The Photochemical Generation of α-Sulfur-Substituted Cyclopropylcarbinyl Radicals and Their Utilization as a Mechanistic Probe for Electron Transfer in the Peroxide–Sulfide Reaction†

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Abstract: The photolytically induced *n*-Bu_3SnH reduction of α-chloro-substituted sulfides **4** and photochemical addition of $BrCCl_3$ to thiones **7** afford α-sulfur-substituted cyclopropylcarbinyl radicals, which rearrange efficiently to afford thioenol ethers as ring-opened products. It is shown that α-sulfur substitution does not significantly influence the propensity for ring opening of these hitherto unknown cyclopropylcarbinyl radical probes. Since in the reaction of cyclopropyl sulfides **1** and benzoyl peroxide, except for sulfoxides **2** (oxygen transfer products), only intact α-benzoyloxy-substituted sulfides **3** (insertion products) are formed, the lack of ring opening is construed as evidence against α-sulfur-substituted cyclopropylcarbinyl radicals in the peroxide–sulfide reaction. Instead of electron transfer between the sulfide and benzoyl peroxide, an S_N2 mechanism is proposed to afford a sulfonium–benzoate ion pair, which serves as a common precursor to the sulfoxide and insertion product (Pummerer rearrangement). The novel photochemical addition of $BrCCl_3$ to thiones **7** constitutes a convenient and efficient synthesis for the previously unknown trichloromethyl-substituted thioenol ethers **8**.

Introduction

The damage of cellular systems caused by active oxygen species, including peroxides, a process known[2] as "oxidative stress", is most effectively combated by glutathione, a tripeptide whose central α-amino acid is cysteine. In this reductive deactivation of peroxides to alcohols the thiol functionality of the cysteine moiety in the glutathione is oxidized to the corresponding disulfide. For this reason, the moderate genotoxic activity of dioxetanes in bacteria and cells[3] was attributed to such efficient deactivation. An electron-transfer-initated process between divalent sulfur compounds and peroxides was postulated[4] (Scheme I).

The reactions between divalent sulfur compounds and diacyl peroxides or peresters were studied for some time.[5-7] As shown in Scheme I, along with the expected sulfoxides (oxygen transfer products), the unusual benzoyloxy sulfides (insertion products) were also observed. Despite considerable efforts, the mechanism of these reactions is until now still the subject of contrary discussion.[6] Either the familiar S_N2 process is invoked, in which the sulfur nucleophile attacks the peroxide bond with displacement of an XO^- fragment, or a radical-mediated process initiated by electron transfer (ET) from the divalent sulfur compound (donor) to the peroxide (acceptor) is postulated. For example, Horner[5] proposed for the reaction of benzoyl peroxide with sulfides an ET mechanism, while Pryor[6] suggested for the reaction of dimethyl sulfide with benzoyl peroxide an S_N2 attack but for *tert*-butyl peroxybenzoate an electron-transfer process. In the latter study the deuterium secondary kinetic isotope effect was employed as a mechanistic probe, in which an inverse one ($k_H/k_D < 1$) was observed for S_N2-type and a normal effect ($k_H/k_D > 1$) for ET-type behavior.

If the insertion product of the reaction of sulfides with peroxides is formed by way of the α-sulfur-substituted methyl radical, which is proposed[4] in Scheme I to arise by deprotonation of the intermediary sulfide radical cation produced in this ET pathway, the cyclopropylcarbinyl mechanistic probe[8] offers an opportunity to detect such transitory radical species. Through the observation of ring-opened rearrangement products at least qualitative mechanistic evidence for such redox processes can be acquired (Scheme II).

It was the purpose of the present investigation to utilize the cyclopropylcarbinyl radical rearrangement as a mechanistic probe in the peroxide–sulfide reaction.

A survey of the literature revealed that no α-sulfur-substituted cyclopropylcarbinyl radicals (Scheme II) appear to have been studied previously.[8,9] Since α-sulfur substitution might stabilize[10] cyclopropylcarbinyl radicals sufficiently so that ring opening is too slow on the time scale that insertion products are formed on (Scheme I), we felt obliged to generate authentic α-sulfur-substituted cyclopropylcarbinyl radicals by alternative routes to assess whether, at least in principle, such species are capable of rearranging. As shown in Scheme III, we pursued two approaches: in path (a) the well-established tributyltin hydride reduction[11] was to be applied to appropriate α-halo-substiuted sulfides and in path (b) the propensity of thiones to scavenge radicals by attachment at the sulfur terminal[12] was to be utilized. The feasibility of the latter approach rests on the fact that vinyl cyclopropanes[13] and

† We dedicate this work to Prof. Dr. Horner, University of Mainz, for his pioneering contributions on the peroxide–sulfide reaction.

(1) Taken from his Diplomarbeit, University of Würzburg, 1989 and presented by him at the 3rd IAPS Meeting, Clearwater Beach, FL, Jan 1–5, 1991.

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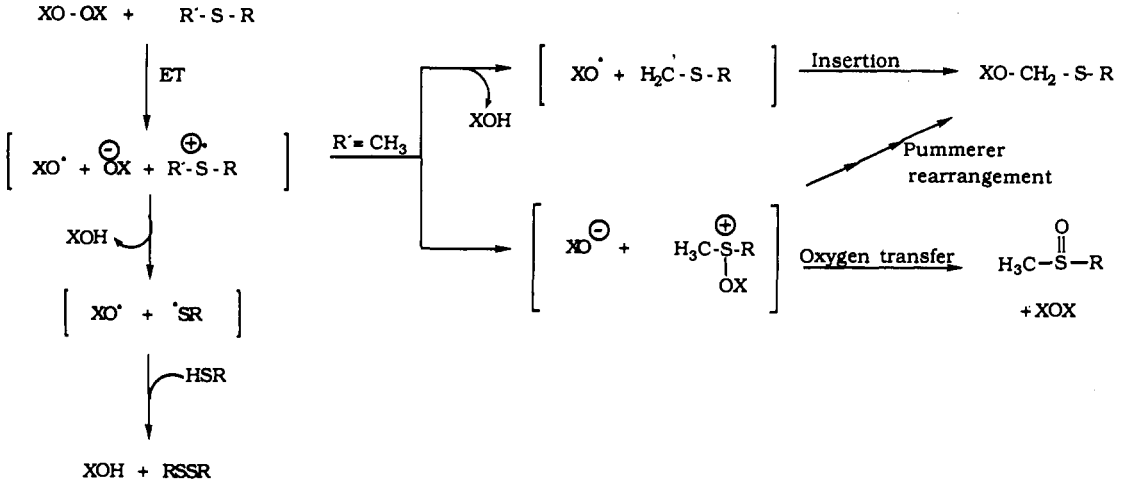
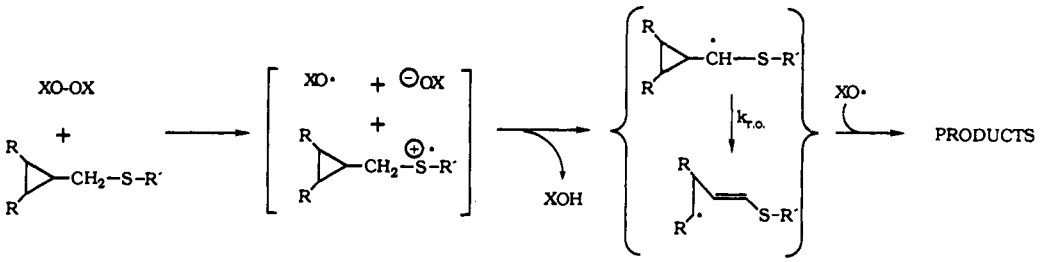
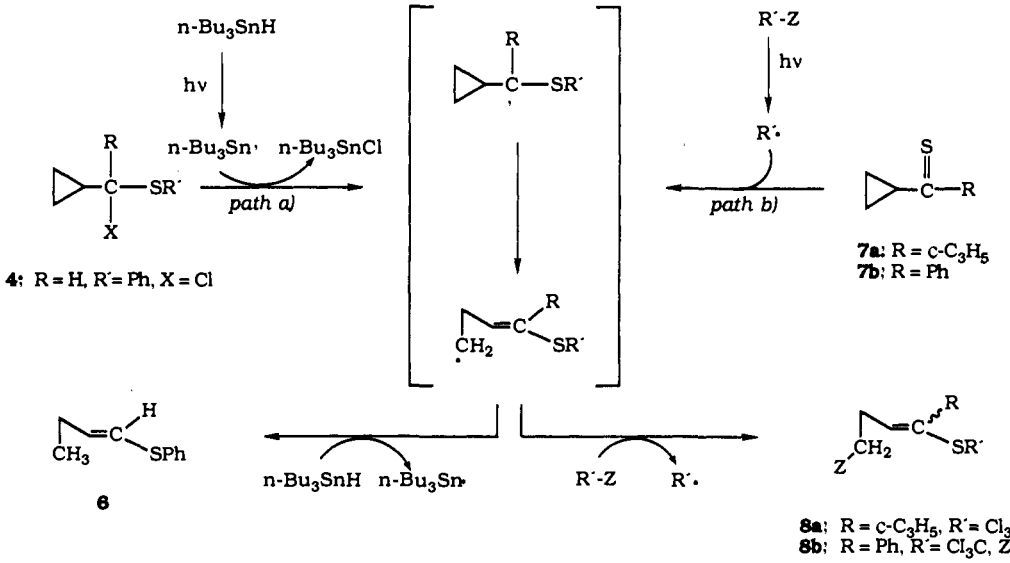
Scheme I



