CAN- and DDQ-Promoted Oxidation of Alkenyl Sulfides

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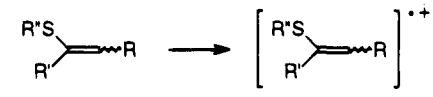
Vinyl sulfides **1** react with CAN in acetonitrile at room temperature to give radical cations **2A** in equilibrium with the thiiranyl radical cations **2B**. The reaction products arise from nucleophilic attack of the nitrate counterion at either the sulfur atom of **2A** or the trivalent carbon of **2B**. The last reaction can proceed through 1,2-shift or displacement of the sulfide moiety. When α-methylenic protons are present in **2B**, deprotonation occurs, leading to allyl radicals and, ultimately, to isomeric allyl alcohols. Reactions of **1** with DDQ in acetonitrile afford charge-transfer complexes and then zwitterionic electron-transfer (ET) complexes which can evolve rapidly through intramolecular proton transfer when *trans* methylenic protons are present. The resulting sulfur–oxygen σ-complexes are responsible for the reaction products mainly through either γ-elimination of $DDQH_2$ or nucleophilic attack at the δ-vinylic carbon followed by displacement of $DDQH^-$.

We have recently discovered that vinyl sulfides **1** react smoothly with dioxygen in mild conditions to give radical cations **2**.[1] These intermediates afforded mainly rearranged carbonyl compounds arising from nucleophilic attack at a vinylic carbon with concomitant 1,2-shift of the sulfur atom. This kind of rearrangement has been observed also in the two-electron anodic oxidation of alkenyl sulfides.[2]

Our present study was aimed at investigating the structure and chemical behavior of radical cations **2** by examining the effect of the substituents and the nature of the oxidant on the reaction products. In this regard, we studied the reaction of vinyl sulfides **1a–g** with cerium (IV) ammonium nitrate (CAN)[3] and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),[4] well-known oxidizing ET reagents that in principle could lead to the sulfide radical cations **2a–g** (Scheme 1).

Scheme 1



1 2

a: R = Bu, R' = H, R" = Ph; **b**: R = Et, R' = Et, R" = Ph;
c: R = ^{t}Bu, R' = H, R" = Ph; **d**: R = Ph, R' = H, R" = Ph;
e: R = Bu, R' = H, R" = $Ph(CH_2)_2$;
f: R = Pr, R' = Pr, R" = Ph; **g**: R = Me, R' = Me, R" = Ph.

Results and Discussion

The CAN-promoted reactions were carried out at room temperature by adding dropwise a saturated acetonitrile solution of CAN to a 0.1 M acetonitrile solution of the appropriate sulfide (**1a–e**). In all cases the reaction was complete within a few minutes, as proved by fading of the yellow color; a slight excess of CAN (1.1–1.5 equiv) was used to obtain complete disappearance of the starting material. The reaction mixture was quenched with water after 3–5 min; TLC analysis showed the presence of very polar, yellow products that disappeared after stirring for several hours. Therefore, the compounds that were isolated by subsequent workup and column chromatography were not the first-formed reaction products; they resulted from hydrolysis of unstable intermediates that might be nitric esters, in agreement with our previous findings.[1]

Hexenyl sulfide **1a** gave 2-(phenylthio)hexanal (**15a**), hexanal (**13a**) (detected by GC–MS), and diphenyl disulfide (**14**) (Scheme 2). Phenylvinyl sulfide **1d** showed a similar behavior, yielding the rearranged aldehyde **15d**, phenylacetaldehyde (**13d**) (detected by GC–MS), and disulfide **14**; this reaction gave also a mixture (15%) of two isomeric products that were identified as adducts of NO_2 onto the carbon–carbon double bond of **1d** (see Experimental Section). In contrast, *tert*-butylvinyl sulfide **1c** furnished mainly vinyl sulfoxide **8** and disulfide **14**, in addition to (possible) 3,3-dimethylbutenyl nitrate (detected by GC–MS). Finally, 3-hexenyl sulfide **1b** gave mainly an equimolar mixture of the regioisomeric allylic alcohols **9** and **10**; a possible nitro derivative was also detected by GC–MS. The nitro derivatives obtained from **1b** and **1d** have no relation with our study and will not be considered any more in this paper: it is well known that CAN also behaves as a nitrating agent.[5]

