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One Electron Transfer Reaction of Phenyl Vinyl Sulfides with Dioxygen. The Fate of the Intermediate Vinyl Sulfide Radical Cations.

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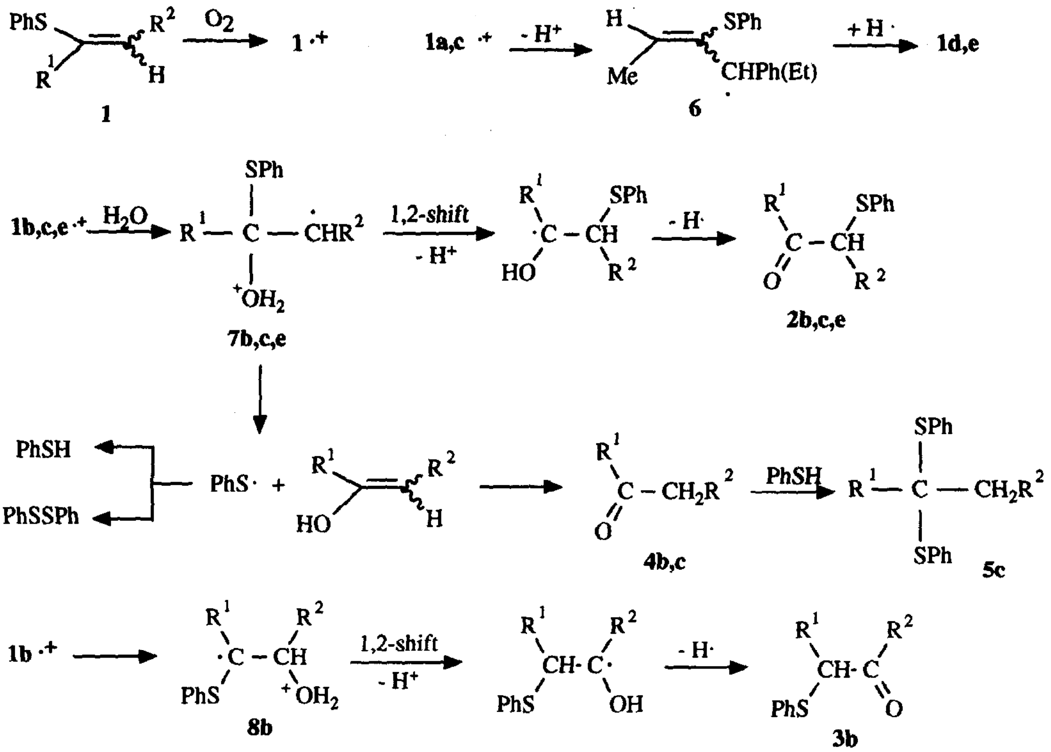
Abstract. Mild reaction of pheyl vinyl sulfides with dioxygen can lead to the eventual formation of rearranged vinyl sulfides and/or carbonyl-containing sulfide products, which are believed to result from decomposition of initially-formed vinyl sulfide radical cations. Supporting evidence is provided by the comparable findings obtained from the one electron oxidation of one vinyl sulfide by cerium (IV) ammonium nitrate.

Organic radical cations, which are now well recognized to be the crucial intermediates in a great variety of processes, can be normally produced from the appropriate organic substrates by one electron metal ion-assisted, electrochemical or photosensitized oxidation[1]. Heterolytic C-H bond fission is the most common reaction pathway available to radical cations, but competing cleavage of a C-C and/or C-X (X = heteroatom) bond often occurs[2]. With π radical cations, nucleophilic addition reactions are also usually encountered[1]. In this note we wish to show that phenyl vinyl sulfides **1** appear to undergo mild one electron transfer reaction with dioxygen to give corresponding radical cations $\mathbf{1}^{\cdot+}$, which lead to a number of decomposition products in a fashion dependent upon the nature of their R^1 and R^2 vinylic substituents.

