distribution is under "ground-state control" (i.e., the product ratio derives from the ground-state distribution of reactive conformations).²⁰ Fortunately, this problem is most since the lowest transition-state enthalpies derive from the lowest energy ground-state conformers; specifically. 1A leads to abstraction from the F residue and 1D leads to abstraction from the E residue. Supporting the idea that the photochemistry is under ground-state control is the observation that the benzophenone moiety dissociates from the β -CD portion to a much larger extent in aqueous CH_2CN than in aqueous *i*-PrOH. In the latter solution most all conformers should be close to a 2propanol molecule, whereas in the former solution those conformers that are not close to a C6 methylene may rid themselves of their excitation energy through bond cleavage.

The mechanism leading from the diradical to 2a and 2b is unclear. The fact that 1 and 2 appear as the LATs disappear suggests that 1 and 2 are formed from an LAT. Other precursors of 1 and 2 can be postulated, but their existence is not consistent with experimental results. Long-lived radicals are unlikely because the benzophenone ketyl portions would undergo coupling to pinacols, which are stable under the reaction conditions. Direct coupling of the radicals giving the cross-pinacol product is another possibility, but this vic-diol should not decompose in the presence of O_2 nor would it give rise to an LAT. Intermolecular coupling to form an LAT (C6-ketyl/benzophenone ketyl) seems unlikely because the process encounters too much steric encumbrance and violates the principle of least motion. We assign the intermediate as the ortho-coupled isomer instead of the para isomer be-

(20) Wagner, P. J. Acc. Chem. Res. 1983, 16, 461-467.

cause the atoms that would bond together are too distant in the latter case and because the *p*-LAT should give some para-coupled product.¹² The *o*-LAT should be favored since the in-plane H-abstraction places the hydroxymethyl radical very close to an ortho position. *o*-LATs do not lead to coupled products, rather, they suffer C–C bond scission, regenerating the benzophenone.¹³ This intermediate can explain the formation of both 1 and 2: O₂-induced scission results in formation of the benzophenone and an alkyl ketyl radical. The latter can lose or gain an H-atom, resulting in 2 or 1, respectively.

Conclusions

Attachment of a benzophenone group to β -CD does not alter the typical benzophenone photochemical pathways. Pinacol formation is efficient when 1 is irradiated in aqueous *i*-PrOH. Without a good H-atom source, the benzophenone abstracts a hydrogen atom from across the β -CD from either the E or F glucose methylene leading to the C6-oxidized products 2 and to a complex mixture of pinacols. Light-absorbing transients (LATs), possibly the intramolecular, ortho-coupled isomers, are observed under anaerobic conditions. They decompose slowly in the presence of air to give 2 and to regenerate 1.

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Registry No. 1, 76700-69-1; **2a**, 133322-44-8; **2b**, 133294-74-3; **3a**, 133322-45-9; **3b**, 133398-17-1; **3c**, 133398-18-2; **4a**, 133294-75-4; **4b**, 133397-41-8; **5**, 82125-70-0; **6**, 133294-76-5; β -CD, 7585-39-9; benzophenone-3,3'-disulfonyl chloride, 17619-15-7; benzophenone, 119-61-9.

Oxidation of Bis(*tert*-butylthio) Selenide at Low Temperatures: Search for a Bis(alkylthio) Selenoxide^{1a}