Scheme II



Scheme III



cyclopropyl ketones[14] afford cyclopropylcarbinyl ring-opened products on addition of radicals or one-electron reduction.

In this paper we present the results of our product studies on the reaction of tetramethyl-1,2-dioxetane and of benzoyl peroxide with cyclopropylcarbinyl-substituted sulfides, in which we demonstrate that no cyclopropylcarbinyl ring-opened products were formed, although independently generated, α-sulfur-substituted cyclopropylcarbinyl radicals rearrange efficiently. The mechanistic implications of these findings with respect to the peroxide–sulfide reaction will be discussed.

Results

Reaction of Sulfides 1 with Peroxides. The reaction of ca. two molar excess of tetramethyl-1,2-dioxetane (TMD) with the previously unknown cyclopropylcarbinyl-substituted sulfide **1c** (for preparation cf. Experimental Section) in chloroform at room temperature (ca. 20 °C) gave after about 15 h (ca. 32% consumption of **1c**) exclusively the sulfoxide **2c**, as established by the ^{1}H NMR of the reaction mixture. Not even traces of the expected insertion product (intact or ring-opened) were detected. For the ring-opened insertion product high accumulation (>150 scans) in the olefinic region (5.2–6.7 ppm) was performed, but within the detection limit (ca. 1%) no cyclopropylcarbinyl rearrangement products were found. That TMD was essentially complete consumed was confirmed by the observation of its deoxygenation into[15] tetramethylene oxide and pinacolone and its cleavage into acetone (main product).

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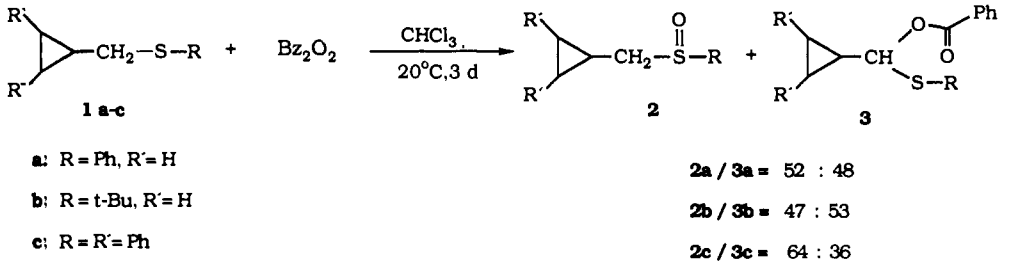
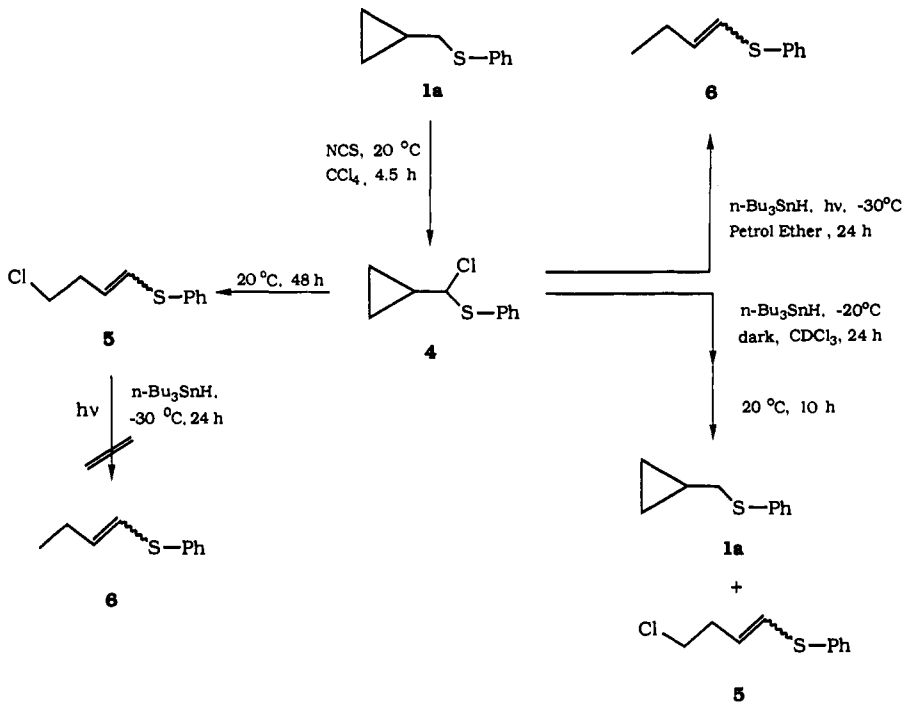
Scheme IV



Scheme V



Treatment of sulfide **1a**[16] with equimolar amounts of benzoyl peroxide at room temperature (ca. 20 °C) until complete consumption (ca. 3 days) of the proxide gave the sulfoxide **2a** and α-insertion product **3a** in nearly equal amounts, as confirmed by ^{1}H NMR of the crude product mixture. Again, not even traces (detection limit ca. 1%) of ring-opened products (Scheme IV) were observed. Similarly, the previously unknown sulfide **1b**, which was prepared analogously to **1a** (cf. Experimental Section), gave also only sulfoxide **2b** and intact insertion product **3b** but no ring-opened products (Scheme IV). In view of the lack of ring-opened products, sulfide **1c** was employed, because it it to date the fastest rearranging cyclopropylcarbinyl system,[17] estimated to ring open faster than diffusion control, i.e., $\geq 2 \times 10^{10}$ s^{-1}.