β-(Phenylthio)styrene[3] **1**, R^1= H, R^2= Ph, remains virtually unchanged upon stirring at room temperature, in the presence of the air, for over 10 days or upon being heated at 90 °C in dioxygen-saturated chloroform for 2 days. On the other hand, under similar conditions 1-phenyl-2-(phenylthio)but-1-ene **1a**[3] undergoes about 30% conversion into isomeric 1-phenyl-2-(phenylthio)but-2-ene **1d**[4]. The rate and the extent of such conversion are essentially unaffected by the presence of an effective radical initiator such as azobis(*iso*-butyronitrile)(AIBN). This fact suggests that no free radical intermediates are primarily involved in the isomerization of the sulfide **1a** to **1d**. In the presence of dioxygen, 1-(phenylthio)hex-1-ene **1b**[3] mainly affords a mixture of diphenyl disulfide, 2-(phenylthio)hexanal **2b**[5], and 1-(phenylthio)hexan-2-one **3b**[6] in ca. 1:1:0.4 ratio, but to an extent highly dependent upon the reaction conditions. In dioxygen-saturated chlorobenzene, at ambient temperature, the above sulfide **1b** reaction hardly occurs, but at 90 °C over 2 days it takes place to about 30 % extent (under the latter conditions additional occurrence of hexanal **4b** is detectable by GC/MS). At room temperature and in the presence of the air, the compound **1b** (in the pure state) can instead undergo ca. 70 % reaction over 10 days. Similarly to that which is observed with the sulfide **1a**, the presence of AIBN does not affect essentially the rate of consumption of the sulfide **1b** nor the composition of its products. Same reaction of the 2-deuterated vinyl sulfide **1b**[7] results in the formation of the 2-deuterated hexanal **2b**[8] and (mainly) the 1-deuterated hexan-2-one **3b**[9]. It therefore follows that the conversion of both vinylic carbons into the corresponding carbonyl carbons would occur with concomitant 1,2-migration of their original phenylthio and hydrogen substituents.

Furthermore, 3-(phenylthio)hex-3-ene **1c**[3], upon being heated in dioxygen-saturated chlorobenzene at 90 °C for ca. 2 days, undergoes ca. 50 % conversion into isomeric 3-(phenylthio)hex-2-ene **1e**[10]. On the other hand, at room temperature and in the presence of the air, the same sulfide **1c** (in the pure state) undergoes almost complete reaction over 10 days to give a rather complex mixture, from which column chromatography

Scheme



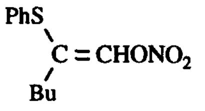
a : R^1 = Et, R^2 = Ph ; b : R^1 = H, R^2 = Bu ; c : R^1 = R^2 = Et ;
d : R^1 = $PhCH_2$, R^2 = Me ; e : R^1 = Pr, R^2 = Me

separated major amounts of 3,3-bis(phenylthio)hexane **5c**[11] and a 2:1 mixture of 4-(phenylthio)hexan-3-one **2c**[6] and 2-(phenylthio)hexan-3-one **2e**[6] along with minor amounts of benzenethiol and diphenyl disulphide as well as little amounts of the rearranged sulfide **1e** and the unchanged sulfide **1c**, in overall yield amounting to ca. 100 %.

The bulk of the general evidence provided by our present dioxygen-promoted reactions of the vinyl sulfides **1a,b,c**, while ruling out the primary intervention of possible free-radical intermediates, would instead suggest the initial occurrence of radical cation **1a,b,c**$^{\cdot+}$ intermediates, from which all the eventual products might conceivably be formed through the reaction pathways outlined in the Scheme.

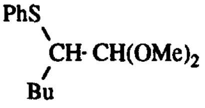
Deprotonation from the α-vinylic methylene carbon of the sulfide radical cation **1a,c**$^{\cdot+}$ would afford a corresponding allylic radical **6** and thence the rearranged sulfide **1d,e** by subsequent hydrogen abstraction reaction. Nucleophilic attack of water (both present in the air and the commercial chlorobenzene solvent) at the α-vinylic carbon of the radical cations **1b,c**$^{\cdot+}$ as well as **1e**$^{\cdot+}$, in turn produced from the rearranged sulfide **1e**, would afford the appropriate radicals **7b,c,e**, from which the corresponding carbonyl products **2b,c,e** might arise through subsequent 1,2-migration of phenylthio group and final elimination of a hydrogen atom.