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Oxidation of bis(tert-butylthio) selenide, t-BuSSeSBu-t (1a), by peracetic acid at -40 °C leads to a monooxidation product (1a-O) whose ¹H (two singlets) and ¹³C NMR spectra (four resonances) show that the two tert-butyl groups in 1a-O are magnetically nonequivalent. It cannot therefore be the bis(alkylthio) selenoxide, t-BuSSe-(O)SBu-t (3a), and is either t-BuS(O)SeSBu-t, 5a (oxidation of 1a at S rather than Se), or t-BuSSeOSBu-t, 4a (formed by rapid isomerization of initially formed 3a). The fact that δ ⁷⁷Se for 1a-O is 289 ppm downfield from δ ⁷⁷Se for 1a is inconsistent with structure 5a and indicates that 1a-O has structure 4a, t-BuSSeOSBu-t. Reaction of t-BuSH with 1a-O gives 1a plus t-BuSOH, in accord with what would be expected for nucleophilic attack of the thiol on the selenium of 4a. While oxidation of 1a by peracid is thought to result initially in 3a, this thioselenoxide apparently isomerizes to 4a so rapidly, even at -40 °C, that 4a is the first oxidation product detectable by NMR. These results are of significance with regard to several steps in the previously proposed (ref 4) mechanism (Scheme I) for the formation of bis(alkylthio) selenides from the reaction of thiols with selenite.

The reaction of selenite with the thiol groups in cysteine residues, glutathione, or coenzyme A to form bis(alkylthio) selenides, RSSeSR (1), is known^{2,3} to be an important pathway by which inorganic selenium is initially incorporated into living systems. Ganther^{2a} established that the

usual combining ratio of thiol to selenite was 4:1 and proposed that the stoichiometry of the reaction was as shown in eq 1.

$$4RSH + H_2SeO_3 \rightarrow RSSeSR + RSSR + 3H_2O \quad (1)$$

1

$$RSH + SeO_2 \xrightarrow{\text{rapid}} RSSeO_2H \qquad (2)$$

3

$$\begin{array}{c} O \\ II \\ RSSeO_2H + RSH \xrightarrow{slow} RSSeSR + H_2O \qquad (3) \\ 2 \qquad 3 \end{array}$$

$$RSH + RSSe = 0 - SR \longrightarrow RSSeSR + RSOH (5)$$

$$\frac{RSH}{(slow when R = I-Bu)} RSSR + H_2O$$
(6a)
RSOH

RSO₂SR (6b)

Kice, Lee, and Pan⁴ investigated the mechanism of the reaction of thiols with selenite using as substrates 1-butanethiol (n-BuSH) and 2-methyl-2-propanethiol (t-BuSH). They found that when the thiol was *t*-BuSH much less disulfide (t-BuSSBu-t) was formed than anticipated from the stoichiometry of eq 1, and that in its place was a sizeable amount (0.3 mol/mol of 1) of tert-butyl 2methyl-2-propanethiosulfonate, t-BuSO₂SBu-t. The kinetic behavior of the reaction showed that the first step was a rapid, and reversible, reaction of the thiol with selenite (as SeO_2) to give an alkylthioseleninic acid (2), $RSSeO_2H$ (eq 2, Scheme I). This was followed by a much slower, and rate-limiting, reaction of thiol with RSSeO₂H, a reaction that, based on the dependence of its rate on various reaction variables, appeared to involve attack of the thiol on the selenium of RSSeO₂H and formation of the bis(alkylthio) selenoxide (3), RSSe(O)SR (eq 3). To account satisfactorily for the further course of the reaction and the final products it was suggested⁴ that 3 then isomerized (eq 4) rapidly to RSSeOSR, 4 (there is precedent⁵ for facile and rapid isomerization of Se=O compounds to the -Se-O- isomer), and that 4 then underwent substitution at selenium by the thiol (eq 5), giving 1 and the sulfenic acid (RSOH). The sulfenic acid either reacted with a fourth molecule of thiol to yield the disulfide (eq 6a) or underwent a reaction sequence resulting in the formation of the thiosulfonate RSO₂SR (eq 6b). Pathway 6b was much important relative to 6a when R was a tertiary alkyl group like $(CH_3)_3C$ and nucleophilic substitution at the sulfur atom was subject to steric hindrance that in other cases⁶ is known to result in rate reductions of up to 10^6 .

