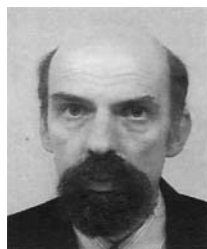


Photochemical and electrochemical oxygenation of thiophenes, benzo[*b*]thiophenes and dibenzothiophenes; photochemical and electrochemical behaviour of their oxygenated intermediates and products

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The photooxygenation of thiophenes, benzo[*b*]thiophenes and dibenzothiophenes is discussed, especially in view of the oxidative removal of these S-containing contaminants from fuels. Furthermore, the photochemistry of the intermediates and the products from these processes is detailed. Finally, an account is given of the electrooxidation of thiophenes and derivatives to the corresponding sulfoxides and sulfones as well as of the electrochemical behaviour of the intermediate thiophene S-oxides.

Keywords: electrochemistry, photochemistry, thiophenes, benzo[*b*]thiophenes, dibenzothiophenes, desulfurisation of fuels

1. Introduction

Sulfur-containing heterocyclic compounds, especially dibenzothiophenes (DBTs, **1**) and higher annelated homologues, e.g., **2**, are ubiquitous contaminants in fossil fuels such as crude oil and natural gas (Fig. 1).¹ Polycyclic sulfur-containing aromatic molecules are found in coal tar,² but they can also be detected in processed products such as in mineral oil³ and lubricating oil.⁴ Also, they can be observed in the flue gases derived from these products such as in the effluents of burnt hard-coal,⁵ where 57 different thiarenes have been identified in a group of 240 polycondensed aromatic compounds (PACs), all of them at levels of over 0.1 mg per kg of coal.⁵ It has been found that S-containing arenes with four and five condensed rings contribute significantly to the cancerogenicity of such effluents.⁵ Minimization of sulfur-containing polycondensed aromatic compounds in fuels is an ongoing concern. Typically, three different strategies are employed for the removal of these contaminants: (a) reductive desulfurisation, frequently

involving the use of heterogeneous metal catalysis,⁶ (b) oxidative ring cleavage of the sulfur containing heterocycle, traditionally involving microbial oxidation (biodesulfurisation),^{1,7} or, (c) chemical oxygenation of the sulfur moiety by a strong chemical oxidant such as hydrogen peroxide or peracids with a subsequent or concomitant removal of the oxidised species by aqueous extraction.^{8,9} The latter approach has merits due to low demands on temperature and pressure and has the advantages of lower operating costs.

Against this background, foregoing the consumption of expensive and potentially hazardous oxidising agents, the use of molecular oxygen, water or an easily recyclable oxidant has been discussed. Therefore, the photochemical and electrochemical oxidation of thiophenes and their benzologues as well as the electro- and photochemical behaviour of the oxygenated thiophene and benzannelated thiophene species, as intermediates in this oxidative transformation, have become of considerable interest.

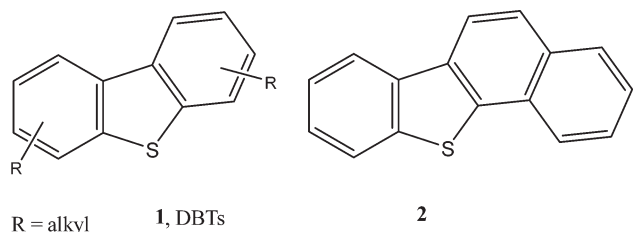
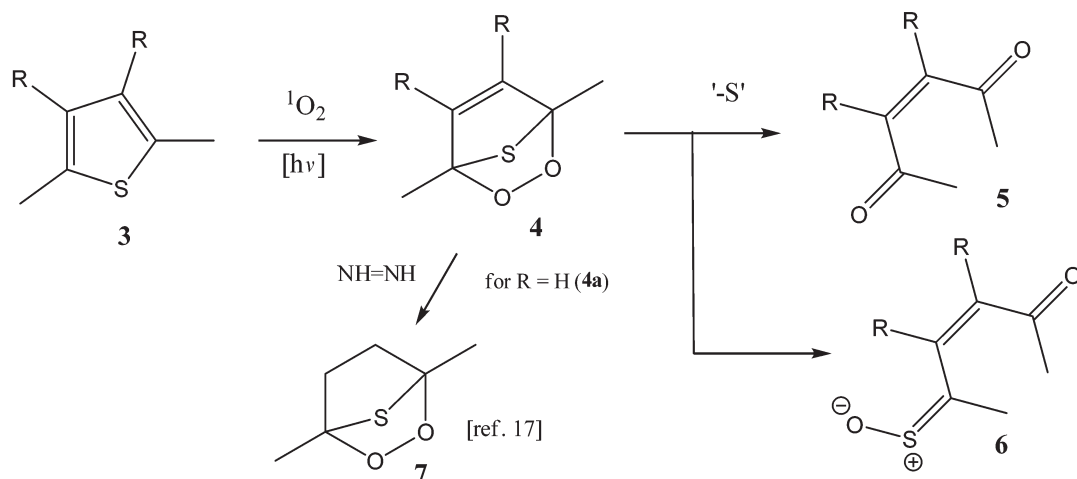


Fig. 1 Sulfur containing contaminants of fossils fuels.

2. Photooxygenation of thiophenes

Thiophene itself, as the parent compound, usually does not undergo oxygenation with photochemically generated singlet oxygen ¹O₂.^{10–14} The same is true for monoalkylated thiophenes such as 2-ethylthiophene.¹⁵ However, 2,5-bis-alkylated or higher alkylated thiophenes **3** react with ¹O₂ to form endoperoxide **4** (Scheme 1), which can be detected at low temperatures by NMR spectroscopy.¹⁴ In the case of endoperoxide **4a** (R = H), resulting from the reaction of 2,5-dimethylthiophene with ¹O₂,^{11,16} diimine reduction has led to the stable endoperoxide **7** (R = H).¹⁷ If the photolysis is carried out at room

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Scheme 1

temperature, endoperoxide **4** reacts further in a thermal reaction to afford either thioketone *S*-oxides **6** or enediones **5** with concomitant extrusion of sulfur (Scheme 1).^{10–14,18} Retro Diels–Alder reaction to thiophene and singlet oxygen is not observed.¹⁹