Again, the reaction of sulfide **1c** with benzoyl peroxide led only to sulfoxide **2c** and intact insertion product **3c**, but no ring-opened products could be detected by ^{1}H NMR spectroscopy (Scheme IV). Insertion product **3a** did not arise from the reaction of benzoic anhydride with sulfoxide **2a** (Pummerer reaction), since in a control experiment, in which **2a** was allowed to react with equimolar amounts of benzoic anhydride in $CDCl_3$, under the sulfide–peroxide reaction conditions (3 days at ca. 20 °C) no insertion product **3a** was observed.

Triarylaminium Radical Ion Oxidation of Sulfide 1a. It was of interest to generate the authentic radical cations of sulfides **1**, in the hope that their deprotonation would afford the desired α-sulfur-substituted cyclopropylcarbinyl radicals (Scheme II) and that ring-opening products would reveal their participation. Proper choice of a sufficiently powerful one-electron oxidant required measuring the oxidation potentials (E_{ox}) of the sulfides **1**. Cyclic voltammetry (cf. Experimental Section for details) gave irreversible E_{ox} values of 1.81 ± 0.02 V for sulfide **1a** and 1.69 ± 0.02 V for **1c** versus the Ag/AgCl electrode in acetonitrile. Thus, tris(2,4-dibromophenyl)aminium radical cation (Magic Green), produced by oxidation of the corresponding triarylamine with antimony pentachloride in CH_2Cl_2,[18] was chosen as oxidant (E_{ox} = 1.74 V versus NHE electrode). When sulfide **1a** was treated with Magic Green in CH_3CN, the sulfide was rapidly consumed, but a complex, intractable reaction mixture resulted, which precluded identification of any ring-opened products. No efforts were made to submit sulfide **1c** to Magic Green oxidation.

Generation of Authentic α-Sulfur-Substituted Cyclopropylcarbinyl Radicals. Photochemically Initiated Tributyltin Hydride Reduction of α-Chloro Sulfide 4. The α-chloro thioether **4** was prepared from sulfide **1a** in 78% yield by *N*-chlorosuccinimide (NCS) chlorination at 20 °C. This chloride was thermally quite labile and rearranged readily at ambient temperature (ca. 20 °C) into its ring-opened isomer **5**. For this reason *n*-Bu_3SnH reduction (0.086 M) was initiated photolytically by irradiating ($\lambda \geq 300$ nm) chloride **4** (0.05 M) at −30 °C for 24 h in petroleum ether, which resulted in the ring-opened thioether **6** as the only product (79% yield), as determined by ^{1}H NMR (Scheme V).

In view of the fact that thioether **4** readily ring opened into the thioenol ether **5**, several control experiments were necessary to establish whether the sequence **4** → **5** → **6** operated. In the dark at −20 °C α-chloro thioether **4** was converted to the extent of 64% (^{1}H NMR monitoring) into **1a** by *n*-Bu_3SnH reduction (Scheme

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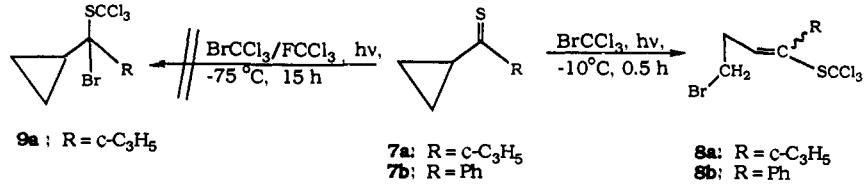
Scheme VI



9a ; R = c-C_3H_5

7a: R = c-C_3H_5
7b; R = Ph

8a: R = c-C_3H_5
8b; R = Ph

V). On warming up to room temperature (ca. 20 °C), the remaining **4** rearranged into the ring-opened **5**. The dechlorinated, ring-opened thioether **6** was not detected by ^{1}H NMR (detection limit ca. 1%). Moreover, under the *n*-Bu_3SnH reduction conditions for **4** → **6**, the chloro-substituted thioenol ether **5** was not dechlorinated to **6** (Scheme V).

Photochemical Addition of Bromotrichloromethane to Thioketone 7a,b. Irradiation (sodium lamp) of a 0.8 M solution of dicyclopropyl thioketone **7a** in $BrCCl_3$ at −10 °C for 30 min resulted in the ring-opened thioenol ether **8a** in 83% (isolated yield) as pure product (Scheme VI). The ^{1}H NMR spectrum of the crude product mixture showed that **8a** was formed as an ca. 60:40 cis/trans ratio of *E,Z* diastereomers. No other products, specifically intact cyclopropylcarbinyl trapping product **9a**, were observed. Even in a low temperature (−75 °C in $FCCl_3$) ^{1}H NMR experiment, on irradiation of **7a** for 15 h in the presence of a two molar excess of $BrCCl_3$, besides **8a** no **9a** was detected. Had **9a** been formed, sufficient amounts should have survived under these conditions for ^{1}H NMR (ca. 1% detection limit) observation. Furthermore, on irradiation (sodium lamp) of a CH_2Cl_2 solution of **7a** in the absence of $BrCCl_3$, no reaction was observed. Thus, although **7a** absorbs in this spectral region, it is photochemically inert and does not ring open. Similar results were observed with thioketone **7b**.

Discussion

Our present qualitative product studies on the ring opening of the authentic α-sulfur-substituted cyclopropylcarbinyl radicals provide compelling mechanistic evidence against the intervention of these transient species in the peroxide–sulfide reaction. It is our task and interest in this section to substantiate the mechanistic implications for this redox process.

With the help of two independent methods, namely the photolytically initiated tin hydride reduction of α-chloro sulfide **4** (Scheme V) and the photochemical addition of bromotrichloromethane to thiones **7** (Scheme VI), we have demonstrated that the intermediary α-sulfur-substituted cyclopropylcarbinyl radicals efficiently rearrange to afford eventually ring-opened products (Scheme III). Although the α-chloro sulfide **4** readily rearranged at room temperature into the ring-opened thioenol ether **5** and tin hydride treatment in the dark at −20 °C afforded the reduced sulfide **1a** (Scheme V), control experiments confirmed that these transformations are heterolytic rather than homolytic in character. If the tin hydride reduction **4** → **1a** + **5** (Scheme V) had taken place by way of cyclopropylcarbinyl radicals, at least detectable quantities of the dechlorinated thioenol ether **6** should have been formed through ring opening. Thus, since α-chloro-substituted thioethers easily ionize to afford carbenium ions[19] and *n*-Bu_3SnH serves as a source of hydride ions,[20] we infer that the tin hydride reduction **4** → **1a** (Scheme V) involves presumably a heterolytic pathway. Some of the intermediary α-sulfur-substituted carbenium ion rearranges to the chloro-substituted thioenol ether **5**, which under the employed conditions is resistant toward *n*-Bu_3SnH reduction, as confirmed by means of a control experiment (Scheme V).