Because eq 3 is the rate-limiting step of the thiol-selenite reaction, direct observation of the postulated rapid isomerization of 3 (eq 4), or of any of the subsequent steps in Scheme I is not possible in a system where 3 is generated from thiol plus selenite. It occurred to us, however, that a bis(alkylthio) selenoxide (3) might also be able to be generated by oxidation of 1 at low temperature with a suitable oxidizing agent. If so, it might then be possible subsequently to observe its isomerization or other chemistry, either at low temperature or by allowing the solution to warm toward room temperature.

The present paper reports a study of the oxidation of bis(tert-butylthio) selenide, t-BuSSeSBu-t (1a, R = t-Bu) at low temperature and of examination of the behavior of the monooxidation product (1a-O).

Results

Preparation and NMR Characterization of 1a. Bis(*tert*-butylthio) selenide⁴ (1a) was prepared by reaction of 2-methyl-2-propanethiol (*t*-BuSH) with selenium dioxide in aqueous acetonitrile, and the crude product was then purified by flash chromatography (removal of *t*-BuSO₂SBu-*t*) followed by fractional vacuum distillation (removal of *t*-BuSSBu-*t*). The ¹H NMR of the purified 1a consisted of a sharp singlet at δ 1.41. The absence of signals at δ 1.32 (*t*-BuSSBu-*t*)⁴ and 1.46 and 1.62 (*t*-BuSO₂SBu-*t*)⁴ showed that the material was not contaminated with a detectable amount of disulfide or thiosulfonate.

The ¹³C NMR (CDCl₃) resonances for the carbons in 1a were found at 30.77 and 47.56 ppm (25 °C); at -40 °C these shift slightly, to 30.37 and 47.50 ppm. The ⁷⁷Se NMR (CDCl₃) resonance for 1a at 25 °C was at 573 ppm (relative to Me₂Se). At -25 °C the same resonance shifted to 565 ppm.

Oxidation of 1a with Peracetic Acid at -40 °C. When t-BuSSeSBu-t (0.12 M in $CDCl_3$) was treated at -40 °C with peracetic acid (also 0.12 M in CDCl₃) the intensity of the singlet at δ 1.41 in the ¹H NMR due to 1a decreased. the extent of the decrease being proportional to the amount of oxidant added, and two singlets of equal intensity appeared at δ 1.45 and 1.46, these being due to a monooxidation product of 1a (1a-O). Besides the strong signals at δ 1.45 and 1.46, there were two very weak signals at δ 1.49 and 1.51. However, there was no evidence of a ¹H NMR signal in this region whose intensity changed with time, such as would be observed if 1a were oxidized initially to a product that then gradually isomerized to 1a-O. Aliquots of peracetic acid solution were added until the singlet at δ 1.41 had disappeared completely; this required the addition of about 1.2 molar equiv of peracid.

The final solution from the oxidation of 1a was then allowed to warm gradually from -40 °C. At -25 °C the two singlets at δ 1.45 and 1.46 coalesced to a single peak (δ 1.45) which sharpened as the temperature was raised to -10 °C. This singlet reverted to a pair of singlets (δ 1.43 and 1.44) when the temperature was raised to 20 °C. All of these temperature-dependent changes in the ¹H NMR were found to be fully reversible on cooling the solution back to -40 °C. In another experiment it was shown that 1a-O

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is apparently reasonably stable in dilute solution at room temperature, since no change in the ¹H NMR of the solution was observed during 3 h at 20 °C.

To establish that the temperature-dependent changes in the ¹H NMR of 1a-O did not represent tangible chemical change, the above experiment was also followed by ¹³C NMR. At -40 °C the ¹³C NMR of 1a-O consisted of four resonances located at 23.99, 30.37, 47.78, and 60.70 ppm. Warming the solution first to -10 °C, and then to 20 °C, did not lead to any significant change in this spectrum (the four resonances being found at room temperature at 24.08. 30.59, 47.69, and 60.61 ppm). This result shows clearly that warming of the solution does not result in any change in the magnetic environment of the carbon atoms in 1a-O.