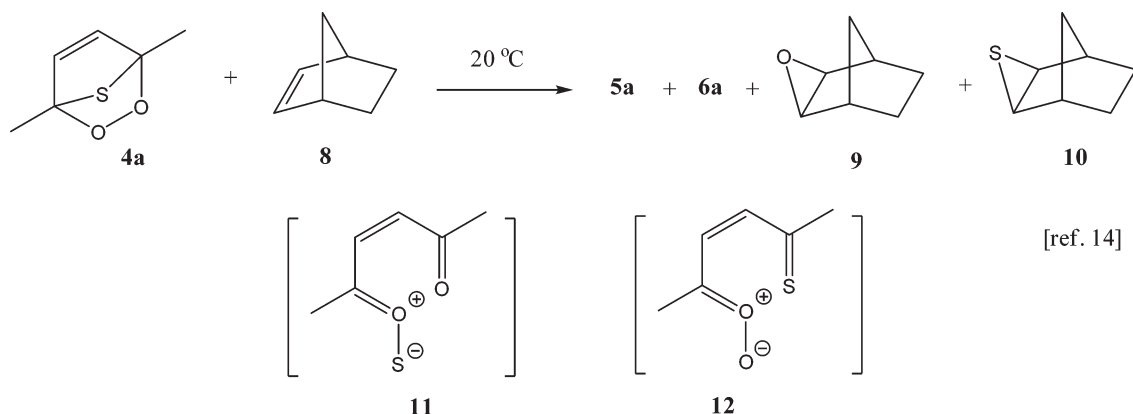
The reaction of the endoperoxides **4**, to **5** and **6** has been described to proceed via intramolecular rearrangement.¹⁸ When endoperoxide **4a** is reacted at 20 °C to form **5a** and **6a** in presence of norbornene **8**, small amounts of norbornene oxide **9** and norbornene sulfide **10** are also formed, indicating the presence of intermediates able to transfer sulfur and oxygen (Scheme 2). Carbon *O*-sulfide **11** and carbonyl oxide **12** have been proposed as possible intermediates. Under identical conditions *cis*-2,5-dimethyl-3-hexene forms mostly the *cis*-oxirane and *cis*-thiirane, whilst the *trans*-alkene forms mostly the *trans*-oxirane and *trans*-thiirane; these findings have discounted radical species as direct sulfur or oxygen transfer agents in these transformations.

In the case of cyclohexeno annelated thiophenes **13**, the endoperoxides **14** formed upon reaction with singlet oxygen can also transfer the sulfur moiety to cycloalkenes transforming these to thiiranes, while themselves forming ene-triones **15**.^{20,21} In the presence of triphenylphosphine, the sulfur moiety is extruded giving triphenylphosphine sulfide, whilst the enetrione **15** cyclises to furan system **16** (Scheme 3).²² An endoperoxide intermediate is also postulated in the methylene blue-sensitized photooxygenation of 2,3-dimethyl-4,5,6,7-tetrahydrobenzo[*b*]thiophene **17** in methanol, which gives cyclic sulfoxide **18** (Scheme 3).¹¹

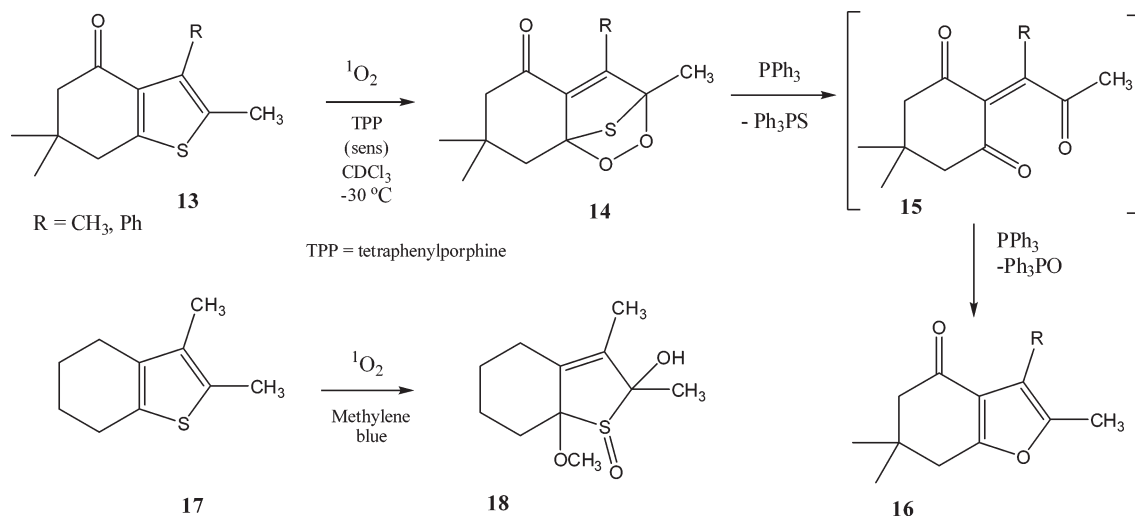
Thiophene itself has been noted to photooxidise with O₂ under UV-irradiation in the presence of Na-ZSM-5 zeolite as a catalyst, although the reaction product has not been characterised.²³ Photooxidation of dialkylated thiophenes, as major sulfur-containing components in FCC light gasoline (light gasoline derived from fluid catalytic cracking), with concomitant liquid–liquid extraction of the products with acetonitrile has been used in a ‘deep desulfurisation process’, typically decreasing the sulfur content of the FCC light gasoline from 309 ppm to 68 ppm.²⁴ Direct photolytic oxidation of 2,5-dimethylthiophene in presence of titanium-pillared montmorillonite has also been found to be viable. Again, the reaction was used in combination with a liquid-liquid oil-acetonitrile extraction process, which proved to be successful in removing 97.4% of the sulfur-containing components from the oil.²⁵

3. Photooxygenation of dibenzothiophenes and benzo[*b*]thiophenes

Extensive research effort has been invested in the potential oxidative removal of dibenzothiophenes from contaminated fuels. The naturally occurring photooxidative degradation of dibenzothiophene (DBT, **1a**) and of alkylated DBTs **1** in contaminated matrices has been found to be slow in comparison to their methylated PAC (polycondensed aromatic compound) analogues. Thus, in crude oil maltenic fractions, spread on deionised water, DBT remained largely unchanged under *in vitro* photooxidation.²⁶ In further experiments, DBT has been shown to be stable under direct photolysis.^{27,28} Nevertheless,



