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SINGLET OXYGEN REACTION – II

ALKYLTHIOSUBSTITUTED ETHYLENE[1]

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Abstract—The reaction of singlet oxygen with tetrakis(ethylthio)ethylene has been shown to afford diethylthiooxalate and diethyl disulfide. The expected diethylthiocarbonate was also obtained as a minor product. A similar reaction with bis(ethylthio)ethylene gave ethylthioglyoxalate together with diethyl disulfide. Formation of diethylthioacetaldehyde was also observed, and is suggested to proceed via the intermediary 1,2-dioxetane or perepoxide followed by preferential migration of the ethylthio group. On the other hand, phenylthioethylene is oxidized with singlet oxygen to give a thiol ester together with disulfide. This suggests that the formation of disulfide probably occurs via a radical pathway. The photooxygenation of disulfide in alcohol was also studied.

During the past 4–5 years, a large body of data has been collected which indicates that electronically excited singlet state molecules are the reactive intermediates in numerous photooxygenation reactions,[2–14] and three types of reaction are formulated: (1) Simple olefins bearing an allylic hydrogen are converted to allylhydroperoxides. The double bond shifts cleanly to the allylic position; the course of the reaction is analogous to the Alder "ene reaction". (2) Singlet oxygen cycloadds to conjugated dienes to give cyclic peroxides in the process like Diels-Alder reaction, and (3) singlet oxygen cycloadds to electron-rich olefins to give 1,2-dioxetanes.

Recent work has shown that the reaction is quite sensitive to the electron density in the double bond of the olefin.[8,15,16] The third mode reaction requires alkenes specially activated, for example, by amine or alkoxy groups, and the absence of very active allylic hydrogens in the molecule. Electron withdrawing substituents such as carbonyl or hydroxyalkyl groups deactivate the olefin.[15]

Reasonably stable tetramethoxy- and diethoxy-1,2-dioxetanes have been obtained in the photooxygenation of tetramethoxyethylene[17] and *cis* and *trans*-diethoxyethylenes,[18] respectively, and these have been observed to decompose cleanly to carbonyl compounds with chemiluminescence.[19,20]

On the other hand, a recent report states that in contrast to tetramethoxyethylene, tetrathioethylene is unreactive particularly toward electrophilic reagents.[21] However, Adam and Liu[22] have recently demonstrated the great reactivity of tetrathiosubstituted ethylene to singlet oxygen. They found that the photooxygenation of these compounds might produce the dioxetane which gave disulfide and dithiooxalate.

We report here similar results supporting the intermediacy of 1,2-dioxetanes in the addition of singlet oxygen to tetraalkylthioethylenes to give ultimately dithiooxalate and disulfide as major products, and to monoalkylthioethylenes to give both thiocarbonate as C–C bond cleavage and disulfide as C–S bond cleavage.

RESULTS AND DISCUSSION

Tetrathioethylene proves to be an excellent substrate for dye-sensitized photooxygenation; the C–S bond is cleaved to give the oxalate and disulfide.[1,22,23] Tetrakis(ethylthio)ethylene (1) in acetone was irradiated with a 100 watt high pressure mercury lamp for 1 hr in the presence of Rose Bengal as sensitizer. The oxygenation proceeded rapidly, and stopped after about 90% of the ethylene was consumed. Evaporative distillation of the solvent followed by gas chromatography of the residue gave diethyl disulfide (63%), diethylthiooxalate (2, 67%), diethylthiocarbonate (3, 7%) and unreactive ethylene (1, 10%). Absolute yields quoted are based on the thioethylene 1, and were determined by GLPC using an internal standard. The structures of these products were determined by comparison of spectra with those of authentic samples and by spectra and elemental analyses. In the absence of a sensitizer, any appreciable reaction could not be observed by irradiation of a solution of the ethylene.