Competing extrusion of benzenethiyl radical by the intermediate radicals **7b** and **7c,e** would additionally result in the eventual formation of hexanal **4b** and hexan-3-one **4c** (and thence its thioketal **5c**), respectively, besides benzenethiol and diphenyl disulfide. Moreover, competing nucleophilic attack of water at the β-vinylic carbon of the intermediate **1b**$^{\cdot+}$ would give the radical **8b**, from which the hexan-2-one **3b** might be produced through 1,2-migration of hydrogen and subsequent hydrogen elimination. The suggested mechanistic interpretation of the present dioxygen-promoted reactions of the sulfides **1a-c,e** was substantiated by the findings obtained by reacting the sulfide **1b** with cerium (IV) ammonium nitrate (CAN), a known powerful one electron oxidant. In anhydrous acetonitrile, at room temperature, the sulfide **1b** underwent total reaction with CAN (1 molar equiv) within ≤ 1 min to give a pale yellow oily mixture being consituted by a main component (TLC), which unfortunately could not be isolated by column chromatography owing to its extensive decomposition. The ^{1}H NMR spectrum of the crude mixture, in addition to aliphatic and aromatic protons, showed a vinylic singlet at δ 7.30; its IR spectrum showed two strong absorption bands at 1650 and 1270 cm^{-1}, ascribable to O-NO_2 stretching vibrations. Upon mild hydrolysis, it furnished the aldehyde **2b** and diphenyl disulfide in 4:1 ratio and in 60 % overall yield, besides tarry material. On this basis we assigned the main product the vinyl nitrate **9** structure. Our structural assignement was further supported by reacting the sulfide **1b** with CAN in acetonitrile/methanol (9:1 v/v). In such case, TLC analysis of the crude product revealed the absence of the presumed nitrate **9** and the presence of two major components which, after column chromatography, were isolated in 50 % overall yield and shown to be the acetal **10**[12] and the alkyl nitrate **11**[13], both conceivably ascribable to further reaction of the vinyl nitrate **9** with methanol. The vinyl nitrate **9** can be envisaged as arising from a mechanistic route analogous to that above postulated to explain the formation of the hexanal **2b** in the corresponding reaction of the sulfide **1b** with dioxygen. This would entail nucleophilic attack of nitrate ion at the α-vinylic carbon of initially formed radical cation **1b**$^{\cdot+}$, followed by 1,2-shift of benzenethiyl radical and eventual elimination of a hydrogen atom.



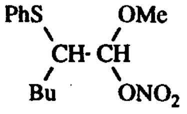
$\mathrm{PhS(Bu)C{=}CHONO_2}$

9



$\mathrm{PhS(Bu)CH{-}CH(OMe)_2}$

10



$\mathrm{PhS(Bu)CH{-}CH(OMe)ONO_2}$

11

In conclusion, we have presently shown that vinyl sulfide radical cations **1**$^{\cdot+}$ are likely to be formed by one electron oxidation of appropriate sulfides **1** by dioxygen (and CAN). A full comprension of the effect of the vinylic substituents on their formation and their decomposition modes clearly requires further investigation, but these intermediates would appear to show a marked tendency to undergo deprotonation from the α-vinylic methylene carbon and/or nucleophilic attack at the α-vinylic carbon.