Scheme 2



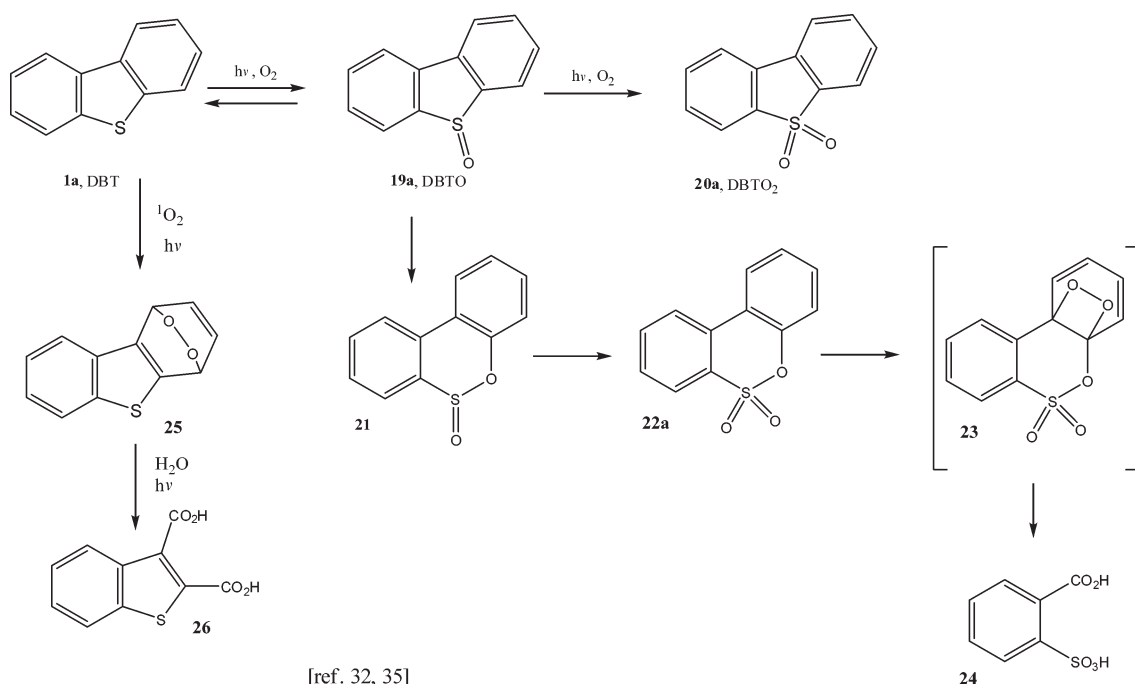
Scheme 3

DBT in sea water, within an oil spill, oxidises to dibenzothiophene *S*-oxide (DBTO, **19**) and to dibenzothiophene *S,S*-dioxide (DBTO₂, **20**) upon photoirradiation with sunlight.²⁹ As DBTO **19** and DBTO₂ **20** are water-soluble and as they can be removed from oils by extraction, the photooxygenation of dibenzothiophenes and congeners in oils, including in light oils, has become of considerable interest.

Dibenzothiophenes have been subjected to photocatalytic oxidation in the presence of chemical oxidants such as H₂O₂ using TiO₂³⁰ or Ti-containing zeolite³¹ as catalysts. Here, the *S*-oxygenated dibenzothiophenes and in the case of alkylated dibenzothiophenes, hydroxyalkyl- or formyl substituted dibenzothiophenes have been reported. Although the authors have noted that a full screening of products had not been achieved, no hydroxybiphenyls or related compounds have been found that would suggest an oxidative cleavage of the C–S bond in these cases. Nevertheless, it has been reported that the oxygenated products move into the aqueous phase, so that

hydroxylated aromatic products cannot be excluded. Earlier, it had been shown by Hirai *et al.* that photoirradiation of a biphasic mixture of dibenzothiophene **1a** in aqueous acetonitrile in the presence of oxygen leads to dibenzothiophene *S*-oxide (DBTO, **19a**), dibenzothiophene *S,S*-dioxide (DBTO₂, **20a**) and dibenzo[*c,e*][1,2]oxathiin 6-oxide (DBT-sultine, **21**).³² Initially, DBTO **19a** is formed. With continuing irradiation, DBTO₂ **20a** and DBT-sultine **21** form, while the concentration of DBTO decreases (Scheme 4).³² DBTO₂ **20a** is not transformed further upon photoirradiation.

Jenks has shown that DBTO **19a** is not photostable,³³ while DBTO₂ **20a** is, at least in solvents that are poor hydrogen donors.³⁴ Further photoirradiation leads to water soluble products, which one might expect to be biphenylsulfonates. Thus, it seems likely that DBT-sultine **21** could undergo oxidative C–S cleavage to anionic compounds. However, Hirai *et al.* observed benzo[*b*]thiophene-2,3-dicarboxylic acid **26** and sulfobenzoic acid **24a** as sole products, apart from DBTO₂



Scheme 4

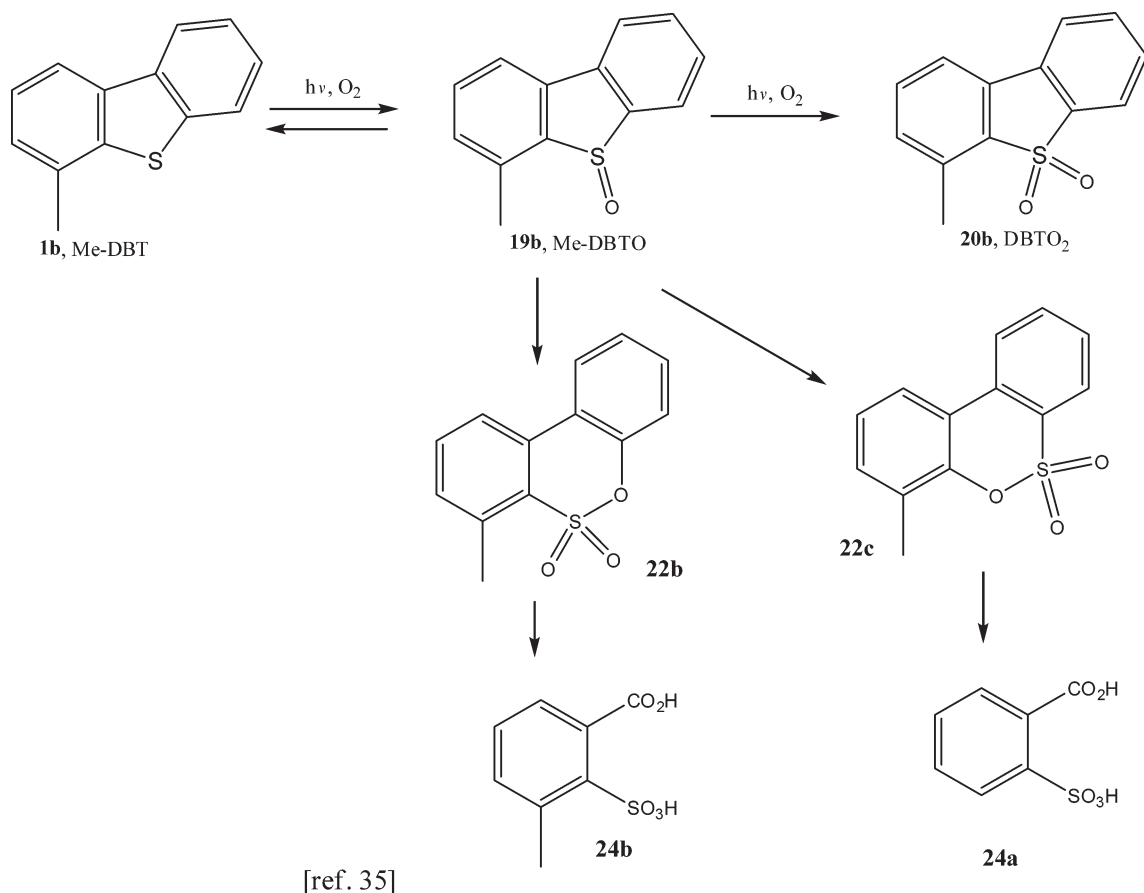
20a, after 30 h of photoirradiation at $\lambda > 280$ nm in acetonitrile–water.³⁵ The authors tentatively explained this result by addition of singlet oxygen to dibenz[*c,e*][1,2]oxathiin-6,6-dioxide **22a**, formed from sultine **21**, to give the dioxacyclobutane **23**. The latter reacts photolytically with water to give final product **24a**.³⁶ On the other hand, Hirai *et al.* envisioned that DBT can also react with singlet oxygen to form endoperoxide **25**, which reacts with water under photoirradiation to give benzo[*b*]thiophene-2,3-dicarboxylic acid **26** (Scheme 4). 4-Methyl-DBT **1b** gives a mixture of sulfobenzoic acids **24a** and **24b** (Scheme 5) as well as 4-methyl-DBTO₂ **20b**, while 4,6-dimethyl-DBT **1c** gave sulfobenzoic acid **24b** and 4,6-dimethyl-DBTO₂ **20c** exclusively (Scheme 6).³⁵ In none of the reactions did Hirai *et al.* observe any formation of dibenzofuran that was reported from a separate experiment by Khudayer,³⁶ nor the formation of biphenyls.³² The order of reactivity was found to be 4,6-dimethyl-DBT **1c** > 4-methyl-DBT **1b** > DBT **1a**.³² Benzo[*b*]thiophene (BT, **27a**) was converted to more polar compounds under the conditions,³² but initially, the products were not identified.³² Nevertheless, Hirai *et al.* revisited the reaction and isolated 2-sulfobenzoic acid **24a** as the main compound after 10 h photoirradiation of BT in wet acetonitrile at $\lambda > 280$ nm (Scheme 7).³⁵