The fact that the ¹³C NMR of 1a-O has four separate resonances, and that its ¹H NMR at -40 °C consists of two singlets, shows that in 1a-O the two tert-butyl groups are not magnetically equivalent. This rules out a symmetric structure for 1a-O, such as t-BuSSe(O)SBu-t.

The ⁷⁷Se NMR spectrum of the monooxidation product of 1a was also determined. In this experiment 1a was oxidized at -40 °C with somewhat less than 1 molar equiv of peracetic acid, and the ⁷⁷Se NMR of the resulting solution (mixture of 1a-O and a lesser amount of residual 1a) was measured at -25 °C. The ⁷⁷Se NMR resonance for the selenium in 1a-O was found 289 ppm downfield from the resonance for the Se in 1a, or at 854 ppm downfield from Me₂Se. Besides the strong signal at 854 ppm a much weaker signal was observed at 845 ppm; this may be due to a minor byproduct formed in the oxidation.

Reaction of the Monooxidation Product of 1a (1a-O) with 2-Methyl-2-propanethiol. The monooxidation product of 1a (1a-O) was allowed to react at -40 °C in CDCl₃ for 6 h with 2 molar equiv of 2-methyl-2-propanethiol (t-BuSH). Observation of the ¹H NMR of the solution during this period showed that the two singlets at δ 1.45 and 1.46 associated with 1a-O disappeared, and the singlet at δ 1.41 associated with 1a reappeared. Only one of the 2 molar equiv of t-BuSH was consumed. Workup of the reaction mixture led to the isolation of la (0.68 mol/mol 1a-O) and tert-butyl 2-methyl-2-propanethiosulfinate,^{4,7} t-BuS(O)SBu-t (0.40 mol/mol 1a-O), consistent with the stoichiometry shown in eq 7 for the reaction of the thiol with 1a-O at -40 °C. 2-Methyl-2-propanesulfenic $1a-O + t-BuSH \rightarrow t-BuSSeSBu-t + t-BuSOH$ (7a)

$$t$$
-BuSOH $\rightarrow \frac{1}{2}t$ -BuS(O)SBu- $t + \frac{1}{2}H_2O$ (7b)

acid (t-BuSOH) is known⁸ to undergo dehydration very easily to form t-BuS(O)SBu-t (eq 7b). The fact that only 1 mol of t-BuSH is consumed per mole of 1a-O shows that under these particular reaction conditions (-40 °C, chloroform solution) dehydration of sulfenic acid to form thiosulfinate (eq 7b) is faster than reaction of the sulfenic acid with thiol to form disulfide (t-BuSH + t-BuSOH \rightarrow t-BuSSBu-t + H₂O). It also shows reaction of t-BuSH with the thiosulfinate does not occur at a significant rate under these conditions.

Oxidation of 1a by Ozone. The oxidation of 1a by ozone was also investigated. In contrast to its oxidation by peracetic acid, where addition of 1 molar equiv of oxidant to 1a at low temperature led to the formation of a monooxidation product (1a-O) in good yield, oxidation of

1a by ozone, even at -78 °C (methylene chloride as solvent), did not. A major source of the difficulty appears to be the relatively low reactivity of 1a toward ozone. at least as compared to alkyl sulfides or selenides, combined with the fact that the product(s) produced initially upon ozonization is(are) more easily ozonized than 1a itself. Thus, even at low flow rates only about 50% of the ozone passed through the solution was absorbed, even at the outset of the ozonization, while an experiment under the same conditions using an alkyl sulfide as substrate gave complete absorption of O_3 up to the point where one mole was taken up.⁹ Workup of the reaction solution after uptake of 1 mol of O_3 per mole of 1a led to the recovery of 44% of the original 1a. The ¹H NMR of this solution prior to workup indicated a plethora of compounds were present, signals being observed at δ 1.34, 1.37, 1.44, 1.45, 1.50, 1.58, and 1.61, in addition to the signal due to unreacted 1a at δ 1.41. However, the only compound beside 1a eluted upon flash chromatography of the reaction mixture was the thiosulfinate t-BuS(O)SBu-t (0.07 mol/ mol of 1a ozonized). The remaining products apparently decomposed on the column because they could not be eluted.

