactive, and less selective species, while the 3,5-dinitroperbenzoic acid (Table 1, entry 10) is more electrophilic, more reactive, and also more selective in this set. In fact, in the Hammett plot of the X_{SO} values a good correlation ($\rho = -0.0987$; $r^2 = 0.991$) was obtained [log $[X_{SO}(X)/X_{SO}(H)]$ *versus* σ(X); X are the substituents of the perbenzoic acids (Table 1, entries 6−10)]. However, the anion of *m*-CPBA (Table 1, entry 17), generated in the H_2O/CH_2Cl_2 biphasic medium with NaOH and tetrabutylammonium hydroxide as phase transfer catalyst gave exclusively SSO_2, the product of the nucleophilic oxidation of SSO.

The steric demand in the peracid oxidation of SSO was probed for the aliphatic peracids with the Et, *i*-Pr, *t*-Bu, and (*n*-Bu)(Et)$CHCH_2$ groups (Table 1, entries 11−14) in comparison to peracetic acid (Table 1, entry 3).

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Clearly, the steric effect is negligible since all five derivatives possess not only nearly constant X_{SO} values of ca. 0.18, but also the *cis*−*trans* ratios of the bisulfoxide SOSO are constant at 17:65 (Table 1, entries 3, 11, and 14).

Since the oxidation of SSO with peracids is conducted under acidic conditions, it was relevant to check whether there might be any isomerization of the *trans*- and the *cis*-SOSO under the influence of acids [PM3 calculations show that the *cis* isomer has a lower enthalpy of formation (19.9 kcal/mol) than the *trans* isomer (23.7 kcal/mol)].[2b] Moreover, even redistribution of the oxygen atoms between the various sulfur oxide products is possible, which would falsify the product ratios. For example, it is known[7] that sulfoxides are acylated by trifluoroacetic anhydride at their nucleophilic oxygen atom and the electrophilically activated sulfoxide may transfer its oxygen atom to organic substrates.[7] Nevertheless, control experiments established that all the reaction mixtures given in Table 1 are invariant in product composition for a few days at room temperature, thus making any isomerization after the oxidation rather unlikely. Furthermore, neither dilute protic acids (acetic acid, trifluoroacetic acid, $HClO_4$) nor acetic anhydride did isomerize the *trans*-SOSO to its *cis* isomer under the applied conditions. However, when trifluoroacetic anhydride was added to the *trans*-SOSO solution, immediate isomerization was found and after several hours a constant *trans*/*cis* ratio of 36:64 was reached. We propose that the isomerization occurs through a sulfurane as was found in the reaction of chiral sulfoxides with acetic anhydride.[8]

Of mechanistic interest is the deep violet color that is immediately generated when trifluoroacetic anhydride is added to a methylene chloride solution of SSO. The absorption maximum at $\lambda = 550$ nm and the characteristic EPR spectrum ($g = 2.0081$) establish that the thianthrene radical cation ($SS^{\bullet+}$) had been formed.[9−11] This radical cation is generally produced when thianthrene is dissolved in fuming sulfuric acid,[9] treated with oxidants like nitrosonium tetrafluoroborate,[10] or submitted to electrolytic oxidation.[11]

Discussion

The present systematic examination of electronic and steric effects in the peracid oxidation of thianthrene 5-oxide (SSO) has revealed valuable information on the oxidative reactivity of the SSO mechanistic probe for nonmetal, peroxidic oxidants. Thus, the fact that the aliphatic peracids (except the strongly electrophilic F_3CCO_3H) all give X_{SO} values within 0.17 ± 0.02 and *cis*,*trans*-SOSO ratios of ca. 17:65 (Table 1, entries 3 and 11−14) convincingly demonstrates that steric effects do not operate in this oxygen transfer. In view of the established S_N2-type mechanism for the oxygen transfer by peracids to sulfides,[12] clearly the alkyl group is too far removed to exercise steric effects (Figure 1).

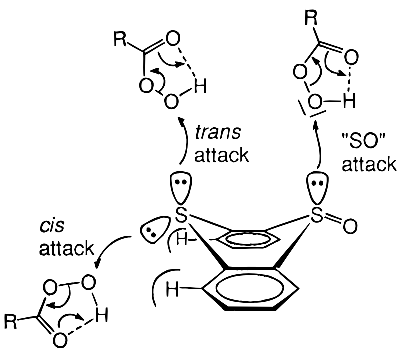
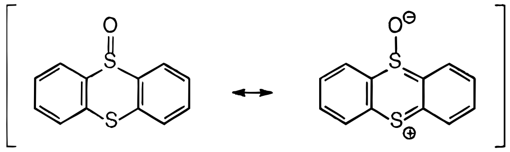


Figure 1. Electrophilic attack of peracids on the lone pairs of the sulfide and sulfoxide functionalities.