Bobinger and Anderson³⁷ had also noted formation of 2-sulfobenzoic acid **24a** when BT **27a** was photoirradiated in a H₂O–MeOH mixture. Both groups formulated benzothio-phenene-2,3-dione **28** as a key intermediate in the reaction (Scheme 7). Later, Hirai *et al.* effectively formulated reaction conditions for the photooxygenation of DBT and BT at $\lambda > 400$ nm, using 9,10-dicyanoanthracene (DCA) as a sensitizer.^{38,39} Here, the products were DBTO and DBTO₂, exclusively. It is thought that the initially formed exciplex is

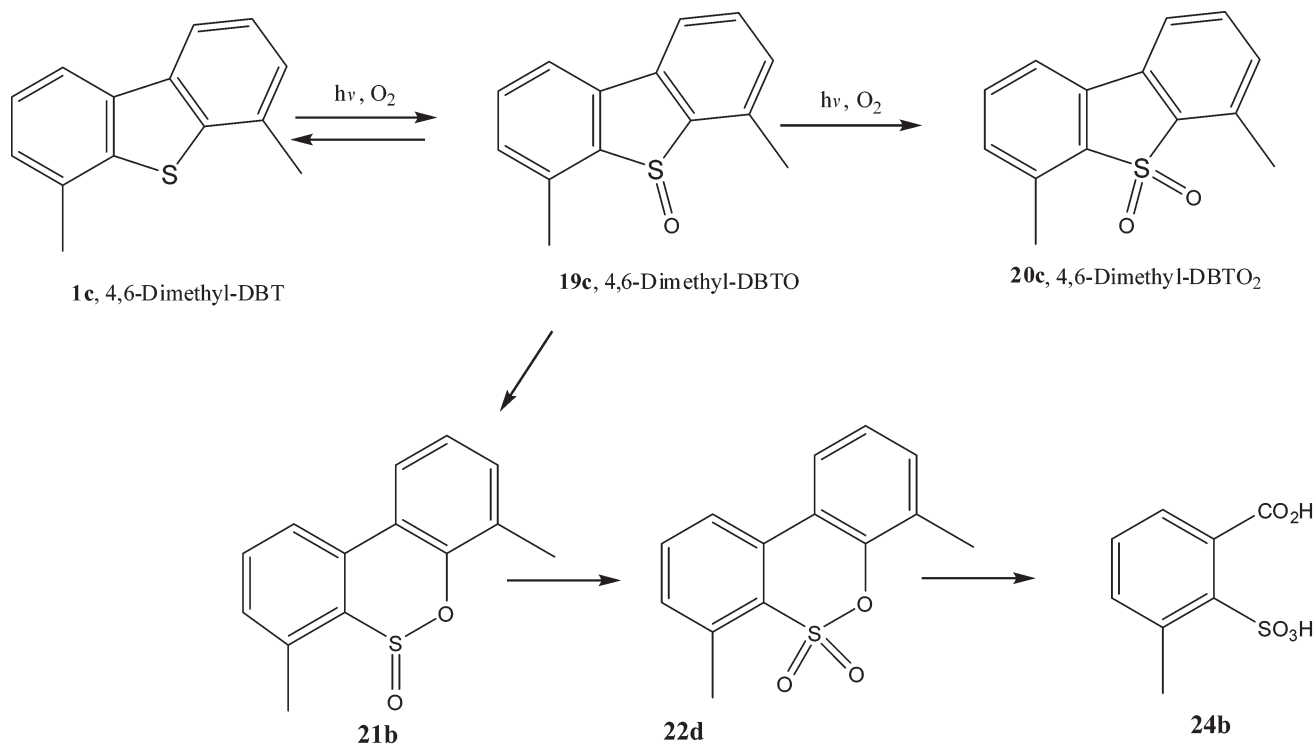
separated into radical ions [DBT⁺ --- DCA⁻] and that DCA⁻ reduces oxygen to the superoxide anion (O₂⁻), with O₂⁻ and DBT⁺ finally forming DBTO. Both 4-MDBT and 4,6-DMDBT were found to undergo slower oxygenation than DBT, although their fluorescence quenching rates of DCA are slightly higher. BT was shown to give benzo[*b*]thiophene-2,3-dione and sulfobenzoic acid under the same conditions.^{38,39} Also, 2- and 3-alkylated benzothiophenes can be oxidised photolytically, when irradiated at $\lambda > 400$ nm in the presence of DCA. Here, 3-methyl-BT **27b** gives benzo[*b*]thiophene-3-carbaldehyde **31a** and benzo[*b*]thiophene-3-carboxylic acid **32a**, while 2,3-dimethyl-BT **27c** is converted to 2-methylbenzo[*b*]thiophene-3-carbaldehyde **31b**, 3-methylbenzo[*b*]thiophene-2-carbaldehyde **31c**, benzo[*b*]thiophene-2,3-dicarbaldehyde **31d** and benzo[*b*]thiophene-2,3-dicarboxylic acid **32b** (Scheme 8).