The reaction products were rationalized through the intermediacy of radical cations **2**, which can give three different kinds of reactivity. (a) The first is nucleophilic attack by the nitrate counterion at the vinylic carbon linked to the sulfur atom with concomitant 1,2-shift of the phenylthio group (with **1a,d**). The resulting intermediates **5a,d** can give the rearranged aldehydes **15a,d**—by loss of NO_2—or nitrates **11a,d** through β-fragmentation with loss of benzenethiyl radicals. Aldehydes

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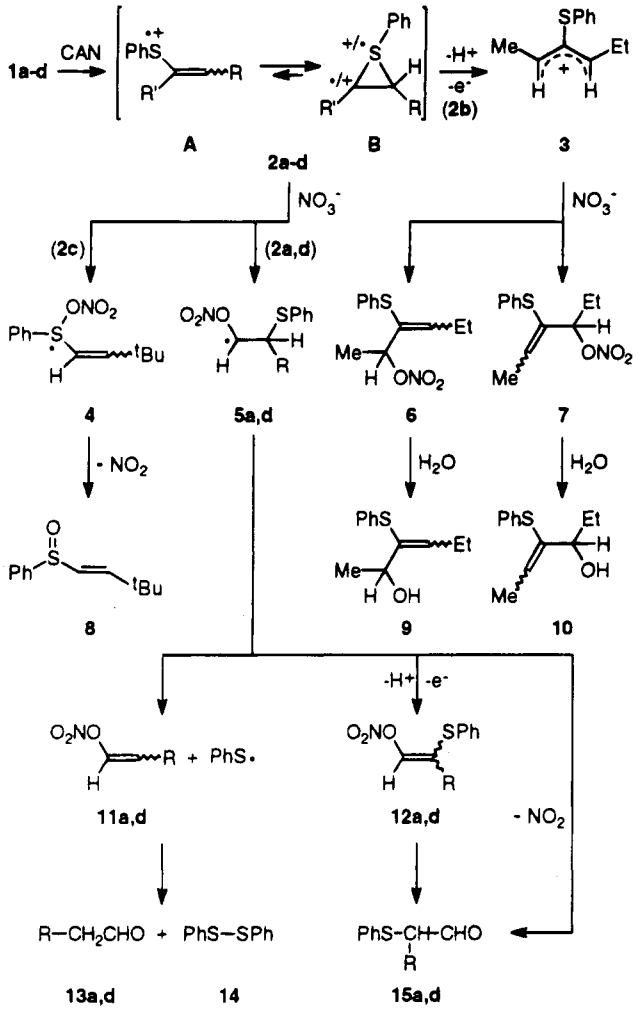
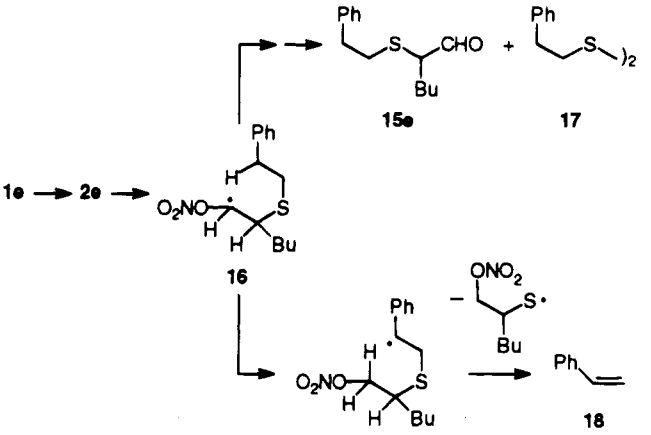
Scheme 2