Under the same conditions, tris(ethylthio)ethylene (5) in acetone took up oxygen (55% reaction at completion) to give ethylthioglyoxalate (6, 19%) and diethyl disulfide (32%) together with some diethylthiooxalate (2, 3%) and ethylthiocarbonate (3, 1%). Additional photooxygenation on the sulfur and oxidative rearrangement as a side reaction gave a sulfoxide and the product 7 in

1–2% yields. The structure of the sulfoxide is unknown, but its IR absorption clearly showed 1057 cm^{-1} (for S—O bond) and 1536 cm^{-1} (for C=C bond).[24] In addition, when the photooxygenation was carried out in methanol solution, the rearrangement product **7** (4%) was formed more efficiently and furthermore, methyl ethanesulfinate was isolated in 12% yield.

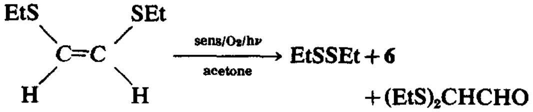
While the mechanism of the conversion of the thioethylenes to carbonyl compounds remains to be established, these experiments particularly, the isolation of the previously unreported cleavage products **3** give an additional evidence that 1,2-dioxetane (**4**) is formed, which is not stable and breaks down to the observed products.

Accepting the intermediacy of the 1,2-dioxetane, the formation of the oxalate and disulfide by C—S bond cleavage rather than the thiocarbonate by C—C bond cleavage is novel. A rationale for this unusual cleavage has been presented based on a comparison of the bond energies[22,25] of C—C and C—S bonds.

An alternative pathway for the product **7** formation could be the formation of a perepoxide intermediate **8**[5] from **5**, followed by expulsion of one O atom to the other molecule.

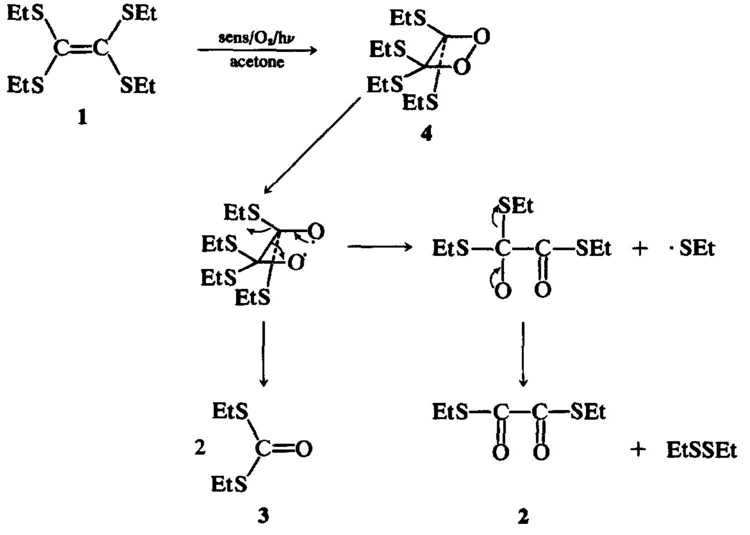
Similar oxidative rearrangements have been previously reported only for monoalkylthio- and 1,1-dialkylthiosubstituted ethylenes, under the autoxidation conditions, tri- and other di-substituted thioethylenes failed to undergo the oxidative rearrangement.[26] Therefore, the product **7** may be formed in the reaction with singlet oxygen.

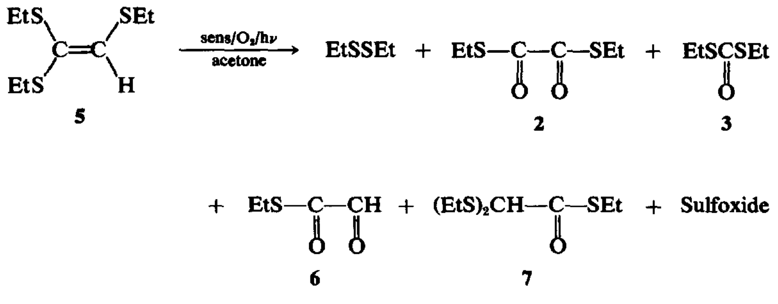
Photosensitized oxidation of cis-bis(ethylthio)ethylene (**9**) was carried out in acetone to give diethylthioacetaldehyde (**10**, 23%) together with diethyl disulfide (19%) and the product **6** (13%) at 72% reaction completion. The expected glyoxal was not detected under the analytical conditions employed.