The exclusive formation of the reduced, ring-opened thioenol ether **6** in the photolytically initiated *n*-Bu_3SnH reaction of α-chloro sulfide **4** even at −30 °C (Scheme V) permits estimating only a limiting value for the rate constant of ring opening (k_{ro}) of the α-sulfur-substituted cyclopropylcarbinyl radical (Scheme II). Taking the ^{1}H NMR detection limit of less than 1% for the thioether **1a** in the tin hydride reduction of the α-chloro sulfide **4** (Scheme V), the ratio of ring opened to intact products should be **6**:**1a** ≥ 100. At the employed *n*-Bu_3SnH concentration of ca. 0.1 M and assuming a value for the rate constant of hydrogen atom abstraction from the tin hydride $k_H \sim 10^6$ M^{-1} s^{-1} at 25 °C,[21] we estimate that $k_{ro} \geq 10^7$ s^{-1} for the α-sulfur-substituted cyclopropylcarbinyl radical. Since the rate constant k_{ro} for the parent cyclopropylcarbinyl radical (secondary to primary radical rearrangement) is of this order of magnitude,[11b] we conclude that α-sulfur substitution has no profound effect on the ring-opening propensity and such α-sulfur-substituted cyclopropylcarbinyl radicals should serve as effective mechanistic probes in radical and redox processes involving sulfur substrates.

Similar conclusions concerning ring opening of α-sulfur-substituted cyclopropylcarbinyl radicals pertain to the novel photochemical addition of $BrCCl_3$ to thiones **7a,b**, which afforded the hitherto unknown thioenol ethers **8a,b** (Scheme VI). As for the analogous vinylcyclopropane case,[13a] a radical chain mechanism (Scheme III) must operate, which leads exclusively to ring-opened products even at low temperatures. Since bromine atom abstraction from $BrCCl_3$ by cyclopropylcarbinyl radicals is almost three orders of magnitude ($k_{Br} = 6.9 \times 10^8$ M^{-1} s^{-1} at 25 °C)[22] faster than hydrogen atom abstraction from *n*-Bu_3SnH ($k_H = 1.1 \times 10^6$ M^{-1} s^{-1} at 25 °C),[21a] it is astonishing that no ring-intact products were observed in the transformation **7** → **8** (Scheme VI). However, this is analogous to the photochemical addition of $BrCCl_3$ to vinylcyclopropane[13a] and implicates that α-sulfur substitution does not influence appreciably the rate of cyclopropylcarbinyl radical ring opening. Of course, the possibility obtains that the intact α-bromo thioether **9a** was indeed formed (Scheme VI) but rearranged through a heterolytic process analogous to the transformation **4** → **5** (Scheme V) to give the ring-opened thioenol ether **8a**. This appears unlikely, because in the control experiment at −78 °C (Scheme VI) some **9a** should have survived for ^{1}H NMR detection at this temperature. It is our contention that of the two photochemical pathways of generating α-sulfur-substituted cyclopropylcarbinyl radicals, namely photolytically initiated tin hydride reduction of α-chloro thioethers (Scheme V) and photochemical addition of $BrCCl_3$ to thiones (Scheme VI), the former is the more reliable. Nevertheless, the photochemical addition of $BrCCl_3$ to thiones **7** constitutes a convenient preparation of the novel thioenol ethers **8**.

We now address the pertinent mechanistic question whether α-sulfur-substituted cyclopropylcarbinyl radicals intervene in the peroxide–sulfide reaction to afford insertion products (Scheme I). Since no ring-opened products are observed in the reaction of benzoyl peroxide with cyclopropyl sulfides **1** (Scheme IV), but α-sulfur-substituted cyclopropylcarbinyl radicals efficiently afford ring-opened products (Schemes V and VI), such species are not viable intermediates in the formation of the insertion products **3** (Scheme IV). At least for the fastest cyclopropylcarbinyl "free-radical clock", namely the *cis*-2,3-diphenylcyclopropylcarbinyl system, which rearranges faster than diffusion control ($k_{ro} \geq 2 \times 10^{10}$ s^{-1}),[17] some ring-opened insertion products should have been detected in the reaction of **1c** with benzoyl peroxide. Assuming a micromolar steady-state concentration of benzoyloxy

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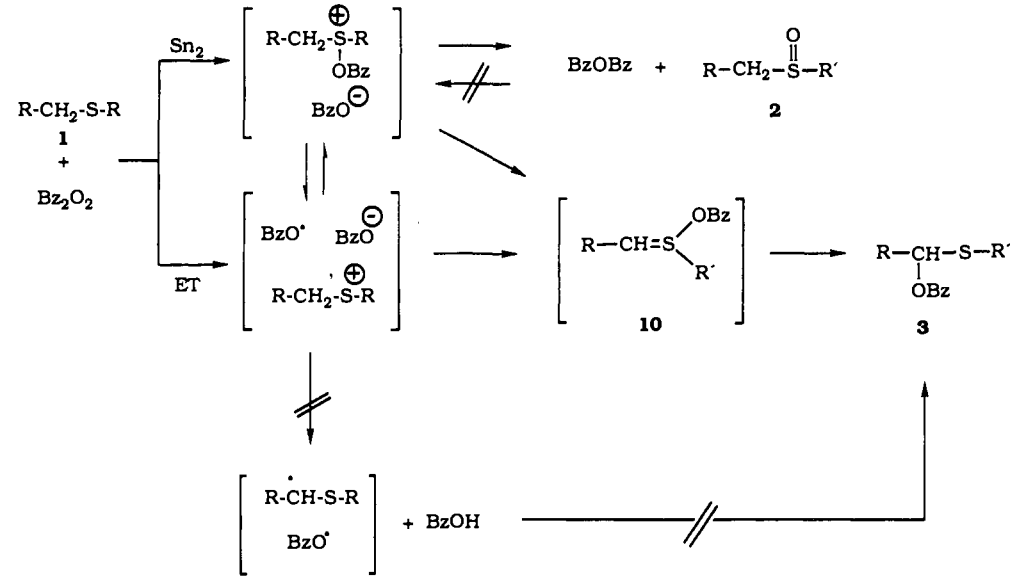
Scheme VII



radicals (X = PhCO in Scheme I) and diffusion-controlled radical combination,[23] the ring-opening rate of the α-sulfur-substituted cyclopropylcarbinyl radical derived from the reaction of sulfide **1c** with benzoyl peroxide should be at least three orders of magnitude slower than that estimated for the *cis*-2,3-diphenylcyclopropylcarbinyl radical ($k_{ro} \geq 2 \times 10^{10}$ s^{-1}).[17] This is not consistent with our experimental evidence (Schemes V and VI) that α-sulfur substitution does not significantly influence the propensity of the cyclopropylcarbinyl ring opening.