Scheme 3



13a,d can then arise from hydrolysis of **11a,d** and disulfide **14** from dimerization of thiyl radicals. An alternative route to compounds **15a,d** could entail oxidation and deprotonation of **5a,d**, followed by hydrolysis of the resulting nitrates **12a,d**. (b) The second is attack of the nitrate ion at the sulfur atom (with **1c**). Elimination of NO_2 from the intermediate **4** can afford sulfoxide **8**. The attack at the sulfur instead of the vinylic carbon is probably due to a steric effect of the bulky *tert*-butyl group. (c) The third is deprotonation from the allylic methylene geminal to the sulfur atom—when it is present, like in **1b**—followed by oxidation of the resulting allyl radical. Addition of the nitrate ion to either terminal carbon atoms of the allyl cation **3** should afford the two isomeric nitrates **6** and **7**; these intermediates can then hydrolyze to allylic alcohols **9** and **10** (Scheme 2).

Phenethyl sulfide **1e** was as easily oxidizable as **1a–d**. Therefore, the charge-delocalization on the phenyl ring linked to the sulfur atom, which is expected in **2a–d**, is not essential to attain a fast ET reaction. Compound **1e** yielded mainly disulfide **17** and the rearranged aldehyde **15e**, besides minor amounts of styrene (**18**) (detected by GC–MS) (Scheme 3). The reactivity of **1e** was very similar to that of **1a–d**; the only difference consisted in the formation of styrene, which was rationalized through a 1,5-shift of a benzylic hydrogen atom of radical **16**, followed by β-scission of the resulting alkylthio-substituted benzyl radical. Similar fragmentations of β-thio-substituted radicals are well documented.[6]

The findings obtained from the above reactions of sulfides **1a–e** with CAN allow us to draw some conclusions on the structure of radical cations **2a–e**. We can observe that the positive charge is centered mainly on the sulfur atom and the linked vinylic carbon. Moreover, deprotonation from the allylic methylene geminal to the phenylthio group—if it exists—is a feasible, easy process. In contrast, deprotonation from the allylic positions *cis* or *trans* to the sulfur atom was not observed at all.

These observations are not in agreement with the intermediacy of an open-chain radical cation (**A** form of **2**, Scheme 2): in this structure one should expect nucleophilic attack at sulfur but not at the linked vinylic carbon with concomitant 1,2-shift of the phenylthio group. Furthermore, in structure **A** the acidity of the methylenic protons *cis* or *trans* to the sulfur atom should be greater than that of the geminal-methylene protons.

On this basis, we suggest that **2A** can be in equilibrium with the thiiranyl radical cation **2B**, responsible for the formation of aldehydes (**15a,d–e** and **13a,d**), alcohols (**9** and **10**), and disulfides (**14** and **17**). With **1c** the preferred formation of the sulfoxide might be due to a more difficult ring closure of **2cA** to **2cB** owing to the hindrance of the *tert*-butyl group.

Attempts to trap radical cations **2** with nucleophiles other than nitrate ion failed. The reaction of **1a** with CAN in the presence of tetrabutylammonium acetate gave disulfide **14** and aldehyde **15a** exclusively. This result would indicate that radical cations **2** are formed as close ion-pairs with the nitrate ion, in accordance with previously reported findings.[7]

When DDQ was added at room temperature to an acetonitrile solution of sulfides **1a–g**, the resulting mixture immediately turned bright-green (with **1a–d,f,g**) or deep-red (with **1e**). The nature of the reaction products depended strongly on the nature of the vinyl sulfide. When a 1:1 *E/Z* mixture of sulfides **1a,b,f,g** was allowed to react with DDQ (1 equiv) we observed complete disappearance of the *E*-isomer after 3–5 min; in contrast, the *Z*-isomer remained unchanged for over 24 h. (*E*)-1-Hexenyl sulfide (*E*)-**1a** afforded diphenyl disulfide (**14**) and the unsaturated ketone **19a**, whereas (*E*)-3-hexenyl sulfide (*E*)-**1b** gave **14** and compound **20** (Scheme 4). The reaction of sulfide **1c** led to slow disappearance of both *E*- and *Z*-isomers: after 70 h the *E*-isomer was completely consumed and 20% of the *Z*-compound was recovered. The final mixture was