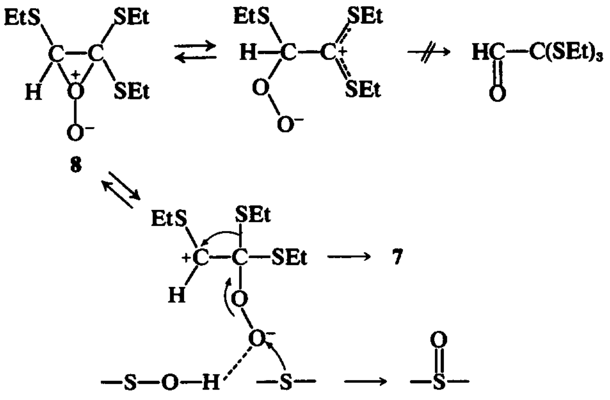


Prolonged oxidation resulted in a lower yield of the aldehyde since it reacts slowly with oxygen to give a mixture of several components.

Now, it is clear that under the above conditions, the di-, tri- and tetrathioethylenes are oxidized easily with singlet oxygen. This chemical behavior







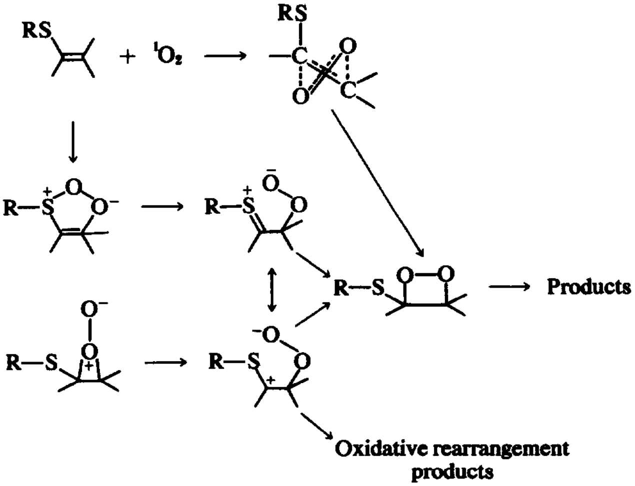
is not consistent with the description that singlet oxygen reacts only with electron rich olefins, because thioethylene is unreactive toward electrophilic and dienophilic reagents.[21]

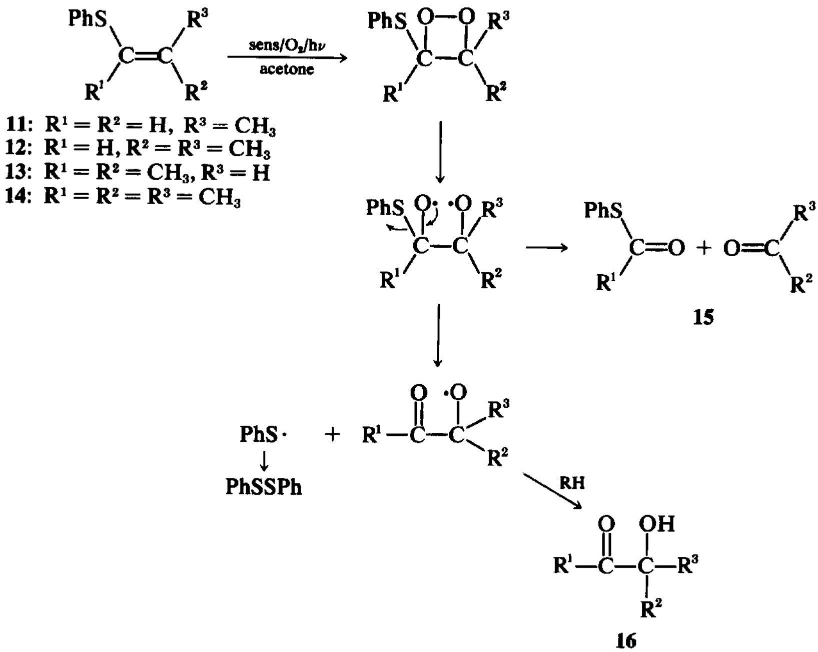
In contrast to "ene reaction", 1,2-dioxetane formation can be correlated with ionization potential and reactivity.[27] However, the remarkable reactivity of ethylthioethylenes suggested that singlet oxygen need not react only with electron rich olefins, but also with the molecules which have lower π-ionization potential. In these cases, either perepoxide or $2s+2a$ direct dioxetane formation appears to be an allowed process.[17,18] However, there is a possibility of initial attack by singlet oxygen on a S atom in the thioethylene (rather than on carbon) followed by transfer to carbon in the fact of Coffen's data that electrophilic species will be directed to one of the sulfur atoms rather than one central C atom and central double bond survives exposure to such reagents.[21]