Benzo[*b*]thiophene-3-carbaldehyde **31a** is also produced from 3-methyl-BT **27b** upon irradiation with UV light ($\lambda > 280$ nm, in acetonitrile) without added sensitizer, but in wet acetonitrile, **31a** is converted further to sulfobenzoic acid **24a** (Scheme 9).³⁵ Under the latter conditions, acetylbenzenesulfonic acid **24c** and benzenesulfonic acid **32** are also produced from 3-methyl-BT **31a**.³⁵ At $\lambda > 280$ nm, 2,3-dimethyl-BT **27c** is converted into sulfobenzoic acid **24a**, 2-acetylbenzenesulfonic acid **24c** and benzenesulfonic acid **32** with trace amounts of 2-methylbenzo[*b*]thiophene-3-carbaldehyde **31b** and 3-methylbenzo[*b*]thiophene-2-carbaldehyde **31c**. Benzo[*b*]thiophene-2,3-biscarbaldehyde **31d** was also detected during the course of photoirradiation (Scheme 10).³⁵

Yazu *et al.* have investigated the photooxygenation of dibenzothiophene and methylated dibenzothiophenes using anthraquinone as sensitizer.⁴⁰ Here, the outcome was found to



Scheme 5



[ref. 35]

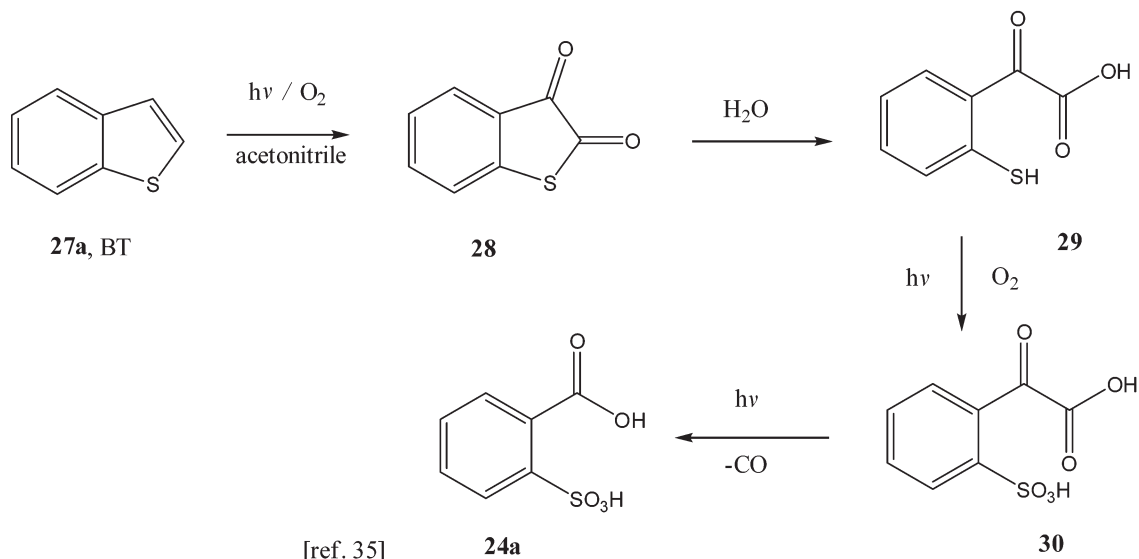
Scheme 6

solvent dependent, with non-polar solvents such as benzene or *n*-octane suppressing the reaction.

Changes to the conditions of the photoirradiation of both DBT and BT derivatives tend to affect the types and the contribution of products obtained. Thus, the use of a YAG laser ($\lambda = 266$ nm) leads to a rapid transformation of DMDBT (10 s for 10^{-6} M solutions in cyclohexane), where an array of products, including CO, methanol and phenol were detected.⁴¹ The photooxidation of DBT over TiO₂ leads to a mixture of DBTO **19a** and DBTO₂ **20a** in addition to small amounts of biphenyl.⁴²

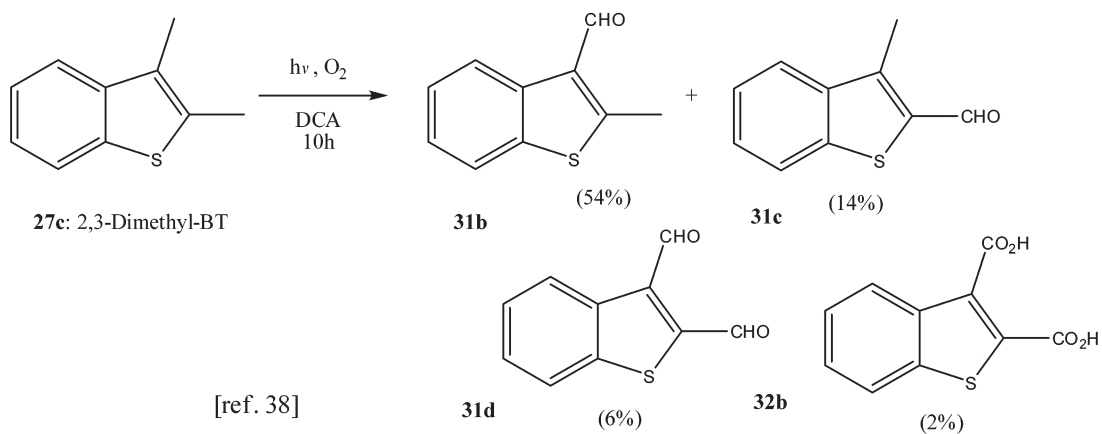
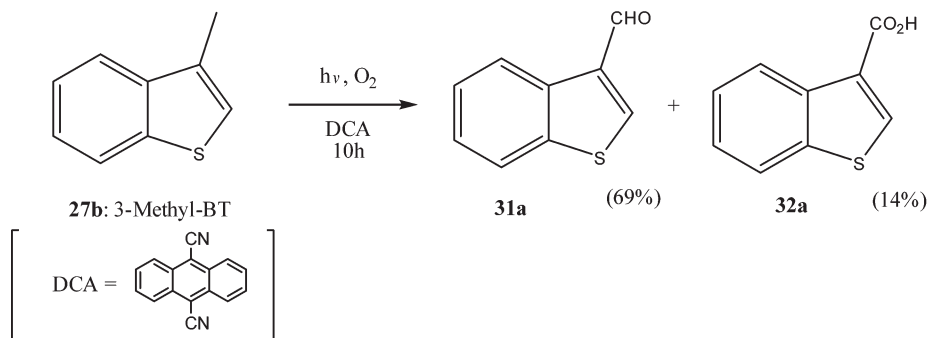
4. Photochemistry of dibenzothiophene *S*-oxides and dibenzothiophene *S,S*-dioxides

To complicate matters, dibenzothiophene-*S*-oxides **19** deoxygenate photochemically to the respective dibenzothiophenes in a number of solvents in the presence of a photosensitiser.^{1,43-46} This reaction is the dominant reaction, when the photoirradiation is carried out in an inert atmosphere. The triplet energy of DBTO **19a** with 61 kcal mol⁻¹ is quite low,³³ so that a number of photosensitisers can be used in the reaction. Often, the dibenzothiophene **1** so formed can itself act as a sensitiser, so that the reaction runs autocatalytically. The exact mechanism