While the *peri* hydrogen atoms do encumber the attack at the *cis* sulfide lone pair so that preferably *trans*-SOSO is produced (Figure 1), the *cis*,*trans*-SOSO ratio remains constant irrespective of the alkyl group attached to the peracid carbon atom. Therefore, the similar X_{SO} values of nearly 0.2 (Table 1, entries 3 and 11−14) display electronic effects in the ease of oxidation at the sulfide *versus* sulfoxide sites for these electrophilic oxidants. Since the electrophilic character of these aliphatic peracids is expected to be nearly constant (except CF_3CO_3H, Table 1, entry 1), the observed chemoselectivity must arise from the distinct oxidative reactivity of the sulfide and sulfoxide sites in the SSO probe, namely their differentiated nucleophilicity.

As suggested for the metal peroxo complexes,[4] also for the electrophilic peracid oxidants the oxygen transfer occurs by nucleophilic attack of the sulfide or the sulfoxide lone pair on the O−O bond of the peroxide. Since sulfides are inherently more nucleophilic than sulfoxides, for such typical electrophilic oxidants as peracids, sulfide oxidation in SSO prevails and low X_{SO} values (<0.2) are observed. Unusual is the fact, however, that for the SSO probe the relative oxidative reactivities of the sulfide *versus* sulfoxide sites are so similar, i.e., only ca. 4-fold (X_{SO} ca. 0.2) compared to over 30-fold for comparable sulfide/sulfoxide pairs.[12] Since the two sulfur functionalities are in conjugation in SSO, delocalization of a sulfide lone pair onto the sulfoxide group (see structures below) leads to a dipolar mesomeric structure, in which the sulfide site (sulfonium character) is now less nucleophilic and the sulfoxide one (sulfurane character) more so. This moderates the relative reactivity of SSO toward electrophilic oxidants, which constitutes an advantage for this intramolecular mechanistic probe by responding more sensitively to the electronic character in the oxygen transfer process. Since the X_{SO} values are accurately determined by quantitative chromatographic analysis of the products SOSO and SSO_2, the oxidative reactivity and chemoselectivity of oxygen transfer agents can be conveniently and reliably assessed by the SSO probe.



Superimposed on this nucleophilic differentiation of the sulfide and sulfoxide oxygen atom acceptor are electronic effects on the electrophilicity of the oxygen donor. This is most clearly expressed in the X_{SO} values (Table 1,

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entries 1 and 3) for CF_3CO_3H (0.02) *versus* CH_3CO_3H (0.16), which confirm that the former is the more electrophilic oxidant. An appreciable differentiation of the electrophilicities is also displayed for the dioxiranes TFD (0.01, Table 1, entry 15) and DMD (0.07, Table 1, entry 16). As expected, the fluorinated dioxirane is definitely the more electrophilic oxidant. The electronic effects of the perbenzoic acids (Table 1, entries 6−10), which fall within the X_{SO} range 0.10 for the dinitro derivative (Table 1, entry 10) and 0.15 for the methoxy case (Table 1, entry 6), are small, but the regular trend confirms the former as the more and the latter as the less electrophilic one in their attack on the lone pairs of the sulfide and sulfoxide functionalities. Be this as it may, the *m*-CPBA anion (Table 1, entry 17), like the hydroperoxy anion[1b] and carbonyl oxides,[2b] definitely is a nucleophilic oxidant. For all of these almost exclusively SSO is oxidized to SSO_2 by nucleophilic addition to the sulfoxide functionality rather than reaction at the lone pair.

Of mechanistic significance is the general fact that for all SSO oxidations reported herein the more electrophilic oxidant is not only the more reactive, as would be expected, but also the more chemoselective. This is particularly evident for the pairs CF_3CO_3H (0.02, Table 1, entry 1) *versus* CH_3CO_3H (0.16, Table 1, entry 3), TFD (0.01, Table 1, entry 15) *versus* DMD (0.07, Table 1, entry 16), and the 3,5-dinitro- (0.10, Table 1, entry 10) *versus* *p*-methoxy-substituted (0.15, Table 1, entry 6) perbenzoic acids. For the latter pair, oxidation by the 3,5-dinitro derivative is essentially instantaneous (ca. 1 min) and the *p*-methoxy one requires ca. 2 h, yet the former is the more selective! This clearly violates the reactivity−selectivity principle (RSP), but numerous exceptions have been documented, especially for orbital-controlled reactions.[13a,b] Presumably, oxygen-transfer reactions to SSO with electrophilic oxidants are also orbital-controlled, and their reactivity and selectivity are dictated by favorable matching of HOMO (oxygen acceptor, SSO) and LUMO (oxygen donor, peroxide) energies. As expected for such cases, the more electrophilic oxidant is the more reactive and also more selective one, as nicely exhibited by the X_{SO} data in Table 1. Indeed, PM3 calculations on CH_3CO_3H *versus* CF_3CO_3H, and DMD *versus* TFD, corroborate this reactivity−selectivity trend.[14] Alternatively, the nucleophilic oxidations with oxygen anions (HOO^-, RCO_3^-, carbonyl oxides, etc.) are charge-controlled.[13c]