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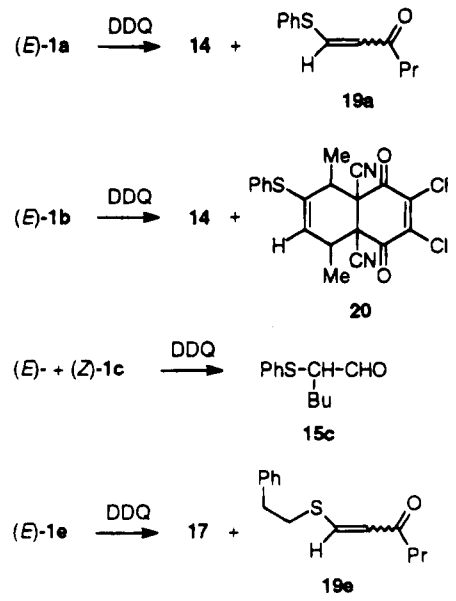
Scheme 4



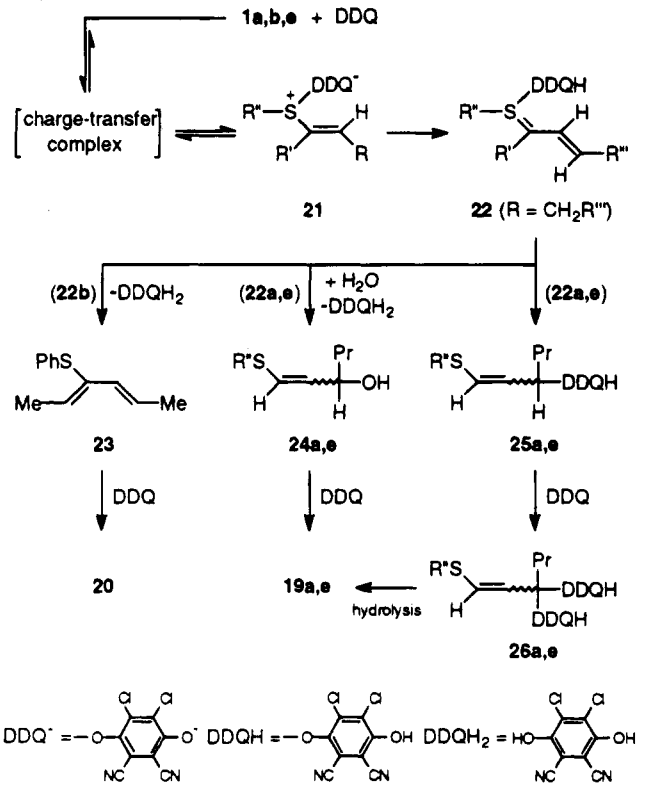
rather complicated: the rearranged aldehyde **15c** was isolated together with other unidentifiable products. The *E/Z* mixture of sulfide **1d** did not react even after 5 days, as was proved by GC–MS analyses; the bright-green color of the solution also persisted. Finally, phenethyl sulfide (*E*)-**1e** disappeared within 5 min; after this time the *Z*-isomer was virtually unchanged, but it decomposed almost completely after 20 h. The reaction mixture obtained after 30 min contained phenethyl disulfide **17** and the unsaturated ketone **19e**.