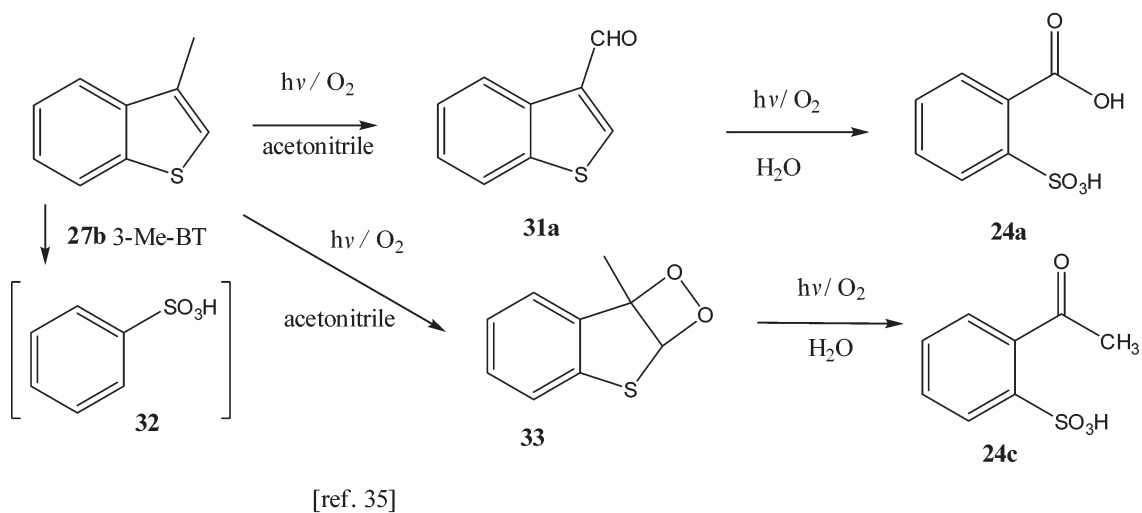


[ref. 35]

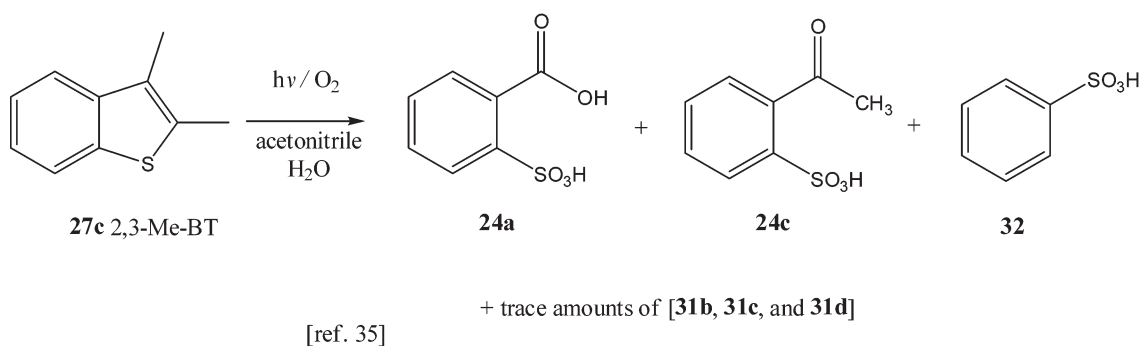
Scheme 7



Scheme 8



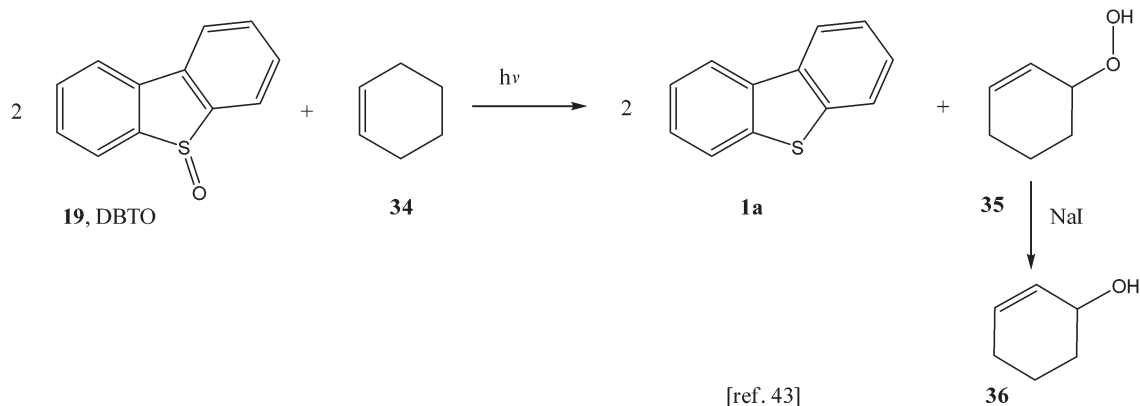
Scheme 9



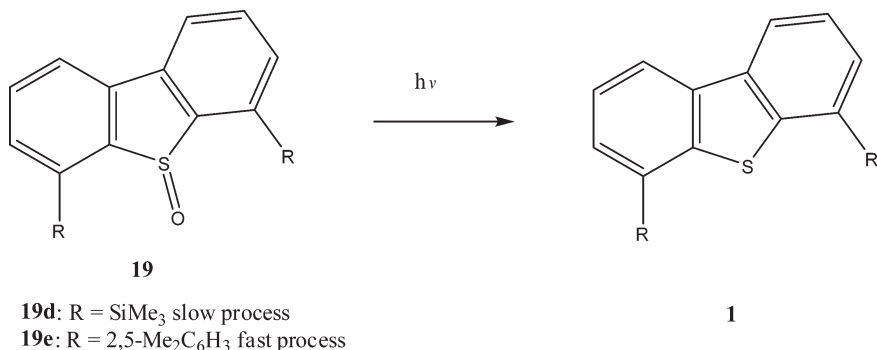
Scheme 10

of the photochemical deoxygenation and especially, the nature of the liberated oxygen species, have been debated for a long time; both bimolecular and monomolecular mechanisms have been formulated. Thus, the involvement of a dibenzothiophene-*S*-oxide dimer, in which a triplet sulfoxide would complex a ground state sulfoxide, has been discussed.^{43,44} This complex would afford two molecules of dibenzothiophene and one molecule of oxygen (O₂).⁴³ Initially, it had been suggested that singlet molecular oxygen ¹O₂ (¹Δ_g) is the product of this reaction. This was supported by the photolysis of dibenzothiophene *S*-oxide (DBTO) in the presence of cyclohexene **34**, from which cyclohexenol **36** could be isolated after reductive work-up with NaI (Scheme 11).⁴³ As the reaction mixture gave positive spot-tests for peroxides before reductive work-up, conversion of cyclohexene **34** to cyclohexene hydroperoxide **35** was formulated by Gurria and Posner⁴³ with a calculated minimum of available oxygen in the sulfoxide as singlet oxygen of 41%.