When the photooxygenation of trimethyl(phenylthio)ethylene (14) was conducted in acetone or methanol solution, three major products, S-acethylthiophenol (15, $R_1 = Me$, 22%), 3-hydroxy-3-methyl-2-butanone (16, $R_1 = R_2 = R_3 = Me$, 8%), and diphenyl disulfide (18%) were obtained in 80% reaction completion. After sulfite reduction of the reaction mixture, new peaks expected from the "ene reaction" products were not observed by GLPC analysis.

The formation of significant amounts of products 15 ($R_1 = Me$) and diphenyl disulfide supported the two step biradical cleavage of the intermediate 1,2-dioxetane which gives homolytic cleavage of the O—O bond followed by C—S bond cleavage to give a thiyl radical and a ketoalkoxy radical. Two thiyl radicals combine together to form disulfide, and ketoalkoxy radical abstracts hydrogen from solvent to form the keto alcohol (16). On the other hand, the C—C bond cleavage in the decomposition of 1,2-dioxetane was also observed to form thiol ester as a favorable process. However, whether the C—C bond cleavage proceeds via a two step diradical or via a molecular concerted path can not be answered with certainty at this moment.

For comparison, Me substituted phenylthioethylenes, 11, 12 and 13 were also prepared and





11: $R^1 = R^2 = H, R^3 = CH_3$
12: $R^1 = H, R^2 = R^3 = CH_3$
13: $R^1 = R^2 = CH_3, R^3 = H$
14: $R^1 = R^2 = R^3 = CH_3$

photooxidized under the identical conditions. In acetone each phenylthioethylene led to two products, phenylthiol ester analogous to **15** and diphenyl disulfide in moderate yields, and some minor product was formed by the fragment of C—S bond cleavage. After sodium sulfite reduction of the reaction mixture, no "ene reaction" products were found. It is obvious from Table 1 that in less substituted ethylenes, the cleavage of the C—S bond occurred effectively, but in tetrasubstituted thioethylenes, the cleavage of C—C bond took place as much as the cleavage of the C—S bond. Both the substituent and solvent have a marked effect on the product ratio, methyl substituents and polar solvents increasing the C—C bond cleavage.

Again, when the photooxygenations were conducted in methanol solution, products resulting from solvent participation to the intermediate 1,2-dioxetane or perepoxide were also obtained in significant amounts together with diphenyl disulfide and C—C bond cleavage products. In a photooxygenation of **11**, diphenyl disulfide was formed in 40% yield along with phenylthioformate (**17**, 2%), acetal (**18**, 5%) and unreacted ethylene (**11**, 2%); the remainder of the reaction mixture consisted of methanol participation products (**19** and **20**, 12%) to the intermediate 1,2-dioxetane. After sodium sulfite reduction of the reaction mixture, products involving "ene reaction" were not obtained. The formation of significant amounts of both **19** and **20** can be accounted for by the previous described dioxetane intermediate mechanism.[28] In the photooxygenation of **13**, diphenyl disulfide and 3-hydroxy-2-butanone were obtained in 43 and 46% yields respectively, together with S-acetylthiophenol (**15**, 21%) and 3-phenylthio-2-butanone (11%).