Discussion

Oxidation of 1a by Peracid. Oxidation of t-BuSSeS-Bu-t (1a) with peracetic acid at -40 °C leads to the formation of a monooxidation product, 1a-O, that ¹H and ¹³C NMR show has a structure where the two *tert*-butyl groups are magnetically nonequivalent; 1a-O is therefore not bis(alkylthio) selenoxide, t-BuSSe(O)SBu-t, (3a).

Two structures can be suggested for 1a-O that are consistent with its ¹H and ¹³C NMR spectra. The first, t-BuS(O)SeSBu-t (5a), would arise if oxidation of 1a by peracid takes place preferentially at sulfur rather than selenium. The second, t-BuSSeOSBu-t (4a), would arise if oxidation occurred at selenium to give 3a, but 3a then isomerized rapidly at -40 °C to give 4a (eq 4). The isomerization of 3a to 4a would have to be fast since the first oxidation product of 1a detectable by ¹H NMR at -40 °C is the one with two nonequivalent tert-butyl groups. That such an isomerization could be rapid at -40 °C is certainly possible given the rapidity of selenoxide to selenenate isomerizations in other cases⁵ ($t_{1/2} = 6 \text{ min at } -80 \text{ °C}$ for the isomerization of *o*-nitrophenyl prenyl selenoxide to the corresponding selenenate^{5a}).

Reaction of 1a-O with t-BuSH at -40 °C leads to the formation of 1a and t-BuS(O)SBu-t (eq 7). This is consistent with what would be expected from nucleophilic attack of the thiol on the selenium atom of either 4a or 5a:

t-

In our opinion the ⁷⁷Se NMR of 1a-O allows a decision in favor of 4a as the structure for 1a-O. Reich and coworkers¹¹ have shown that the ⁷⁷Se chemical shift for the divalent selenium atom in selenoseleninate 6 (540 ppm) is slightly upfield from the 77 Se resonance (559 ppm) for

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the corresponding diselenide 7. The same is true¹¹ in the cyclic selenoseleninate 8 (Se=O, 693 ppm; Se, 273 ppm) and the related cyclic diselenide 9 (Se, 289 ppm). While



no ⁷⁷Se NMR data are available for compounds with an S(O)Se functionality, the data for 6 vs 7, and 8 vs 9, suggest to us that the ⁷⁷Se chemical shift for the selenium in 5a would not be expected to differ much from that for the selenium in 1a (565 ppm at -25 °C). The fact that the ⁷⁷Se chemical shift for the Se in 1a-O (854 ppm) is ~300 ppm downfield from δ ⁷⁷Se for the selenium in 1a is therefore hardly consistent with 1a-O having structure 5a. On the other hand, if it has structure 4a the δ ⁷⁷Se for the selenium in 1a-O would be expected to be far downfield from δ ⁷⁷Se for 1a.

The chemical shift for the Se in 1a-O is actually in the region (800–870 ppm) typically associated with selenium atoms in Se=O groups.¹² The δ ⁷⁷Se for the Se's in the selenenate esters and selenenic acids that have been measured (such as 10 and 11) are even further downfield



(1060–1280 ppm).^{11,13} However, since the ¹H and ¹³C NMR clearly show that 1a cannot have structure 3a, we believe that the δ^{77} Se for 1a-O of 854 ppm is not indicative of its having structure 3a. Rather we suggest that the -S-Se-O-S- structure in 4a is sufficiently different from a typical selenenate ester functionality (>C-Se-O-C<) that it would not be surprising if the chemical shift of the Se in 4a, while well downfield from that for 1a, were in a different region than for ordinary selenenate esters.