In order to gain support of one mechanism over another, dibenzothiophene *S*-oxides with sterically demanding substituents at positions C4 and C6 were prepared and photoirradiated. These dibenzothiophene *S*-oxides were thought, on steric grounds, to be unable to form an exciplex. Indeed, the photodeoxygenation of 4,6-bis(trimethylsilyl)dibenzothiophene *S*-oxide **19d** proceeded only very sluggishly, indicating the potential intervention of an excited state dimer in the photodeoxygenation process, which, in this case, could not form due to steric constraints.^{45,46} However, the photodeoxygenation of the equally sterically encumbered 4,6-bis(2,5-dimethylphenyl) dibenzothiophene *S*-oxide **19e** proceeded normally, so that in the former case a substituent effect and not a steric effect is now deemed to be the driving force (Scheme 12).^{45,46}



Scheme 11

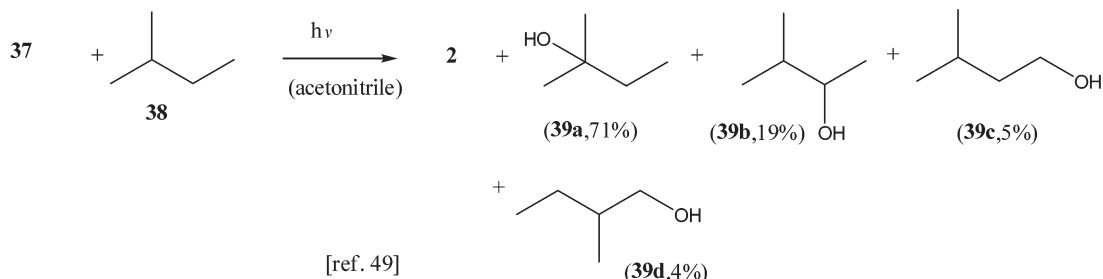
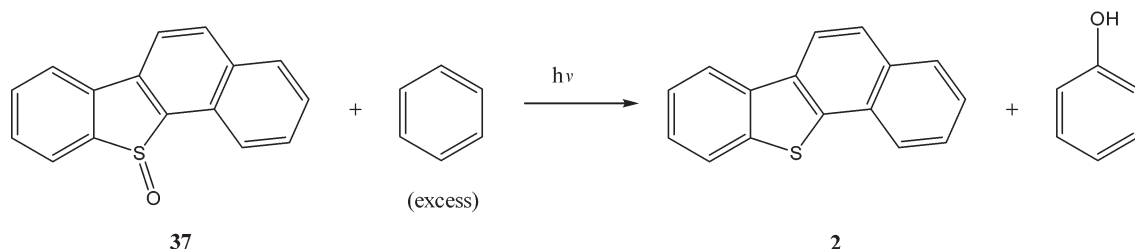


Scheme 12

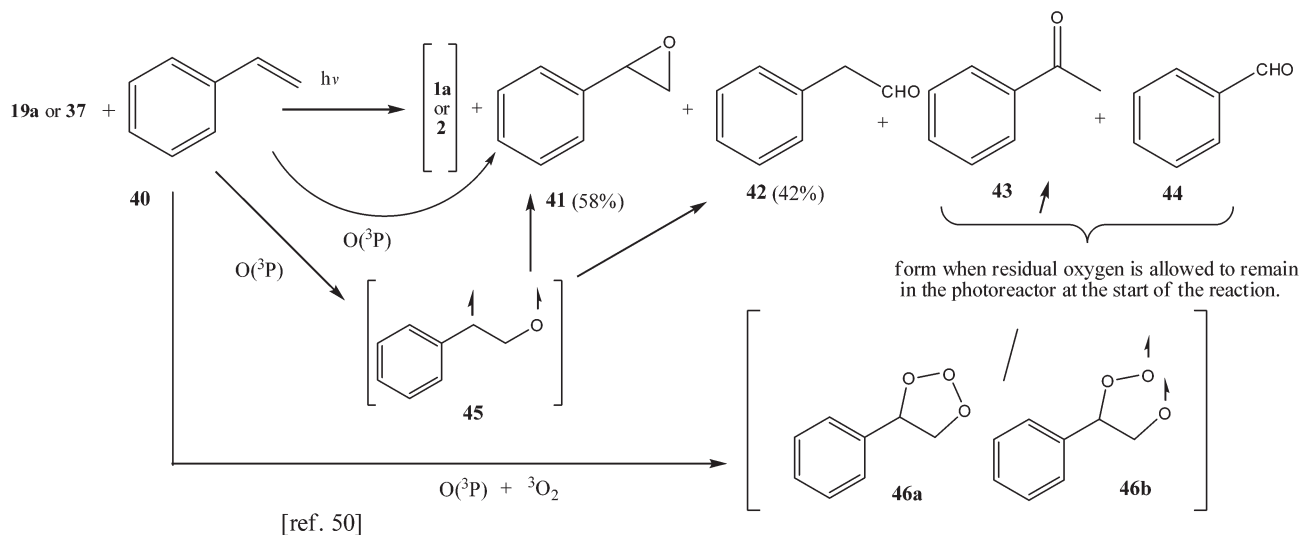
Subsequently, Jencks *et al.* suggested that in the photodeoxygenation of DBTO triplet-ground-state atomic oxygen, O(³P), or a closely related non-covalent complex is an initial product,^{47,48} which, as a very reactive species, would react with available substrates, including with the solvent. The proposal was based on reaction kinetics of O(³P) and quantum yield data. Further evidence for O(³P) has been derived from the selective oxidation of 2-methylbutane **38** in acetonitrile to 2-methyl-2-butanol **39a** upon photodeoxygenation of the dibenzothiophene *S*-oxide analogue **37** (Scheme 13).⁴⁹ It would be expected that, in contrast to O(³P), a potentially possible singlet ground-state atomic oxygen, O(¹D) reacts with primary, secondary and tertiary sites indiscriminately.

Greer has found that styrene **40** forms styrene oxide **41** and phenylacetaldehyde **42** upon photoirradiation both of **19a** (at $\lambda = 385$ nm) and of **37** (at $\lambda = 350$ nm) in an inert atmosphere, under the complete exclusion of molecular oxygen (Scheme 14).⁵⁰ If trace amounts of molecular oxygen are present in the photoreaction vessel prior to irradiation, benzaldehyde **44** and acetophenone **43** can also be obtained as products. These compounds may derive from a formal ozonolysis of styrene, where O(³P) has reacted with the residual molecular oxygen ³O₂ to form ozone. Additionally, it was found that the photodeoxygenation of benzene by **37** affords phenol (Scheme 13).⁴⁹

Recently, the photoreaction of the water soluble hydroxy-methyl substituted dibenzothiophene *S*-oxides **47** and **49** was shown to give formyldibenzothiophenes **48b** and **50b** and diformylbenzothiophenes **48c** and **50c** respectively, apart from the expected products **48a** and **50a** (Scheme 15).⁵¹ The quantum yield of the photodeoxygenation in water was found to be much higher than that in organic solvents. The distribution of products **48/50a-b** was found to be pH dependent,



Scheme 13



Scheme 14

where under neutral and acidic conditions, again an S=O bond fission with the formation of monoatomic oxygen $O(^3P)$ is very likely, while under basic conditions the creation of O^- and after protonation of OH radicals cannot be ruled out.⁵¹ Furthermore, it may be noted that photoirradiation of **19** in the presence of benzophenone as sensitizer does in fact yield the triplet of **19**. However, continued irradiation of triplet **19** does not lead to deoxygenation, so that simple S–O bond cleavage of **19*** does not seem to be involved in the deoxygenation reaction.⁵² Recently, this issue has been readdressed by Jenks *et al.*⁵³