A mechanism is required for the formation of insertion product in the benzoyl peroxide–sulfide reaction which does not involve α-sulfur-substituted alkyl radical, cf. Scheme VII. As previously proposed,[6] in this mechanism either S_N2 displacement by the sulfide nucleophile on the peroxide yields the sulfonium–benzoate ion pair of electron transfer (ET) yields the radical pair. These interconverting species may both generate the sulfurane **10**, which by Pummerer rearrangement[24] would lead to the insertion product **3**. Alternatively, the sulfonium–benzoate ion pair may afford the sulfoxide **2** and benzoic anhydride; however, under the present reaction conditions the sulfoxide **2** and benzoic anhydride (the usual Pummerer reaction) do not give the insertion product **3**, as confirmed by means of a control experiment (Scheme VII). Whatever the fate of the interconverting ion and radical pairs, our experimental results establish that α-thioalkyl radicals are not involved, because cyclopropylcarbinyl radical ring-opened products should have been observed.

As to the S_N2 versus ET alternatives (Scheme VII), our present results do not permit an experimental differentiation. Although Oae[25] provided evidence that the enzymatic dealkylation of sulfides by cytochrome P-450 involves electron transfer that leads to sulfur-centered radical cations, for the benzoyl peroxide–sulfide reaction Pryor[6] favors, on the basis of kinetic isotope effects, the S_N2 mechanism. Since the oxidation potentials of aryl sulfides are about by 1 V higher than for the corresponding amines,[26] for which an ET mechanism has been proposed in their reaction with benzoyl peroxides to give insertion products,[6,27] on the basis of the Marcus theory[26] direct formation of the radical pair in Scheme VII by electron transfer is less likely. Besides, recently Steckhan[28] has shown that in the triarylamine-catalyzed anodic oxidation of sulfides the intermediary sulfur-centered radial cations fragment into carbenium ions and thiyl radicals, as evidenced by the formation of nucleophilic trapping products from the former and disulfides of the latter. Such products are not observed in the benzoyl peroxide–sulfide reaction, which also renders the ET mechanism in Scheme VII unlikely.

On the basis of the cyclopropylcarbinyl radical probe employed in our present mechanistic study we conclude that the formation of insertion products in the peroxide–sulfide reaction is not necessarily indicative of redox or electron-transfer chemistry. Since in the reaction of tetramethyl-1,2-dioxetane (TMD) with the cyclopropyl sulfides **1** not even traces of insertion products **3** are formed, such mechanistic scrutiny is rendered difficult. Nevertheless, had insertion products been formed with TMD, like those for benzoyl peroxide, ring-opened derivatives through cyclopropylcarbinyl radical rearrangement would appear improbable. The fact that the major product derived from TMD in its reaction with sulfide **1c** is acetone, which constituted the cleavage product of this dioxetane, but at temperatures (ca. 20 °C) much below its thermolysis (ca. 70 °C),[29] suggests that electron-rich partners induce electron exchange-catalyzed decomposition of dioxetanes.[3b] Such reaction channels seem to reflect more reliably the electron-transfer chemistry of dioxetanes and should be worthwhile for mechanistic pursuit.

Experimental Section

General Aspects. Boiling and melting points are uncorrected; the latter were taken on a Reichert Thermovar Kofler apparatus.

^{1}H and ^{13}C NMR spectra were run on either a Bruker AC 200 or AC 250 spectrometer at the appropriate frequencies. IR spectra were measured on a Perkin-Elmer 1420 spectrophotometer and mass spectra (MS) on a Varian MAT CH7. Combustion analyses for elemental composition were obtained either in-house or from Prof. Maier's staff of the Institute of Organic Chemistry (Giessen). For column chromatography silica gel (60–230 mesh) from Woelm or silylated silica gel from Merck were used. Kugelrohr distillations were carried out on a Büchi GKR-50 apparatus. Photochemical experiments were conducted either in Pyrex vessels by using a mercury arc (Hanau Td 150 lamp) or in Pyrex test tubes when irradiating with a 150-W Philips G 128/2 sodium lamp. Cyclic voltammetry was performed on a Princeton Applied Research PAR 170 instrument in acetonitrile and $LiClO_4$ (electrolyte) at 20 °C against a Ag/AgCl reference electrode.

Commercial reagents and solvents were purchased from standard chemical suppliers and purified to match the reported physical data.

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Known compounds were prepared according to literature procedures. Commercial benzoyl peroxide was recrystallized from $CHCl_3/CH_3OH$.

***tert*-Butyl Cyclopropylmethyl Sulfide (1b).** Sulfide **1b** was prepared analogously to sulfide **1a**[16] by stirring equimolar amounts of cyclopropylmethyl tosylate and sodium *tert*-butylthiolate in ethanol for 15 h at 20 °C to yield 79% of sulfide **1b**, bp 59–60 °C at 15 Torr: IR (neat, cm^{-1}) ν 3090, 2980, 1460, 1360, 1240, 1160, 1040, 1020, 965; ^1H NMR (200 MHz, $CDCl_3$) δ 0.35 (m, 4 H, CH_2CH_2), 0.92 (m, 1 H, CH), 1.32 (s, 9 H, *t*-Bu), 2.47 (d, J = 7.1 Hz, 2 H, CH_2S); ^{13}C NMR (50 MHz, $CDCl_3$) δ 5.6 (t, CH_2), 10.8 (d, CH), 30.9 (q, *t*-Bu), 33.9 (t, CH_2S), 41.5 (s); MS (70 eV) m/z (%) = 144 (21) [M^+], 88 (18), 60 (14), 57 (100) [*t*-Bu], 55 (40), 41 (33).

***trans*-2,3-Diphenylcyclopropylmethyl Phenyl Sulfide (1c).** To thiophenol (0.421 g, 3.83 mmol), dissolved in 5 mL of dry DMF, was added a solution of 0.900 g (3.85 mmol) of sodium in 5 mL of ethanol, and the excess ethanol was evaporated at 20 °C and 15 Torr. After addition of 1.10 g (3.83 mmol) of *trans*-2,3-diphenylcyclopropylmethyl bromide[17] in 5 mL of DMF, the solution was heated to 90–100 °C for 1 h. The reaction mixture was allowed to cool to room temperature, 25 mL of water were added with rapid stirring, and the precipitate was collected. The crude thioether was purified by column chromatography (silica gel, CH_2Cl_2 as eluent), and recrystallization from petroleum ether (bp 50–60 °C) afforded 0.920 g (76%) of pure sulfide **1c** as white needles, mp 76–77 °C: IR (KBr, cm^{-1}) 3020, 1990, 1580, 1570, 1480, 1460, 1410, 1270, 1230, 1180; ^1H NMR (200 MHz, $CDCl_3$) δ 1.95–2.10 (m, 1 H, CH), 2.40 (d, J = 5.6 Hz, 2 H, CHPh), 3.22 (d, J = 6.7 Hz, 2 H, CH_2S), 6.83–7.45 (m, 15 H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.5 (d), 32.3 (d), 38.8 (t, CH_2S), 125.8 (d), 126.2 (d), 127.7 (d), 128.9 (d), 128.9 (d), 129.7 (d), 136.5 (s), 137.4 (s); MS (70 eV) m/z (%) = 316 (35) [M^+], 199 (50), 193 (100) [$M^+ - PhSCH_2$], 178 (15), 129 (39), 115 (66), 91 (36), 77 (13). Anal. Calcd for $C_{22}H_{20}S$: C, 83.49; H, 6.37. Found: C, 83.78; H, 6.20.