In conclusion, the sulfoxide entity in SSO can be oxidized either by electrophilic oxidants (RCO_3H) through S_N2-type attack of the sulfoxide lone pair to the peroxide bond or with nucleophilic oxidants (RCO_3^-) by nucleophilic addition to the sulfoxide functionality to afford SSO_2, both in competition with the electrophilic oxidation at the sulfide site to produce SOSO. Thus, for nucleophilic oxidants (HOO^-, RCO_3^-, carbonyl oxides, etc.) the X_{SO} values are definitely larger than 0.5, and as X_{SO} tends to unity, the nucleophilicity of the oxidant increases. For electrophilic oxidants, e.g., RCO_3H, dioxiranes, etc., the X_{SO} values are definitely less than 0.5, and as X_{SO} tends to zero, the electrophilicity of the oxidants increases. However, for such electrophilic oxidants both the sulfide and sulfoxide functionalities are oxidized, respectively, to SOSO and SSO_2 by attack of the sulfur lone pair on the peroxide bond. For these electrophilic oxidants the X_{SO} values differentiate their relative electrophilic character through the inherent nucleophilicity difference of the sulfide and sulfoxide sites in SSO. Apparently, this electrophilic oxygen transfer to the heteroatom is orbital-controlled so that the more electrophilic oxidant is the more reactive but also more chemoselective, i.e., preferential oxidation of SSO to SOSO, as confirmed for peracids (CF_3CO_3H *versus* CH_3CO_3H) or dioxiranes (TFD *versus* DMD). Thus, the SSO probe (X_{SO} value) is a convenient and informative mechanistic tool to assess the electronic nature of an oxygen transfer agent.

Experimental Section

General Aspects. The HPLC analyses were carried out as described elsewhere[1b] on an HPLC analytical system equipped with a C-18 reversed-phase column by using the ternary solvent mixture of $CH_3OH/H_2O/CH_3CN$ (64:34:2) as eluent. Detection was performed at $\lambda = 254$ nm, and the identification of the peaks was verified by their UV spectra (250−450 nm) on a KONTRON detector 430. As internal standard *trans*-1-phenyl-1-penten-3-one was added in chloroform after the reaction in the dark to avoid photoisomerization. The EPR spectrum was recorded on a Bruker EPR 420 spectrometer.

All oxidations were run in distilled solvents (CH_2Cl_2 over P_2O_5, MeOH over Mg). Acetic acid and trifluoroacetic acid were used without further purification.

Methylene chloride solutions of the peroxy acids RCO_3H (R = Et, *i*-Pr, *t*-Bu, (*n*-Bu)(Et)$CHCH_2$−, Ph, *p*-$MeOC_6H_4$−) were prepared from their corresponding acid chlorides by treatment with H_2O_2/NaOH according to reported procedures.[15] The solutions of the peracids with R = *p*-$NO_2C_6H_4$−, 3,5-$(NO_2)_2C_6H_3$− in CH_2Cl_2 were prepared from their corresponding acids[16] with H_2O_2 in $MeSO_3H$. The peroxide content of the peracid solutions was determined by iodometry, and the solutions were stored over at −20 °C.

General Procedures for the Oxidation of Thianthrene 5-Oxide (SSO) with Peracids. To a solution of thianthrene 5-oxide (23.2 mg, 0.100 mmol) in CH_2Cl_2 (5 mL) was added the peracid stock solution (0.2−0.5 equiv). After the peroxide was consumed (as tested by KI/starch paper), the residue was analyzed by HPLC as described above without any workup. The results are summarized in Table 1.

Reaction of Thianthrene 5-Oxide with UHP/F_3C-CO_2H. A solution of thianthrene 5-oxide (21.0 mg, 0.0904 mmol), F_3C-CO_2H (103 mg, 0.904 mmol), and UHP (4.60 mg, 0.0489 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature. After 10 d the peroxide test was negative and the sample was submitted to HPLC analysis as described above. The results are summarized in Table 1.