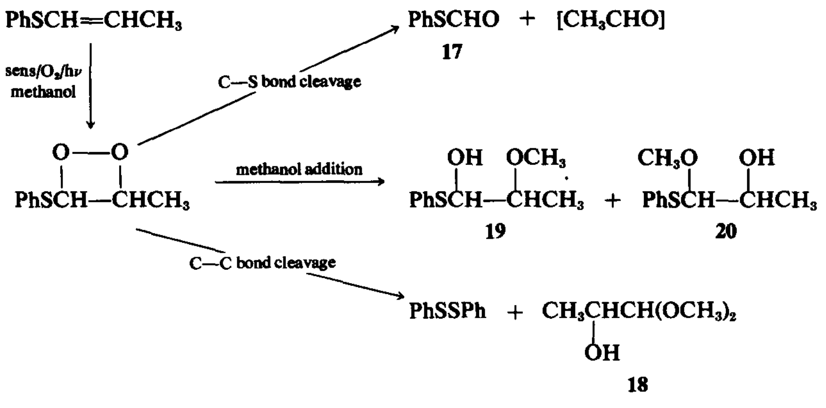
Table 1. Ratio of C—C and C—S bond cleavage in the photooxygenation of phenylthioethylenes

Ethylene	Product ratio (C—C/C—S bond cleavage) In acetone	 In methanol
$PhSCH{=}CHCH_3$ (**11**)	0·22	0·05
$PhSCH{=}C(CH_3)_2$ (**12**)	0·41	0·22
$PhSC(CH_3){=}CHCH_3$ (**13**)	1·08	0·48
$PhSC(CH_3){=}C(CH_3)_2$ (**14**)	1·20	1·05

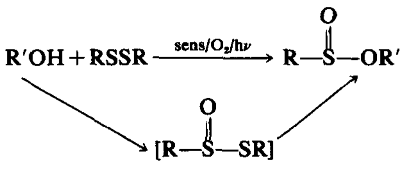
Relative reaction rates were obtained by competitive techniques. A solution containing 2·95 mmole of **1** and 2·31 mmole of **14** were oxidized as described above. After 50 ml of oxygen was consumed, the relative product ratio of the oxalate **2** and S-acetylthiophenol **15** was determined by gas chromatography, and found to be 1·2 ± 0·1. Considering that singlet oxygen was comsumed by **14** to give diphenyl disulfide and S-acetylthiophenol at equal ratio, the relative ease of photooxygenation of **1** and **14** is approximately 0·6, which suggests methyl and thiyl groups comparably effect dioxetane formation in the reaction of ethylenes with singlet oxygen.

We have turned our attention to photooxygenation of disulfides, although there are some reports that sulfur atom is reactive to singlet oxygen to give sulfoxide.[15, 29–31]

Photosensitized oxidation of alkyl disulfides, **21**, **22**, **23** and **24**, in alcohol leads to the oxidation



of the disulfide to give alkylsulfinate in high yield. In a typical experiment, the photooxygenation of dimethyl disulfide in methanol in the presence of Rose Bengal gave methyl methanesulfinate in 33% yield (45% reaction completion), and in ethanol to give ethyl methanesulfinate in 49% (63% reaction completion). The yields are based on dimethyl disulfide and were determined by GLPC using an internal standard. The structures of these sulfinates were identified by comparing GLPC retention times and IR and NMR spectra with those of authentic samples.



21: $R = CH_3$, $R' = CH_3$ 73% yield
22: $R = CH_3$, $R' = C_2H_5$ 78
23: $R = C_2H_5$, $R' = CH_3$ 79
24: $R = C_2H_5$, $R' = C_2H_5$ 68

The photosensitized oxidation of di-t-butyl disulfide in methanol did not produce the corresponding sulfinate. The oxidation could be due to form initially thiolsulfinate and then reaction of the thiolsulfinate with alcohol to give alkylsulfinate.

EXPERIMENTAL

Instruments. IR spectra were recorded on a Hitachi Infracord Model EPI-G3. NMR spectra were recorded on a Varian A-60D spectrometer in CCl_4 solutions with an internal TMS standard. Gas-liquid partition chromatography was used extensively for the separation and purification of products and for yield determinations. The internal standard method was used in yield determinations. The GLPC columns used included (A): 10% SF-96, 2 m × 6 mm, on Celite 22, and (B): 10% Carbowax 20M, 2 m × 6 mm, on Celite 22.