Chlorocyclopropylmethyl Phenyl Sulfide (4). *N*-Chlorosuccinimide (0.814 g, 6.10 mmol) was added to a solution of 1.00 g (6.10 mmol) of sulfide **1a** in 20 mL of dry CCl_4. After 4.5 h of stirring at room temperature **1a** was completely consumed (^1H NMR monitoring). The solution was filtered, and the solvent was evaporated at ca. 20 °C and 15 Torr to afford 0.950 g (78%) of a colorless oil, which in view of its thermal instability was stored at −78 °C without further purification: ^1H NMR (200 MHz, $CDCl_3$) δ 0.58 and 0.76 (m, 4 H, CH_2CH_2), 1.43 (m, 1 H, CH), 4.72 (d, J = 8.8 Hz, 1 H, CHCl), 7.28–7.57 (m, 5 H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$) δ 6.7 (t), 7.4 (t), 19.5 (d), 74.8 (d), 128.3 (d), 128.9 (d), 129.1 (s), 133.0 (d).

4-Chloro-1-(phenylthio)but-1-ene (5). On standing at room temperature for 48 h α-chloro sulfide **4** (1.00, 5.04 mmol) rearranged completely into its ring-opened isomer **5**, as was established by ^1H NMR spectroscopy of the crude material. The thioenol ether **5** was purified by Kugelrohr distillation to yield 450 mg (45%) of a colorless oil, which consisted of a 53:47 mixture of E/Z isomers: IR (neat, cm^{-1}) 3090, 3000, 2960, 1580, 1435, 1290, 1240, 1070, 1030, 1020; ^{13}C NMR (63 MHz, $CDCl_3$) δ 32.2 (t), 36.0 (t), 43.5 (t, 2c), 125.5 (d), 126.5 (d), 126.6 (d), 126.7 (d), 127.1 (s), 127.5 (s), 127.9 (d), 120.0 (d), 129.1 (d), 130.3 (d), 135.4 (s), 135.6 (s); ^1H NMR of (*E*)-**5** (250 MHz, $CDCl_3$) δ 2.58 (dt, J = 7.0, 7.0 Hz, 2 H, CH_2—CH=), 3.54 (t, J = 7.0 Hz, 2 H, CH_2Cl), 5.87 (td, J = 15.0, 7.0 Hz, 1 H, CH_2CH=), 6.27 (d, J = 15.0 Hz, 1 H, =CH—S), 7.25 (m, 5 H, Ph); ^1H NMR of (*Z*)-**5** (250 MHz, $CDCl_3$) δ 2.71 (dt, J = 6.9, 6.9 Hz, 2 H, CH_2—CH=), 3.59 (t, J = 6.9 Hz, 2 H, CH_2Cl), 5.83 (td, J = 9.4, 6.9 Hz, 1 H, CH_2CH=), 6.36 (td, J = 9.4, 1.3 Hz, 1 H, =CH—S), 7.25 (m, 5 H, Ph); MS (70 eV) m/z (%) = 198 (53) [M^+], 149 (100), 134 (21), 123 (29), 116 (50), 109 (27), 77 (18). Anal. Calcd for $C_{10}H_{11}ClS$: C, 60.44; H, 5.58. Found: C, 60.50; H, 5.33.

Reaction of Sulfide 1c with Tetramethyldioxetane (TMD). Tetramethyl-1,2-dioxetane[29] (25.3 mg, 0.218 mmol) and sulfide **1c** (44.4 mg, 0.140 mmol) were dissolved in 0.5 mL of $CDCl_3$ at 20 °C. After 15 h the TMD was completely consumed (^1H NMR monitoring) to yield acetone, tetramethylene oxide, and pinacolone, as confirmed by comparison of the ^1H NMR spectra with those of the authentic compounds. Under these conditions sulfide **1c** was converted in ca. 32% yield exclusively into sulfoxide **2c**. The olefinic region (5.2–6.7 ppm) was examined for ring-opened products under high signal accumulation (150 scans), but none were found (detection limit <1%).

General Procedure for the Reaction of Sulfides 1a–c with Benzoyl Peroxide. The reactions were performed according to Horner's procedure[4] by stirring 0.2–0.3 M solutions of equimolar amounts of benzoyl peroxide and sulfides **1a–c** in dry chloroform for 3 days. Conversion of the sulfides and the product distributions were estimated by quantitative ^1H NMR spectroscopy directly on the crude product mixture. The only sulfide-derived products (detection limit <1%) were the sulfoxides **2a–c** (oxygen transfer products) and the benzoyloxy sulfides **3a–c** (insertion products). The solvent was removed at 20 °C and 15 Torr, and the residue was refluxed with 30 mL of 2 N NaOH for 15 min to hydrolize the benzoic anhydride. The separated oil was washed with 15 mL of 2 N NaOH, taken up in ether (20 mL), washed with water (2 × 10 mL), and dried over sodium sulfate. After evaporation of the solvent at 20 °C and 15 Torr, the mixture of products **2** and **3** was separated either by Kugelrohr distillation or by column chromatography. The individual experiments are described below.

Oxidation of Sulfide 1a. Sulfoxide **2a** and sulfide **3a** were obtained in a 52:48 ratio from 2.00 g (9.15 mmol) of sulfide **1a** and 2.95 g (9.15 mmol) of benzoyl peroxide. They were separated by Kugelrohr distillation to yield 659 mg (40%) of **2a** as a colorless oil (bp 130–140 °C at 0.1 Torr), which solidified upon cooling, mp 29–31 °C (lit.[16] 32–33 °C), and 909 mg (35%) of **3a** as a colorless oil (bp 170–175 °C at 0.1 Torr).

Sulfoxide 2a: IR (CCl_4, cm^{-1}) 3100, 3040, 2920, 1485, 1450, 1410, 1310, 1240, 1180, 1110, 1060 (S=O); ^1H NMR (250 MHz, $CDCl_3$) δ 0.30 and 0.60 (m, 4 H, CH_2CH_2); 0.37 (m, 1 H, CH), 2.69 (dd, J = 13.2, 7.5 Hz, 1 H, CHSO), 2.87 (dd, J = 13.2, 7.1 Hz, 1 H, CHSO), 7.72 (m, 5 H, aromatic H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 4.7 (d, CH), 4.8 and 5.1 (t, CH_2CH_2), 63.1 (t, CH_2SO), 124.3 (d), 129.1 (d), 131.1 (d), 143.6 (s).

Sulfide 3a: IR (neat, cm^{-1}) 3080, 3010, 1720 (C=O), 1600, 1470, 1450, 1435, 1310, 1250, 1180; ^1H NMR (200 MHz, $CDCl_3$) δ 0.53–0.73 (m, 4 H, $-CH_2CH_2-$), 1.28–1.38 (m, 1 H, CH), 5.85 (d, J = 8.4 Hz, 1 H, −OCHS−), 7.25–7.30 (m, 3 H, aromatic H), 7.40–7.60 (m, 5 H, aromatic H), 8.01–8.06 (m, 2 H, aromatic H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 4.1 (t), 5.4 (t), 15.7 (d), 94.1 (d, −OCHS−), 128.2 (d), 128.3 (d), 128.8 (d), 129.6 (s), 129.8 (d), 131.7 (s), 133.1 (d), 134.1 (d), 165.2 (s, C=O); MS (70 eV) m/z (%) = 284 (<1) [M^+], 175 (5), 126 (14), 109 (8), 105 (100) [PhCO], 77 (33), 55 (51). Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.83; H, 5.63. Found: C, 71.71; H, 5.53.