These results indicate that DDQ and alkenyl sulfides give rise to charge-transfer complexes which can evolve rapidly only if allylic methylenes *trans* to the sulfur atom ((*E*)-**1a,b,e–g**) are present. The eventual reaction products derive from oxidation of these allylic positions. It is worth pointing out that the reaction is highly stereospecific, although the oxidation potentials of (*E*)- and (*Z*)-vinyl sulfides are virtually identical.[2]

We can suggest that the charge-transfer complex can undergo an ET process leading to the σ-adduct **21** and then to the intermediate **22** through an intramolecular proton transfer from the *trans* allylic-methylene to the anionic oxygen of the DDQ-moiety. Such a proton transfer should be too sterically hindered in the *Z*-isomer, as shown by analysis of molecular models.

The intermediate **22** could be responsible for the products through (a) proton loss from the allylic methylene geminal to the sulfur with concomitant elimination of $DDQH^-$; the resulting diene **23** is trapped by the excess of DDQ to give the Diels–Alder adduct **20**; and (b) displacement of $DDQH^-$ through nucleophilic attack at the γ-vinylic carbon, reasonably by the water present in the reaction mixture. The resulting allyl alcohols **24a,e** can be easily oxidized by DDQ to the unsaturated ketones **19a,e**. We cannot exclude that $DDQH^-$ itself can act as the nucleophile, giving allyl ethers **25a,e**; subsequent oxidation and hydrolysis of the resulting acetals **26a,e** could afford **19a,e** (Scheme 5). It is well known that DDQ can easily oxidize both allyl alcohols[8] and allyl ethers.[9] As far as disulfides **14** and **17** are concerned, their formation is still unclear.

Scheme 5



In agreement with our suggestion, the oxidation did not occur (**1d**) or was very slow (**1c**) in the absence of allylic methylenes. With **1c** the reaction yielded aldehyde **15c**, which probably arises from radical cation **2c** through a mechanism analogous to that described for CAN-mediated reactions.

Experimental Section

Structural assignment to the reaction products was generally made on the basis of ^1H NMR and MS spectral data in addition to elemental analysis. ^1H NMR spectra were recorded in $CDCl_3$ solutions on a 200-MHz instrument with tetramethylsilane as internal standard. GC–MS analyses were performed on a Carlo-Erba QMD 1000 instrument equipped with a Quadrex 007-2-25-0.25F capillary column. Column chromatography was carried out on silica gel (0.040–0.063 particle size) by gradual elution with light petroleum (bp 40–70 °C)/diethyl ether. Mass spectra were recorded by the electron impact method on a VG 7070E instrument.

Starting Materials. The alkenyl sulfides **1a–d,f,g**[10] and **1e**[6] were obtained as previously described. Cerium(IV) ammonium nitrate (CAN) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were commercially available and were used as received.

Reaction of Alkenyl Sulfides 1a–e with CAN. A 0.1 M acetonitrile solution of CAN (20–30 mL, 1–1.5 equiv) was added dropwise at room temperature to a solution of the appropriate alkenyl sulfide **1a–e** (2 mmol) in acetonitrile (20 mL) until quick fading of the yellow color was observed. At this time, a TLC analysis showed complete disappearance of the starting sulfide. The resulting solution was stirred for a further 20–30 min and then hydrolyzed with water. The mixture was allowed to stand overnight and then extracted with diethyl ether. The organic layer was separated and analyzed by GC–MS. The solvent was evaporated and the residue chromatographed on silica gel column. All of the reactions described below were performed according to this procedure.

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(9) Hayashi, Y.; Mukaiyama, T. *Chem. Lett.* **1987**, 1811.
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From Hex-1-en-1-yl Phenyl Sulfide (1a). Chromatography gave diphenyl disulfide (**14**) (60 mg, 27%) and 2-(phenylthio)hexanal (**15a**) (185 mg, 45%). GC–MS analysis of the reaction mixture had evidenced the presence of these compounds in addition to hexanal (**13a**). This reaction was repeated in the presence of tetrabutylammonium acetate (1.2 g, 4 mmol): workup and column chromatography yielded disulfide **14** (80 mg, 35%) and aldehyde **15a** (145 mg, 35%) as the only identifiable products.