Reaction of Thianthrene 5-Oxide with UHP/$(H_3C-CO)_2O$. A solution of thianthrene 5-oxide (25.2 mg, 0.109 mmol), acetic anhydride (5.00 mL), and UHP (6.54 mg, 0.0695 mmol) in CH_2Cl_2 (11 mL) was stirred at room temperature (ca. 20 °C). After 8 d, CH_2Cl_2 (20 mL) was added, and the solution was washed with 10% aqueous $NaHCO_3$ solution (10 mL) and subsequently with water (2 × 20 mL). The organic layer was washed with water (2 × 20 mL) and dried over $MgSO_4$. The

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(14) The LUMO of CH_3CO_3H (0.29 eV) is significantly higher than that of CF_3CO_3H (−1.06 eV), as expected for the electron-accepting properties of the fluoro atoms of the latter, while in SSO the higher-energy HOMO (−8.87 eV) is located on the sulfide and the HOMO-1 (−9.30 eV) on the sulfoxide functionality. Thus, the lowest energy gap pertains to the HOMO(sulfide)−LUMO(CF_3CO_3H) interaction, which implies a higher reactivity as well as chemoselectivity for this combination. The PM3 parameters were taken from: Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209−221; **1991**, *12*, 320−341. Software package VAMP 5.0: Rauhut, G.; Chandrasekhar, J.; Alex, A.; Steinke, T.; Clark, T. University of Erlangen-Nürnberg, Germany, 1993.

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solvent was evaporated (30 °C/12 Torr), and the residue was taken up in 5 mL of CH_2Cl_2/ethanol (1:1) and submitted to HPLC analysis as described above. The results are summarized in Table 1.

Reaction of Thianthrene 5-Oxide with H_2O_2/Cl_3C-CN. Thianthrene 5-oxide (23.2 mg, 0.0999 mmol) was dissolved in CH_2Cl_2 (0.5 mL) and methanol (10 mL). Trichloroacetonitrile (0.700 mL, 6.92 mmol) and a methanolic H_2O_2 solution (0.620 mL, 1.61 M, 0.999 mmol) were added at room temperature and stirred. After 1 d, the peroxide was quenched with 0.5 mL of dimethyl sulfide. The solvent was evaporated (30 °C/12 Torr), and the residue was taken up in 4 mL of CH_2Cl_2/ethanol (1:1) and submitted to HPLC analysis as described above. The results are summarized in Table 1.

Reaction of Thianthrene 5-Oxide with *m*-Chloroperbenzoic Acid (*m*-CPBA)/NaOH. A methylene chloride solution of *m*-CPBA (0.302 mL, 0.153 M, 0.0463 mmol) was added to a well-stirred solution of NaOH (95.0 mg, 2.38 mmol) and *n*-Bu_4NOH (0.200 mL, 0.386 M, 0.0771 mmol) as phase-transfer catalyst in water (1.00 mL) at ambient temperature. To this well-stirred two-phase mixture was added a solution of thianthrene 5-oxide (20.0 mg, 0.0861 mmol) in CH_2Cl_2 (3.00 mL). After 1 h the peroxide test was negative, 3.00 mL of CH_2Cl_2 was added, and the organic layer was washed with water (2 × 10 mL) and separated. Small aliquots of the organic layer were directly submitted to HPLC analysis as described above. The results are summarized in Table 1.

Attempted Isomerization of *trans*-SOSO by Acids. To separate solutions of *trans*-SOSO (0.844 mg, 3.40 μmol) in 5.50 mL of CH_2Cl_2 at 25 °C was added F_3CCO_2H (1.65 mL, 21.5 mmol) or $HClO_4$ (0.303 mL, 15 M, 4.55 mmol). The reaction mixtures were directly injected into the HPLC, and their *trans/cis* ratio was determined. No isomerization of *trans*-SOSO was found even after 2 days of treatment.

Isomerization of *trans*-SOSO by Trifluoroacetic Anhydride. To a solution of *trans*-SOSO (0.844 mg, 3.40 μmol) in 5.50 mL of CH_2Cl_2 at 25 °C was added $(F_3CCO)_2O$ (22.3 mg, 0.108 mmol). After 26 h the reaction mixture was submitted to the HPLC analysis and the *trans/cis* ratio determined to be 36:64, which was invariant after that time. Acetic anhydride (541 mg, 5.30 mmol) did not cause any isomerization under these conditions.

Reaction of SSO with Trifluoroacetic Anhydride. To a solution of SSO (0.790 mg, 3.40 μmol) in 5.50 mL of CH_2Cl_2 at 25 °C was added a solution of trifluoroacetic anhydride (22.3 mg, 0.108 mmol) in CH_2Cl_2. Immediately a violet color appeared (λ_{max} = 550 nm) and an EPR spectrum showed the characteristic signal at $g = 2.0081^{9-11}$ for the thianthrene radical cation.

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