Oxidation of Sulfide 1b. Sulfoxide **2b** and sulfide **3b** were obtained in a 47:53 ratio from 2.00 g (14.0 mmol) of sulfide **1b** and 3.36 g (14.0 mmol) of benzoyl peroxide. Separation by Kugelrohr distillation afforded, at 90 °C and 0.1 Torr, 351 mg (16%) of sulfoxide **2b**, which on recrystallization from petroleum ether (bp 50–60 °C) was obtained as white needles, mp 62–63 °C, and 1.31 g (35%) of sulfide **3b** at 130 °C and 0.1 Torr, mp 65–66 °C, after recrystallization from petroleum ether (bp 50–60 °C).

Sulfoxide 2b: IR (KBr, cm^{-1}) 3090, 3040, 3020, 2980, 2930, 2870, 1465, 1390, 1290, 1035 (S=O); ^1H NMR (250 MHz, $CDCl_3$) δ 0.29–0.74 (m, 5 H, cyclopropyl-H), 1.23 (s, 9 H, *t*-Bu), 2.21 (dd, J = 13.0, 16.0 Hz, 1 H, CHSO), 2.58 (dd, J = 13.0, 16.0 Hz, 1 H, CHSO); ^{13}C NMR (63 MHz, $CDCl_3$) δ 5.1 (t), 5.7 (t), 5.9 (d), 22.9 (q), 51.7 (t), 52.6 (s); MS (70 ev) m/z (%) = 160 (4) [M^+], 57 (100), 55 (67), 41 (35), 39 (14), 29 (38). Anal. Calcd for $C_8H_{16}SO$: C, 59.94; H, 10.10. Found C, 59.85; H, 10.44.

Sulfide 3b: IR (KBr, cm^{-1}) 3120, 3080, 2980, 1765 (C=O), 1650, 1630, 1540, 1500, 1420, 1370; ^1H NMR (250 MHz, $CDCl_3$) δ 0.46–0.66 (m, 4 H, $-CH_2CH_2-$), 1.33 (s, 9 H, *t*-Bu), 1.35 (m, 1 H, CH), 6.05 (d, J = 7.8 Hz, 1 H, −OCHS−), 7.47 (m, 2 H, aromatic H), 7.55–8.08 (m, 3 H, aromatic H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 4.1 (t), 4.8 (t), 16.8 (d), 31.4 (q), 43.8 (s), 81.2 (d, OCHS), 128.4 (d), 129.8 (d), 133.1 (d), 130.2 (s), 165.9 (s, C=O); MS (70 eV) m/z (%) = 264 (<1) [M^+], 175 (10), 105 (100), 85 (5), 77 (22), 57 (13), 51 (5), 41 (9). Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.20; H, 7.57. Found: C, 68.54; H, 7.64.

Oxidation of Sulfide 1c. Sulfoxide **2c** and sulfide **3c** were obtained in a 64:36 ratio from 624 mg (2.03 mmol) of **1c** and 491 mg (2.03 mmol) of benzoyl peroxide. Separation on a silica gel column by eluting first with CH_2Cl_2, followed by a 1:1 CH_2Cl_2/ether mixture, resulted in 235 mg (27%) of sulfoxide **2c** (first fraction) as white needles, mp 100–101 °C, after recrystallization from petroleum ether (bp 50–60 °C). A second fraction was obtained, 312 mg (46%) of sulfoxide **2c**, white needles, mp 146–147 °C, after recrystallization from ethanol.

Sulfoxide 2c: IR (CCl_4, cm^{-1}) 3080, 3040, 2980, 1600, 1500, 1450, 1260, 1205, 1100, 1060 (S=O); ^1H NMR (250 MHz, $CDCl_3$) δ 2.05 (m, 1 H, CH), 2.34 (dd, J = 9.8, 4.7 Hz, 1 H, CHPh), 2.43 (dd, J = 9.8, 7.0 Hz, 1 H, CHPh), 3.10 (dd, J = 13.4, 5.7 Hz, 1 H, CHSO), 3.17 (dd, J = 13.4, 4.7 Hz, 1 H, CHSO), 6.78–7.13 and 7.40–7.67 (m, 15 H, aromatic H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.6 (d), 31.6 (d), 31.8 (d), 62.2 (t, CH_2SO), 124.2 (d), 126.0 (d), 126.2 (d), 127.7 (d), 127.9 (d), 128.6 (d), 129.2 (d), 129.2 (d), 131.1 (d), 136.4 (s), 136.7 (s), 143.6 (s); MS (70 eV) m/z (%) = 332 (<1) [M^+], 207 (4), 193 (9), 178 (6), 129 (26), 115 (16), 91 (100), 77 (10). Anal. Calcd for $C_{22}H_{20}SO$: C, 79.45; H, 6.06. Found: C, 79.12; H, 6.07.

Sulfide 3c: IR (CCl_4, cm^{-1}) 3060, 2960, 1720 (C=O), 1600, 1500, 1450, 1250, 1200, 1070, 1020; ^1H NMR (250 MHz, $CDCl_3$) δ 2.32 (m, 1 H, CH), 2.65 (dd, J = 9.8, 6.9 Hz, 1 H, CHPh), 2.79 (dd, J = 9.8, 4.8 Hz, 1 H, CHPh), 6.30 (d, J = 7.9 Hz, 1 H, OCHS), 6.84, 7.06, 7.25, 8.08 (m, 20 H, aromatic H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 29.5 (d),

30.1 (d), 31.7 (d), 83.2 (d, OCHS), 126.1 (d), 127.8 (d), 128.5 (d), 128.8 (d), 128.9 (d), 129.0 (d), 129.8 (d), 133.3 (d), 134.4 (d), 129.8 (s), 131.0 (s), 136.3 (s), 136.6 (s), 172.5 (s, C=O); MS (70 eV) m/z (%) = 327 (2, M^+ - PhS), 314 (2, M^+ - $PhCO_2$), 251 (2), 225 (19), 193 (6), 115 (25), 105 (100), 77 (23).

Irradiation of α-Chloro Sulfide 4 in the Presence of Tributyltin Hydride. A solution of 2.50 g (8.59 mmol) of n-Bu_3SnH in 50 mL of petroleum ether (bp 30-50 °C) was cooled to -30 °C while passing a stream of dry nitrogen gas. After addition of 0.960 g (4.84 mmol) of α-chloro sulfide **4**, the solution was irradiated for 24 h at λ ≥ 300 nm. The solvent was evaporated, and the residue was purified by double column chromatography on silica gel by eluting with a 1:4 CH_2Cl_2/petroleum ether (bp 30-50 °C) solvent mixture to yield 320 mg (79%) of (*E*,*Z*)-1-butenyl phenyl sulfide (**6**). The ^1H and ^{13}C NMR spectral data were consistent with those reported.[30]