From Hex-3-en-3-yl Phenyl Sulfide (1b). Chromatography gave **14** (10 mg, 5%), a mixture of inseparable, unidentifiable products (80 mg) containing a main compound that was possibly 3-nitro-4-(phenylthio)hex-3-ene [GC–MS *m/z* (rel inten) 237 (M^+, 30), 207, 191, 149 (100), 135, 105], and an inseparable 47:53 mixture of 4-(phenylthio)hex-4-en-3-ol (**10**) and 3-(phenylthio)hex-3-en-2-ol (**9**) (125 mg, 30%) [^{1}H NMR δ_{10} = 0.85 (3H, t, J = 7.5 Hz), 1.65 (2H, m), 1.85 (3H, d, J = 7.2 Hz, collapsing to a singlet upon irradiation at δ = 6.38), 4.05 (1H, t, J = 6.5 Hz), 6.38 (1H, q, J = 7.2 Hz), 7.1–7.3 (5H, m); δ_9 = 0.95 (3H, t, J = 7.5 Hz), 1.30 (3H, d, J = 7.0 Hz), 2.30 (2H, m, collapsing to a quartet, J = 7.5 Hz, upon irradiation at δ = 6.30), 4.30 (1H, q, J = 7.0 Hz, collapsing to a singlet upon irradiation at δ = 1.30), 6.30 (1H, t, J = 7.0 Hz), 7.1–7.3 (5H, m); IR ν_{max} 3600 (sharp) and 3400 (broad) cm^{-1}; GC–MS showed two chromatographic peaks *m/z* (first isomer) (rel inten) 208 (M^+, 80), 190 (30), 179 (40), 161 (100), 149 (60), 110 (70); *m/z* (second isomer) (rel inten) 208 (M^+, 80), 190 (70), 161 (20), 110 (100). Anal. Calcd for $C_{12}H_{16}OS$: C, 69.19; H, 7.74; S, 15.39. Found: C, 68.96; H, 7.71; S, 15.42]. GC–MS analysis of the reaction mixture showed the absence of the above hexanols **9** and **10** before column chromatography.

From 3,3-Dimethylbut-1-en-1-yl Phenyl Sulfide (1c). Chromatography gave **14** (45 mg, 20%), a mixture of inseparable, unidentifiable products (90 mg), and (*E*)-3,3-dimethylbut-1-en-1-yl phenyl sulfoxide (**8**) (120 mg, 30%) [^{1}H NMR δ = 1.10 (9H, s), 6.40 (2H, AB system, J_{AB} = 15 Hz, inner lines separation = 17 Hz), 7.6 (5H, m); MS *m/z* (rel inten) 208 (M^+, 20), 160 (30), 159 (30), 145 (100). Anal. Calcd for $C_{12}H_{16}OS$: C, 69.19; H, 7.74; S, 15.39. Found: C, 68.94; H, 7.70; S, 15.43]. GC–MS analysis of the reaction mixture showed the presence of a major product that was possibly 3,3-dimethylbut-1-en-1-yl nitrate [MS *m/z* (rel inten) 145 (M^+, 10), 116 (20), 115 (20), 83 (70), 70 (60), 43 (100).

From β-Styryl Phenyl Sulfide (1d). Chromatography gave **14** (40 mg, 18%), 2-phenyl-2-(phenylthio)acetaldehyde (**15d**) (135 mg, 30%) [^{1}H NMR δ = 4.75 (1H, d, J = 4.2 Hz), 7.3–7.6 (10H, m), 9.55 (1H, d, J = 4.2 Hz); MS *m/z* (rel inten) 228 (M^+, 15), 199 (100), 91 (20). Anal. Calcd for $C_{14}H_{12}OS$: C, 73.65; H, 5.30; S, 14.04. Found: C, 73.40; H, 5.27; S, 14.10], and a 1:1 mixture of (*E*)- and (*Z*)-α-nitro-β-(phenylthio)styrene as a pale-yellow oil (80 mg, 15%) [^{1}H NMR δ = 7.3–7.55 (20H, m), 7.6 (1H, s), 8.52 (1H, s); IR ν_{max} 3050, 3022, 1608, 1585, 1556, 1505, 1439, 1322, and 1294 cm^{-1}; the two isomers showed similar GC–MS spectra with peaks at *m/z* (rel inten) 257 (M^+, 30), 211 (30), 178 (50), 125 (100), 110 (40), 109 (40).