We therefore feel that the δ ⁷⁷Se NMR of 1a-O points toward 1a-O having structure 4a. That being the case we conclude that 1a is apparently oxidized initially at selenium by the peracid, giving the bis(alkylthio) selenoxide 3a (eq 8a), but that even at -40 °C the rearrangement of 3a to 4a is very rapid (eq 8b). As a consequence our hope that we could generate 3 by oxidation of 1 at low temperatures and then study the isomerization to 4 (eq 4) has not been able to be realized. That 4 once formed would react with a molecule of thiol in the manner postulated in eq 5 has, however, been demonstrated.

$$t-\text{BuSSeSBu-}t \xrightarrow[-40 \circ C]{\text{AcOOH}} t-\text{BuSSe(O)SBu-}t \quad (8a)$$

$$t-BuSSe(O)SBu-t \xrightarrow[-40 \circ C]{fast} t-BuSSeOSBu-t \quad (8b)$$

Oxidation of 1a by Ozone. The rate of uptake of ozone by a solution of **1a** shows that the bis(alkylthio) selenide is oxidized by O_3 much less readily than are alkyl sulfides or selenides. Further, the fact that after uptake of 1 mol

of ozone by the solution almost half of the 1a remained unchanged shows that the initial oxidation product(s) from the reaction of 1a with O_3 is(are) more easily oxidized by ozone than is 1a itself. This clearly contrasts with the oxidation of 1a by a peracid where addition of 1 mol of oxidant gave a good yield of the monooxidation product and only a small amount of 1a remained unoxidized. The reason for this marked difference in behavior between O_3 and AcOOH as oxidants for 1a is not known.

Experimental Section

Synthesis and Purification of Bis(tert-butylthio) Selenide (1a). This compound was prepared by a modification of a previously published⁴ procedure. 2-Methyl-2-propanethiol (9.0 g, 0.1 mol) was added dropwise over 1 h to a well-stirred solution of 2.2 g (0.02 mol) of selenium dioxide in 100 mL of 80% (v/v)acetonitrile-water. Stirring was continued for 2 h after the addition was complete. During this time an oily yellow phase containing 1a separated. Most of the acetonitrile was removed under reduced pressure by rotary evaporation, and the residual two-phase mixture was extracted several times with methylene chloride. The combined methylene chloride extracts were washed with water and dried $(MgSO_4)$, and the methylene chloride was removed under reduced pressure to give a residue consisting of 1a (¹H NMR, δ 1.41) containing significant amounts of *tert*-butyl disulfide (δ 1.32) and tert-butyl 2-methyl-2-propanethiosulfonate (δ 1.46 and 1.62). To purify the crude 1a it was first subjected to flash chromatography on silica gel using hexane as eluent; this separates the thiosulfonate from the other two compounds. The 1a-disulfide fractions from the flash chromatography were then fractionally distilled under vacuum giving 3.7 g (72%) of pure 1a:⁴ bp 48-49 °C (0.15 Torr); ¹H NMR (CDCl₃) δ 1.41 (s); ¹³C NMR (CDCl₃) 30.77 and 47.56 ppm (T = 25 °C), 30.37 and 47.50 ppm (T = -40 °C); ⁷⁷Se NMR (CDCl₃) 573 ppm (25 °C, Me₂Se as δ^{77} Se = 0), 565 ppm (-25 °C).

Oxidation of 1a with Peracetic Acid. Separate solutions of 1a and peracetic $acid^{14}$ in $CDCl_3$ (both 0.117 M) were made up. A 0.5-mL aliquot of the solution of 1a was placed in a 5-mm NMR tube and cooled to -40 °C. The peracetic acid solution was also cooled to -40 °C, and a measured amount was added dropwise by micropipet over a 5-min period with good mixing. The NMR tube was then placed in the probe of a Chemagnetics A200 NMR spectrometer, which was thermostated at -40 °C, and allowed to equilibrate briefly, and spectra were then obtained in the usual manner.