Acknowledgments

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3. All the starting vinyl sulfides **1** were isomeric (E)/(Z) mixtures as obtained from the free radical addition of benzenethiol to the appropriate alkyne (cfr. Benati, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1*, **1991**, 2103).
4. ^{1}H NMR (200 MHz) [(E) or (Z) isomer] δ 1.85 (3H, d, J 7.0 Hz), 3.45 (2H, br s), 5.93 (1H, q, J 7.0 Hz), 7,0-7.6 (10H, m); ^{1}H NMR (200 MHz) [(Z) or (E) isomer] δ 1.90 (3H, d, J 7.0 Hz), 3.55 (2H, s), 6.05 (1H, q, J 7.0 Hz), 7.0-7.5 (10H, m). The two isomers showed similar GC-MS spectra with peaks at m/z 240 (M$^+$), 149, 135, 134, 130, 129, 116, 115, 105, and 91 (100).
5. ^{1}H NMR, (200 MHz) δ 0.9 (3H, t, J 7 Hz), 1.2-1.9 (6H, m), 3.53 (1H, dt, J_t 7.5, J_d 4.4 Hz), 7.2-7.6 (5H, m), and 9.4 (1H, d, J 4.4 Hz). IR, υ_{max} 1720 and 1690 cm^{-1}. MS, m/z 208 (M$^+$, 30), 190 (20), 179 (60), 147 (50), 123 (100), and 69 (60).
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7. 2-Deutero-1-(phenylthio)hex-1-ene was obtained as ca. 1:1 isomeric (E)/(Z) mixture in 80 % isotopical purity by radical addition of PhSD to hex-1-yne (cfr. ref. 3). ^{1}H NMR (200 MHz) δ 0.95 (6H, t, J 7.5 Hz), 1.2-1.5 (8H, m) 2.1-2.4 (4H, m), 6.15 (1H, br s), 6.22 (1H, br s), 7.1-7.4 (10H, m).
8. Obtained in ca. 80 % isotopical purity, as indicated by ^{1}H NMR and GC-MS analysis.
9. Obtained in ca. 50 % isotopical purity, as indicated by GC-MS analysis.
10. ^{1}H NMR (200 MHz) [(E) or (Z) isomer] δ 0.82 (3H, t, J 7.5 Hz), 1.50 (2H, 8 lines, J 7.5 Hz), 1.87 (3H, d, J 6.5 Hz), 2.08-2.26 (2H, m), 6.0 (1H, q, J 6.5 Hz), and 7.1-7.4 (5H, m). ^{1}H NMR (200 MHz) [(Z) or (E) isomer] δ 0.90 (3H, t, J 7.5 Hz), 1.58 (2H, m), 1.78 (3H, d, J 7.0 Hz), 2.22 (2H, t, J 7.5 Hz), 5.97 (1H, q, J 7.0 Hz), and 7.1-7.5 (5H, m). The two isomers showed similar GC-MS spectra with peaks at m/z 192 (M$^+$, 100), 164, 149, 135, 110, and 87.
11. ^{1}H NMR (200 MHz) δ 0.86 (3H, t, J 7.0 Hz), 1.1 (3H, t, J 7.0 Hz), 1.5-1.7 (6H, m), 7.3-7.4 (6H, m), 7.7-7.8 (4H, m); MS, m/z 193 (100), 151, 137, 123, 109, 83, and 55.
12. ^{1}H NMR (200 MHz) δ 0.85 (3H, t), 1.2-1.7 (6H, m), 3.38 (3H, s), 3.42 (3H, s), 3.3-3.45 (1H, m), 4.65 (1H, d, J 4.0 Hz), 7.2-7.35 (3H, m), and 7.4-7.55 (2H, m); MS, m/z 254 (M$^+$, 10), 153 (40), 145 (100), 113 (25), 109 (12), 81 (50), 75 (45), 71 (33), and 45(58).
13. Obtained as diastereoisomeric mixture; ^{1}H NMR (200 MHz) δ 0.85 (3H, t), 0.90 (3H, t), 1.2-2.0 (12H, m), 3.45 (3H, s), 3.5 (3H, s), 4.50 (1H, d, J 7.5 Hz), 4.70 (1H, d, J 4.2 Hz), 5.06 (1H, ddd, J_1 10, J_2 7.5, J_3 3.6 Hz), 5.20 (1H, ddd, J_1 7.4, J_2 4.5, J_3 4.2 Hz), 7.2-7.35 (6H, m), and 7.4-7.5 (4H, m). MS, m/z 285 (M$^+$, 7), 208 (15),179 (34), 176 (50), 153 (40), 130 (23), 123 (50), 110 (22), 109 (38), 101 (57), 85 (100), and 69 (50).

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