From Hex-1-en-1-yl Phenethyl Sulfide (1e). Chromatography gave phenethyl disulfide (**17**) (75 mg, 27%), 2-(phenethylthio)hexanal (**15e**) (60 mg, 25%) [^{1}H NMR δ = 0.9 (3H, t), 1.2–1.9 (6H, m), 2.7–3.0 (4H, m), 3.07 (1H, ddd, J_1 = 9.5 Hz, J_2 = 8.0 Hz, J_3 = 4.7 Hz,), 7.1–7.4 (5H, m), 9.15 (1H, d, J = 4.7 Hz); MS *m/z* (rel inten) 236 (M^+, 15), 207 (65), 173 (60), 151 (50), 105 (100), 104 (90), 91 (60). Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53; S, 13.56. Found: C, 70.87; H, 8.48; S, 13.62], and a mixture of inseparable, unidentifiable products (110 mg). GC–MS analysis of the reaction mixture showed the presence of minor amounts of styrene (ca. 3–5%).

Reaction of Alkenyl Sulfides 1a–g with DDQ. DDQ (225 mg, 1 mmol) was added under stirring to a solution of a 1:1 *E/Z* mixture of the appropriate alkenyl sulfide **1a–g** (1 mmol) and diphenyl (internal standard) in acetonitrile (10 mL). The solution became immediately deep red in the case of phenethyl sulfide **1e** or deep green in all the other cases. After appropriate times, the reaction mixtures were quantitatively analyzed by GC to follow the disappearance of the starting sulfide. The (*E*)-sulfides (*E*)-**1a,b,e–g** disappeared after 5 min. The phenyl sulfides (*Z*)-**1a,b,f,g** were found to be largely unchanged (over 90%) after 24 h, whereas phenethyl sulfide **1e** was found to be virtually unchanged after 1 h, but somewhat decomposed (50–60%) after 24 h. Both (*E*)- and (*Z*)-**1c** remained unchanged for over 30 min, but the decomposition was evident after 24 h and virtually complete after 4–5 days. Both (*E*)- and (*Z*)-**1d** were found to be unreacted after 5 days.

The reactions of sulfides **1a–c,e** were repeated on a 2 mmol scale. The reaction mixtures were worked up after suitable times with aqueous sodium carbonate and extracted with diethyl ether. The organic layer was separated, the solvent evaporated, and the residue chromatographed. All the reactions described below were performed according to this procedure.

From Hex-1-en-1-yl Phenyl Sulfide (1a). The reaction mixture was worked up after 20 h. Chromatography gave unreacted (*Z*)-**1a** (95%), **14** (15 mg, 8%), and a 2:1 *E/Z* mixture[11] of 1-(phenylthio)hex-1-en-3-one (**19a**) as an oil (170 mg, 65%) [^{1}H NMR $\delta_{(E)\text{-isomer}}$ = 0.92 (3H, t, J = 7.5 Hz), 1.5–1.8 (2H, m), 2.45 (2H, t, J = 7.5 Hz), 6.08 (1H, d, J = 15.5 Hz), 7.3–7.5 (5H, m), 7.75 (1H, d, J = 15.5 Hz); $\delta_{(Z)\text{-isomer}}$ = 0.98 (3H, t, J = 7.5 Hz), 1.5–1.8 (2H, m), 2.52 (2H, t, J = 7.5 Hz), 6.40 (1H, d, J = 9.5 Hz), 7.25 (1H, d, J = 9.5 Hz), 7.3–7.5 (5H, m); the two isomers showed similar GC–MS spectra with peaks at *m/z* (rel inten) 206 (M^+, 20), 163 (100), 109 (30). Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84; S, 15.54. Found: C, 69.59; H, 6.80; S, 15.62].