Materials. The reagents, dimethyl, diethyl and di-t-butyl disulfides were obtained commercially and used without further purifications. Tetrakis(ethylthio)-, tris-(ethylthio)- and *cis*-bis(ethylthio)ethylenes were prepared by displacement on the corresponding chloroethylenes by sodium ethylmercaptide.[32] Tetrakis(ethylthio)ethylene had a m.p. 52–53°, NMR: 1·23 (t, 3H) and 2·82 ppm (q, 2H). Tris(ethylthio)ethylene had peaks at 1·23 ppm (t, 6H), 1·33 ppm (t, 3H), 2·65 ppm (q, 4H), 2·72 ppm (q, 2H) and 6·33 ppm (t, 1H); b.p. 102–105°/1·5 mmHg. *cis*-Bis(ethylthio)ethylene had NMR peaks at 1·27 (t, 6H), 2·66 (q, 4H) and 5·99 ppm (s, 2H); b.p. 114–115°/25 mmHg. Phenylthioethylenes (**11–14**) were prepared in 40–70% yields, starting from allyl phenyl sulfide (for **11** and **12**),[33] thiophenol and ethyl methyl ketone (for **13**) or isopropyl methyl ketone (for **14**),[34] following the known procedures.

Sensitized photooxygenation of tetrakis(ethylthio)ethylene (**1**). A soln of 0·5 g Rose Bengal, 2·4 mmole of **1** in 120 ml acetone was irradiated in a water cooled circulated apparatus through which O_2 was recirculated. The light source was a Rikosha 100 watt high pressure mercury lamp. After 30–60 min irradiation, a soln was condensed and injected directly into column A. The major products, diethylthiooxalate **2** and diethyl disulfide were collected. The NMR spectrum of the oxalate **2** had peaks at 1·33 (t, 6H), and 2·96 ppm (q, 4H); IR spectrum: 1677 cm^{-1}. (Found: C, 40·81; H, 6·02; S, 36·30. Calcd. for $C_6H_{10}O_2S_2$: C, 40·43; H, 5·65; S, 35·97%). The minor product, diethylthiocarbonate **3** was collected. The NMR spectrum of **3** had peaks at 1·30 (t, 6H), and 2·96 ppm (q, 4H); the IR spectrum had a thiolcarbonate peak at 1648 cm^{-1}. (Found: C, 39·89; H, 6·58. Calcd. for $C_5H_{10}OS_2$: C, 39·97; H, 6·71%). Other photooxygenations were run similarly; the products had analogous spectra and properties. Appropriate control experiments were performed. Under the reaction conditions, there was insignificant decomposition of the solvent and the products were neither isomerized nor destroyed.

Photooxygenation of tris(ethylthio)ethylene (**5**). A soln of 3 mmole of **5** and 0·5 g Rose Bengal and 120 ml acetone was irradiated at 20–25°, and worked up by the procedure described previously. Analysis of the mixture by GLPC indicated a yield of 32% diethyl disulfide, 19% aldehyde **6**, 1% diethylthiocarbonate **3**, 3% diethylthiooxalate **2** (identified by comparison of the retention time of known samples), 2% compound **7**, 2% a sulfoxide and 45% unreacted ethylene **5**. Compound **6** was tentatively identified as ethylthioglyoxalate by NMR and IR spectra; NMR: 1·34 (t, 3H), 3·00 (q, 2H) and 9·20 ppm (s, 1H); IR spectrum had CO peaks at 1740 and 1675 cm^{-1}. (Found: C, 40·38; H, 5·19; S, 26·93. Calcd. for $C_4H_6O_2S$: C, 40·68; H, 5·12; S, 27·10%). Compound **7** had NMR peaks at 1·27 (t, 9H); 2·68 (q, 4H), 2·91 (q, 2H), and 4·36 ppm (s, 1H). The IR spectrum had a peaks at 1682 cm^{-1} corresponding to thiolester. (Found: C, 42·41; H, 7·18; S, 42·74. Calcd. for $C_8H_{16}OS_3$: C, 42·85; H, 7·19; S, 42·81%). The sulfoxide was tentatively identified as the oxidation product on the sulfur of **5**, but which S atom is oxidized is not clear. The NMR spectrum had peaks at 1·16 (t, 3H), 1·43 (t, 6H), 2·82 (q, 6H) and 7·37 ppm (s, 1H). The IR spectrum had peaks at 1057 cm^{-1} (for S—O bond) and 1536 cm^{-1} (for C=C bond): (The IR spectrum of **5** had a peak at 1513 cm^{-1} for C=C bond). (Found: C, 42·75; H, 7·04; S, 42·55. Calcd. for $C_8H_{16}OS_3$: C, 42·85; H, 7·19; S, 42·81%).