Photoinitiated Addition of Bromotrichloromethane to Cyclopropylmethane Thiones 7a,b. Thione 7a. A solution of 204 mg (1.60 mmol) of dicyclopropylmethane thione[31] in 2 mL (20.3 mmol) of bromotrichloromethane was irradiated for 30 min at -10 °C with a 150-W sodium lamp, which resulted in complete decoloration of the thione **7a**. The ^1H NMR spectra of the crude product mixture showed complete consumption of the thione **7a** and consisted exclusively of 4-bromo-1-cyclopropyl-1-((trichloromethyl)thio)-but-1-ene (**8a**) as a 60:40 ratio of *E*,*Z* isomers. On purification by column chromatography on silylated silica gel by eluting with a 1:1 CH_2Cl_2/petroleum ether (bp 50-60 °C) solvent mixture 323 mg (83%) of the *E*,*Z* isomers as colorless oil was obtained. IR (neat, cm^{-1}) 3090, 3010, 2960, 1440, 1260, 1205, 960, 750, 710; ^1H NMR of (*Z*)-**8** (250 MHz, $CDCl_3$) δ 0.75 and 0.91 (m, 4 H, cyclopropyl-CH_2), 1.79 (m, 1 H, CH), 2.99 (td, J = 6.8, 6.8 Hz, 2 H, =CH—CH_2), 3.40 (t, J = 6.8 Hz, 2 H, CH_2Br), 6.48 (td, J = 7.1, 1.5 Hz, 1 H, =CH—); ^1H NMR of (*E*)-**8** (250 MHz, $CDCl_3$) δ 0.75 and 0.91 (m, 4 H, cyclopropyl-CH_2), 1.96 (m, 1 H, CH), 2.99 (td, J = 6.8, 6.8 Hz, 2 H, =CH—CH_2), 3.51 (t, J = 6.8 Hz, 2 H, CH_2Br). 6.15 (td, J = 7.1, 1.2 Hz, 1 H, =CH—); ^{13}C NMR (63 MHz, $CDCl_3$), δ 8.0 (t), 8.7 (t), 13.6 (d), 19.1 (d), 30.5 (t), 31.5 (t), 32.7 (t), 33.2 (t), 98.7 (s, CCl_3), 137.4 (s), 138.2 (s), 137.8 (d), 145.9 (d); MS (70 eV) m/z (%) = 324 (6) [M^+], 298 (3) [M^+ - Cl], 243 (2) [M^+ - Br], 205 (32) [M^+ - CCl_3], 125 (31), 93 (21), 85 (68), 77 (66), 65 (43), 39 (100). Anal. Calcd for $C_8H_{10}BrCl_3S$: C, 29.61; H, 3.11. Found: C, 29.62; H, 3.19.

Thione 7b. Following the above procedure, a solution of 19.9 mg (0.123 mmol) of thione **7b** in 0.5 mL (5.04 mmol) of bromotrichloromethane was irradiated at -10 °C for 40 min. The excess $BrCCl_3$ was removed by evaporation in 20 °C and 19 Torr, and the residue was taken up in $CDCl_3$ and analyzed by ^1H NMR spectroscopy. Thione **7b** was converted exclusively into the thioenol ether **8b**: ^1H NMR (250 MHz, $CDCl_3$) δ 3.22 (dt, J = 7.0, 7.0 Hz, 2 H, =CH—CH_2), 3.50 (t, J = 7.0 Hz, 2 H, CH_2Br), 6.63 (t, J = 7.0 Hz, 1 H, =CH), 7.39 (m, 5 H, aromatic H).

Control Experiments. Reaction of Benzoic Anhydride with Sulfoxide 2a. A mixture of 20.0 mg (0.111 mmol) of sulfide **2a** and 25.0 mg (0.111 mmol) of benzoic anhydride in 0.5 mL of $CDCl_3$ was allowed to stand at ca. 20 °C for 3 days. No reaction was detected by ^1H NMR spectroscopy.

Irradiation of Thione 7a in the Absence of Bromotrichloromethane. In a control experiment, a 0.5 M solution of thione **7a** was irradiated in CH_2Cl_2 at -10 °C for 1 h. Under these conditions thione **7a** was stable, as confirmed by ^1H NMR monitoring.

Attempts of Detecting α-Bromo Sulfide 9. In a control experiment a solution of thione **7a** (ca. 0.3 M) and $BrCCl_3$ (ca. 0.6 M) in $FCCl_3$ was irradiated at -75 °C for 15 h and examined by low-temperature (-70 °C) ^1H NMR spectroscopy. Only the ring-opened product, namely thioenol ether **8a** was observed.

Oxidation Potentials of Sulfides 1a,c. Cyclic voltammetry curves for sulfides **1a** and **1c** were obtained at a platinum electrode by employing a 500 mV/s sweep rate against a Ag/AgCl reference electrode at 20 °C. The sulfide concentrations were ca. 7.5 M in 0.10 M $LiClO_4$ solution of acetonitrile. Both sulfides showed irreversible oxidation reactions at 1.81 ± 0.02 V for **1a** and 1.69 ± 0.02 for **1b**.

Oxidation of Sulfide 1a by Tris(2,4-dibromophenyl)ammoniumyl Hexachloroantimonate (Magic Green). To a solution of 0.328 g (2.00 mmol) of sulfide **1a** in 10 mL of CH_3CN was added dropwise a solution of 2.11 g (2.00 mmol) of Magic Green[19] in 15 mL of CH_3CN. The green color of the radical cation disappeared at once. After addition of 20 mL of water, the solution was extracted with ether (3 × 20 mL), and the ethereal phase washed with 20 mL of 10% $NaHSO_3$ solution. Drying over Na_2SO_4 and evaporation of the solvent at 20 °C and 18 Torr yielded a dark oil. ^1H NMR and TLC revealed that, besides tris(2,4-dibromophenyl)amine, a complex, intractable mixture of sulfide-derived products were formed. No efforts were made to characterize these products.

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Substituent Effects on the Stabilities of Phenoxyl Radicals and the Acidities of Phenoxyl Radical Cations

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Abstract: Oxidation potentials for 35 phenoxide ions and 3 naphthoxide ions have been combined with their pK_{HA} values to estimate homolytic bond dissociation energies (BDEs) for the O-H bonds in phenols. Comparison with literature values shows that there is remarkably good agreement between ΔBDE values determined by different methods. A plot of oxidation potentials for *m*-phenoxides vs pK_{HA} values was found to be linear over a range of 18 kcal/mol, pointing to the presence of an inherent group electronegativity factor, related to basicity, that strengthens the O-H bond in phenols. Deviations of points for para substituents from this line have provided a measure of their radical-stabilizing ability that is devoid of such inherent bond-strengthening effects. A good correlation of $E_{ox}(A^-)$ values for p-$GC_6H_4O^-$ phenoxide ions with σ^+ constants was observed over a range of greater than 40 kcal/mol. The acidities of 35 phenoxyl radical cations have been estimated from pK_{HA}, $E_{ox}(A^-)$, and $E_{ox}(HA)$ values. A good correlation of $E_{ox}(HA)$ vs $pK_{HA}^{\bullet+}$ was observed for m-$GC_6H_4OH^{\bullet+}$ radical cations, but the points for para donors were found to deviate from the line.

Proximate substituent effects on radicals vary with the nature of the radical. The radical-stabilizing energies (RSEs) of methyl radicals, $GCH_2^\bullet$, where G is an α-donor substituent as judged by the homolytic bond dissociation energies (BDEs) of GCH_2-H relative to that of CH_3-H (105 kcal/mol), increase in the following order: F (5) < Me (7) MeO (12) < Ph (17) < Me_2N (21).[1a] (The numbers in parentheses are in kilocalories per mole, hereafter

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