A series of preliminary experiments established that somewhat more than 1 mol of peracid per mole of 1a needed to be added for complete disappearance of the singlet (δ 1.41) due to the protons of 1a. The need to add slightly more than 1 mol of peracid is presumably due to the fact that some peracid is consumed in further oxidation of the monooxidation product, but the problem of further oxidation of the initial oxidation product is minor compared to the situation in the ozonization of la (vide infra). Addition of ~ 1.2 mol of peracid per mol of 1a gave optimum results. After addition of this amount of peracid the ¹H NMR of the solution at -40 °C in the δ 0.0-3.0 region consisted of strong singlets at δ 2.16 (CH₃ of AcOH) and 1.45 and 1.46 (monooxidation product of 1a, 1a-O), together with two quite weak singlets at δ 1.50 and 1.51 (presumed to be due to products of further oxidation of 1a-O). The ¹³C NMR exhibited resonances at δ 21.26, 23.99, 30.37, 47.78, 60.70, and 178.63. The signals at δ 21.26 and 178.63 were shown to be due to the carbons in acetic acid. The remaining four peaks were due to the oxidation product having ¹H NMR signals at δ 1.45 and 1.46.

The solution was allowed to warm from -40 °C, and ¹H NMR spectra were taken at -25, -10, 5, and 20 °C, while ¹³C NMR spectra were obtained at -10 °C and 20 °C. The specifics of these spectra are outlined in the Results.

The behavior of the 77 Se NMR upon oxidation of 1a with peracetic acid was investigated in a separate experiment in which 1.5 mL of a 0.47 M solution of peracetic acid in CDCl₃ was added

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slowly at -40 °C to 1.5 mL of a 0.53 M solution of 1a in the same solvent contained in a 10-mm NMR tube, and the tube was then transferred to the probe of a Bruker 200 MHz NMR spectrometer that was thermostated to -25 °C. A total of 1825 scans were taken at -25 °C. The resulting ⁷⁷Se NMR had a peak at 565 ppm (relative to Me₂Se) due to unoxidized 1a and a much stronger peak 289 ppm downfield from this (i.e., at 854 ppm) due to the monooxidation product (1a-O). There was also a very weak peak at 847 ppm, which may be due to a product resulting from further oxidation of 1a-O.

Reaction of 2-Methyl-2-propanethiol with 1a-O. NMR Studies. A 0.5-mL aliquot of a 0.117 M solution of 1a in CDCl₃ was oxidized at -40 °C with sufficient 0.117 M peracetic acid in CDCl₃ to lead to the complete disappearance of the singlet for 1a at δ 1.41. With the solution still at -40 °C, 0.5 mL of a 0.234 M solution of 2-methyl-2-propanethiol in CDCl₃ was then added, and the ¹H NMR of the solution was observed as a function of time. The pair of singlets of the oxidation product at δ 1.45 and 1.46 were seen to decrease in intensity, and accompanying this was the appearance and increase in intensity of a singlet at δ 1.41. After 6 h at -40 °C only 1 mol of t-BuSH had reacted, the ¹H NMR showed a strong singlet at δ 1.41, and the original pair of singlets at δ 1.45 and 1.46 were gone.

Product Isolation Studies. To a solution of 0.5 g (1.95 mmol) of 1a in 16.6 mL of reagent grade chloroform was added dropwise at -40 °C 23.6 mL of a 0.1 M solution of peracetic acid in chloroform. After the addition was complete the solution was allowed to stand at -40 °C for several hours, and then 0.35 g (3.88 mmol) of 2-methyl-2-propanethiol in 16.6 mL of chloroform was added dropwise at -40 °C over a 20-min period. After the addition of the thiol the solution was allowed to stand for 4 h. At the end of that time the volume of the solution was reduced to less than 10 mL by rotary evaporation, and the residual solution was subjected to flash chromatography on silica gel using hexane, followed by 3:1 hexane-ether, as eluents. The fraction eluted with hexane (0.34 g) was identical in all respects with a known sample of 1a. The fraction eluted with 3:1 hexane-ether (0.15 g) was identical in its spectral and other properties with a known sample of tert-butyl 2-methyl-2-propanethiosulfinate,47 t-BuS(O)SBu-t.