Photooxygenation of cis-*bis(ethylthio)ethylene* (**9**). A soln of 2 mmole of **9**, 0·5 g Rose Bengal and 120 ml acetone was irradiated at 25–30° for 45 min, and worked up as described previously. Analysis of the mixture by GLPC indicated a yield of 19% diethyl disulfide, 13% of **6**, 23% compound **10** and 28% of uncreacted ethylene **9**. The compound **10** was identified as the diethylthioacetaldehyde by the NMR spectrum, which had peaks at 1·29 (t, 6H), 2·61 (q, 4H), 4·09 (d, 1H, d = 4·5 c/s) and 9·09 ppm (d, 1H, d = 4·5 c/s). The IR spectrum had peaks at 1717 and 2705 cm^{-1} corresponding to C=O and C—H of aldehyde. (Found: C, 45·02; H, 7·50; S, 38·27. Calcd. for $C_6H_{12}OS_2$: C, 43·87; H, 7·36; S, 39·03%). The product was unstable at room temp and satisfactory analytical data were not obtained.

Photooxygenation of 1-phenylthio-2-methylethylene (**11**). A soln of 10 mmole of **11** in 120 ml acetone containing 0·5 g Rose Bengal was photooxidized at 20–25° for 45 min after which time all of the **11** was consumed (230 ml of O_2 was taken up). After distillation of solvent, gas chromatography on column A gave 38% of diphenyl disulfide and 9% of phenylthioformate (**17**).

The IR spectrum of **17** had prominent peaks at 3050, 2813, 1688, 1479, 1442, 784, 730 and 691 cm^{-1}. The NMR spectrum had peaks at 7·46 (s, 5H) and 10·20 ppm (s, 1H). This compound was also prepared from thiophenol, formic acid and Ac_2O in the presence of a catalytic amount of pyridine.[35]

Photooxygenation of 1-phenylthio-2,2-dimethylethylene (**12**). A soln of 12·2 mmole of **12** in 120 ml acetone containing 0·5 g Rose Bengal was irradiated as the previously described. After 40 min, 270 ml of O_2 was taken up (98% reaction completion). By means of retention time and IR spectrum, the products were found to be diphenyl disulfide and **17**. 2·0 g of Na_2SO_3 was added to the mixture and allowed to stand at room temp for 24 hr. After working up the mixture, new products could not be detected by GLPC.

Photooxygenation of 1-phenylthio-1,2-dimethylethylene (**13**). A soln of 11·1 mmole of **13** in 120 ml acetone containing 0·5 g Rose Bengal was irradiated as described previously. After 40 min, 190 ml of O_2 was taken up (89% reaction completion). The mixture was analyzed by GLPC after Na_2SO_3 reduction for 24 hr at room temp. Analytical gas chromatography on column A served to separate dipehyl disulfide and S-acetylthiophenol (**15**, R^1 = Me). The NMR spectrum of **15** (R^1 = Me) had peaks at 2·35 (s, 3H) and 7·43 ppm (s, 5H). The IR spectrum had prominent peaks at 1715, 1483, 1444, 1356, 1120, 1093, 954 and 752 cm^{-1}. This product was also prepared in 56% yield from thiophenol and acetyl chloride in the presence of some pyridine,[36] b.p. 117–119/23 mmHg.

Photooxygenation of trimethyl(phenylthio)ethylene (**14**). A soln of 9·55 mmole of **14** in 120 ml acetone containing 0·5 g Rose Bengal was photooxygenated at 20–25° for 45 min as previously described. 200 ml of O_2 was taken up (94% reaction completion). Analysis of mixture by GLPC indicated 3 major products. Two of them were found to be diphenyl disulfide and **15** (R^1 = Me) by comparison of their retention times and IR spectra with those of authentic samples. The third product was tentatively identified as 3-hydroxy-3-methyl-2-butanone by the NMR spectrum, which had peaks at 1·32 (s, 6H), 2·17 (s, 3H) and 3·54 ppm (broad s, 1H). This product was also compared with an authentic sample.[37] After Na_2SO_3 reduction of the mixture, no additional products were observed in GLPC.