From Hex-3-en-3-yl Phenyl Sulfide (1b). The reaction mixture was worked up after 20 h. Chromatography gave unreacted (*Z*)-**1b** (90%), **14** (40 mg, 35%), a mixture of two inseparable, unidentifiable products with M^+ 206 and 208, respectively (40 mg, 20%), and 1,4,4a,5,8,8a-tetrahydro-2,3-dichloro-4a,8a-dicyano-5,8-dimethyl-7-(phenylthio)naphthalene-1,4-dione (**20**) as a pale-yellow solid (85 mg, 20%), mp 133–135 °C [^{1}H NMR δ = 1.18 (3H, d, J = 7.5 Hz), 1.52 (3H, d, J = 7.5 Hz), 3.10 (1H, bq, collapsing to dq, J_q = 7.5 Hz, J_d = 2.2 Hz, upon irradiation at δ = 5.97), 3.35 (1H, m, collapsing to dq, J_q = 7.5 Hz, J_d = 2.3 Hz, upon irradiation at δ = 5.97), 5.97 (1H, m), 7.2–7.4 (5H, m); MS *m/z* (rel inten) 416 (M^+, 15), 190 (100), 110 (40), 81 (35). Anal. Calcd for $C_{20}H_{14}Cl_2N_2O_2S$: C, 57.56; H, 3.38; Cl, 16.99; N, 6.71; S, 7.68. Found: C, 57.43; H, 3.36; Cl, 17.07; N, 6.75; S, 7.74].

From 3,3-Dimethylbut-1-en-1-yl Phenyl Sulfide (1c). The reaction mixture was worked up after 70 h. Chromatography gave unreacted (*Z*)-**1c** (20%), a fraction containing mainly 3,3-dimethyl-2-(phenylthio)butanal (**15c**) (40 mg, ca. 8–10%) as shown by GC–MS and NMR analyses [^{1}H NMR δ = 1.20 (9H, s), 3.20 (1H, d, J = 5.5 Hz), 7.2–7.5 (5H, m), 9.45 (1H, d, J = 5.5 Hz, collapsing to a singlet upon irradiation at δ = 3.20); GC-MS *m/z* (rel inten) 208 (M^+, 30), 190 (30), 179 (30), 175 (80), 152 (100), 123 (50), 69 (80), 57 (80)], and a mixture of inseparable, unidentifiable products.

From Hex-1-en-1-yl Phenethyl Sulfide (1e). The reaction mixture was worked up after 30 min. Chromatography gave unreacted (*Z*)-**1e** (70%), **17** (35 mg, 20%), and a 2:1 *E/Z* mixture[11] of 1-(phenethylthio)hex-1-en-3-one (**19e**) (100 mg, 35% on the basis of reacted **1e**, 43% on the basis of (*E*)-**1d**) [^{1}H NMR δ = 0.93 (3H, t, J = 7.5 Hz), 1.55–1.75 (2H, m), 2.44 (2H, t, J = 7.5 Hz), 2.9–3.1 (4H, m), 6.13 (0.7H, d, J = 15.2 Hz), 6.28 (0.3H, d, J = 9.5 Hz), 6.98 (0.3H, d, J = 9.5 Hz), 7.2–7.4 (5H, m), 7.60 (0.7H, d, J = 15.2 Hz); the two isomers showed similar GC–MS spectra with peaks at *m/z* (rel inten) 234 (M^+, 50), 191 (80), 130 (60), 129 (100), 105 (85), 104 (50). Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74; S, 13.68. Found: C, 71.47; H, 7.69; S, 13.75].

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(11) ^{1}H NMR analysis of the reaction mixture before chromatography showed the two isomeric ketones in a ca. 1:1 ratio.