Ozonization of 1a. Ozone was generated by passing oxygen through a Monitor Labs NO_x Analyzer ozone unit at a rate of 50 cm³/min. Calibration was accomplished by passing the resulting O_2/O_3 exit stream through a saturated KI solution and titrating the iodine produced. For ozonization of 1a 0.10 g of t-BuSSeSBu-t was dissolved in 5 mL of methylene chloride, and the solution

was placed in a midget impinger. The solution was cooled to -78 °C and the O_2/O_3 stream from the ozone generator was passed through the solution for a selected period of time. The exhaust stream from the midget impinger was passed through a bubbler containing saturated potassium iodide. The amount of iodine formed in the bubbler was determined by titration at the conclusion of the experiment. The amount of ozone consumed by the reaction solution, determined by difference from the known rate of O_3 generation (calibration experiment) and the amount getting through the reaction solution. This contrasted with the 100% uptake until 1 mol/mol substrate had been taken up that was observed when diethyl sulfide, rather than 1a, was the substrate.

The ¹H NMR of the final reaction solution was determined at -55 °C in a run in which 1.2 mol of O₃ had been consumed per mol of 1a. The spectrum showed peaks at δ 1.34, 1.37, 1.41, 1.44, 1.50, and 1.61. The peak at δ 1.41 is due to unreacted 1a (vide infra). At least one of the other compounds is quite unstable thermally, since warming of the solution resulted in the deposition of a red precipitate (probably selenium).

In a separate experiment 0.26 g of 1a in 12.5 mL of methylene chloride was treated with ozone at -78 °C until 1.0 mol of O₃/mol 1a had been taken up by the reaction solution. The final reaction solution was then flash chromatographed on silica gel using 1.5:1 ether-hexane as eluent. The first material eluted (0.114 g) was identical with a known sample of 1a, and amounts to 44% of the original 1a being recovered unreacted. The only other material that could be eluted from the column (0.015 g) was shown to be identical with a known sample of *tert*-butyl 2-methyl-2-propanethiosulfinate,^{4,7} t-BuS(O)SBu-t. The inability to elute additional compounds suggests that they decomposed on the column.

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Supplementary Material Available: 13 C NMR spectrum of the monooxidation product of *t*-BuSSeSBu-*t* (1 page). Ordering information is given on any current masthead page.

Occurrence of Single-Electron Transfer during the Reduction of α -Halo Sulfones with Zinc

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In order to study the frontier between inner sphere (polar) and outer sphere (monoelectronic transfer) mechanisms, the reduction of α -halo sulfones with zinc has been investigated using as starting materials 5endo-[(1'-halo-1'-methylethyl)sulfonyl]-5-exo-cyano-2-norbornenes 1, efficient radical clock precursors. For the bromo as well as for the chloro sulfone, the tricyclic compound characteristic of the rearrangement of a radical intermediate has been detected: the yields are lower in methanol (1-2%) than in hexamethylphosphoramide (3-11%). These reductions could therefore proceed at least partly, via two monoelectronic transfers leading to the intermediate α -sulfonyl carbanion.

When alkyl halides react with nucleophiles, attack on the carbon center with displacement of the halide ion is usually observed. But, if the normal S_N^2 reaction on the carbon is made difficult or if appropriate nucleophiles are selected, nucleophilic substitution at X may take over. This kind of reactions, named substitutions on "positive" halogen¹ or X-philic reactions,² may occur chiefly in the presence of substituents which stabilize the carbanion and if the carbon atom is made less accessible by bulky groups. α -Halo sulfones are well known to undergo nucleophilic

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