Photooxygenation of 1-phenylthio-2-methylethylene (**11**) *in methanol*. A soln of 9 mmole of **11**, 0·5 g Rose Bengal and 120 ml MeOH was irradiated at 20–25° for 45 min and worked up as the described previously. 2 g Na_2SO_3 was added to the mixture which then was kept at room temp for 24 hr. Analysis of the mixture by GLPC indicated the formation of 2 major products and 5 minor products. The major products were found to be phenylthioformate and diphenyl disulfide by comparison of their retention times and spectra with those of authentic samples. The minor products had a yield of 12% of **19** and **20**, 5% of **18**, 2% of compound Y and 2% of compound Z. The compound **19** was identified as 3-hydroxy-3-phenylthio-2-methoxy ropane by spectral and elemental analysis, but this compound also contained isomer **20** in ratio 3:2. The NMR spectrum had peaks at 1·23 and 1·25 (d, 3H), 2·53 (broad s, 1H), 3·48 and 3·52 (s, 3H), 3·4–3·8 (m, 1H), 4·26 and 4·29 (d, 1H) and 7·3 ppm (m, 5H). The IR spectrum had prominent peaks at 3500–3400, 3050, 2925, 1581, 1480, 1148, 1076, 1026 and 742 cm^{-1}. (Found: C, 66·75; H, 6·50. Calcd. for $C_{10}H_{14}O_2S$: C, 60·57; H, 7·12. Calcd. for dehydrated product $C_{10}H_{12}OS$: C, 66·63; H, 6·71%). The compound **18** was identified as an acetal by NMR spectrum, which had peaks at 1·09 (d, 3H), 0·95–1·35 (m, 1H), 3·32 and 3·36 (s, 6H), 3·6 (m, 1H) and 3·97 ppm (d, 1H). Compound Y was identified as 1-hydroxy-2-propane by the NMR spectrum, which had peaks at 2·13 (s, 3H), 2·87 (s, 1H) and 4·13 ppm (s, 2H). The IR spectrum had peaks at 3400–3395, 1728, 1425–1408, 1361, 1087 cm^{-1}, which was independently prepared from bromoacetone.[38] Compound Z was identified as phenylthioacetone by its NMR spectrum, which had peaks at 2·20 (s, 3H), 3·53 (s, 2H) and 7·25 ppm (s, 5H). The IR spectrum had a CO peak at 1715–1725 cm^{-1}. The formation of the compounds Y and Z may arise via radical process, although it is not established.

Photooxygenation of disulfides in alcohols. A soln of 20–40 mmole dialkyl disulfide and 0·5 g Rose Bengal in alcohol was photooxygenated for 1 hr at 20–25° (approximately 50% reaction completion) in a 150 mm × 20 mm Pyrex test tube having an oxygen bubbler, resulting in the formation of a corresponding sulfinate in high yield. Spectral and analytical data of the sulfinates are shown below. **21**: NMR 2·51 (s, 3H), 3·68 ppm (s, 3H); IR: 1128, 1010 cm^{-1}. (Found: S, 33·25. Calcd. for $C_2H_6O_2S$: S, 34·06%). **22**: NMR 1·35 (t, 3H), 2·51 (s, 3H), 4·02 ppm (q, 2H); IR: 1134, 1026, 887 cm^{-1}. (Found: S, 29·23. Calcd. for $C_3H_8O_2S$: S, 29·65%). **23**: NMR 1·23 (t, 3H), 2·64 (t, 2H), 3·70 ppm (s, 3H); IR: 1125 and 975 cm^{-1}. (Found: S, 29·81. Calcd. for $C_3H_8O_2S$: S, 29·65%). **24**: NMR 1·22 (t, 3H), 1·34 (t, 3H), 2·63 (q, 2H) and 4·03 ppm (q, 2H); IR: 1127, 1009 and 890 cm^{-1}. (Found: S, 26·08. Calcd. for $C_4H_{10}O_2S$: S, 26·24%).

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