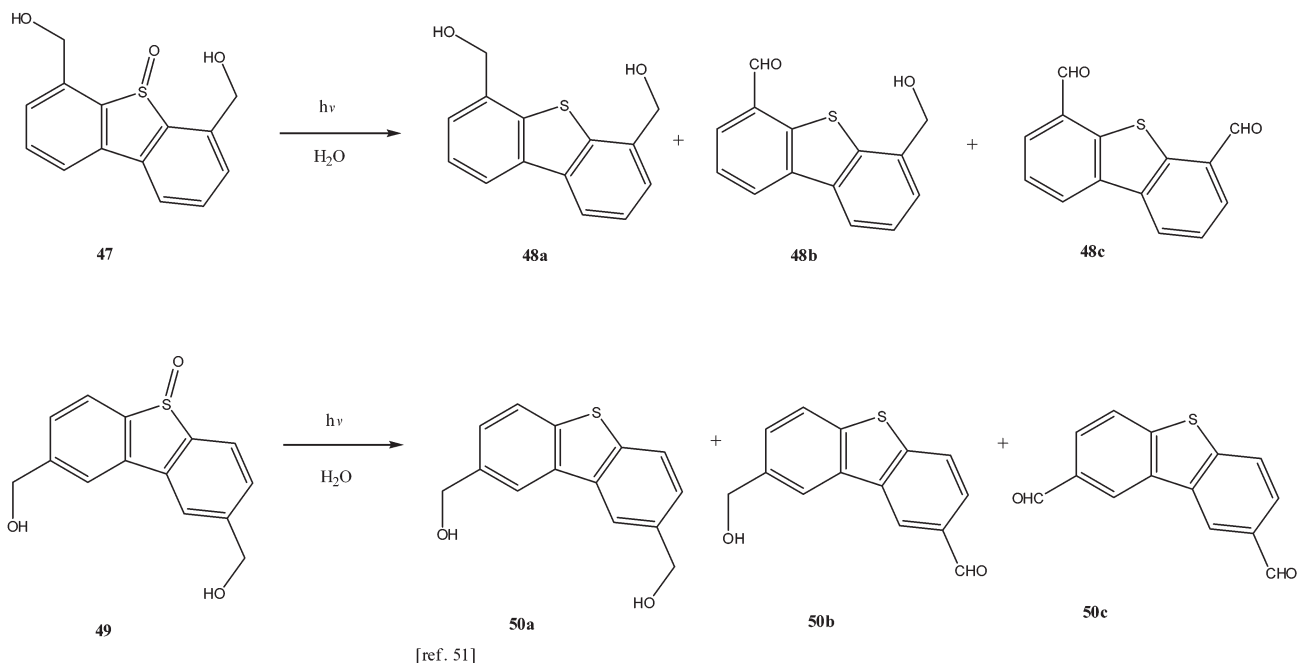
While it has been stated that DBTO₂ **20** is photostable in non-hydrogen donating solvents, this sulfone does undergo photochemical transformation in alcohols, especially in isopropanol, where biphenyl **54** is obtained as the major product (Scheme 16).³⁴ It is believed that biphenylsulfonic acid **52** is an intermediate in the transformation. Although **52** could not be detected unambiguously in the reaction, Jenks *et al.* showed that independently synthesised **52** indeed gave **54** under identical photochemical conditions. Sultine **21** could be ruled out as an intermediate as the photolysis of **20** in isopropanol yields

2-phenylphenol **55** (Scheme 16), which was not observed as a product in the photoirradiation of **20**.³⁴

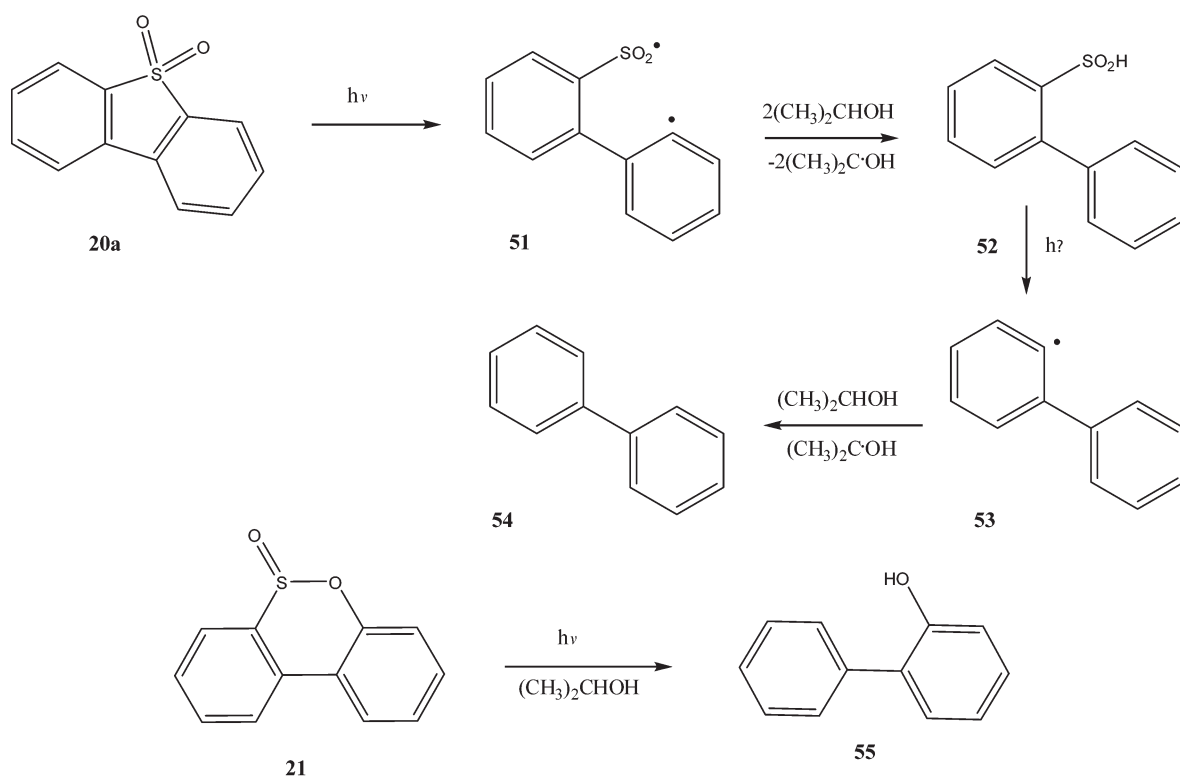
From a practical standpoint, it may be interesting to point out that the photoreactivity of DBTO has been used in the hydroxylation and esterification of interior sites within polyolefinic films. A PE film is doped with DBTO at 15 mmol kg⁻¹.⁵⁴ It is then irradiated with a high-pressure Hg arc lamp at 400 W. During this process DBTO is deoxygenated, thereby reverting back to the dibenzothiophene, oxidising the PE-film (*i.e.*, hydroxylation). The dibenzothiophene is washed out of the film in a second process. The hydroxylated positions within the film can be esterified subsequently.⁵⁴

5. Photochemistry of benzo[*b*]thiophene *S*-oxides and benzo[*b*]thiophene *S,S*-dioxides

Although a certain amount of photodeoxygenation can be found for some benzo[*b*]thiophene *S*-oxides (BTOs), the characteristic photoreactivity of substituted BTOs, which has been studied extensively by Geneste *et al.*,^{55–57} differs markedly from that of dibenzothiophene *S*-oxides and thiophene *S*-oxides. BTOs carrying various substituents at



Scheme 15



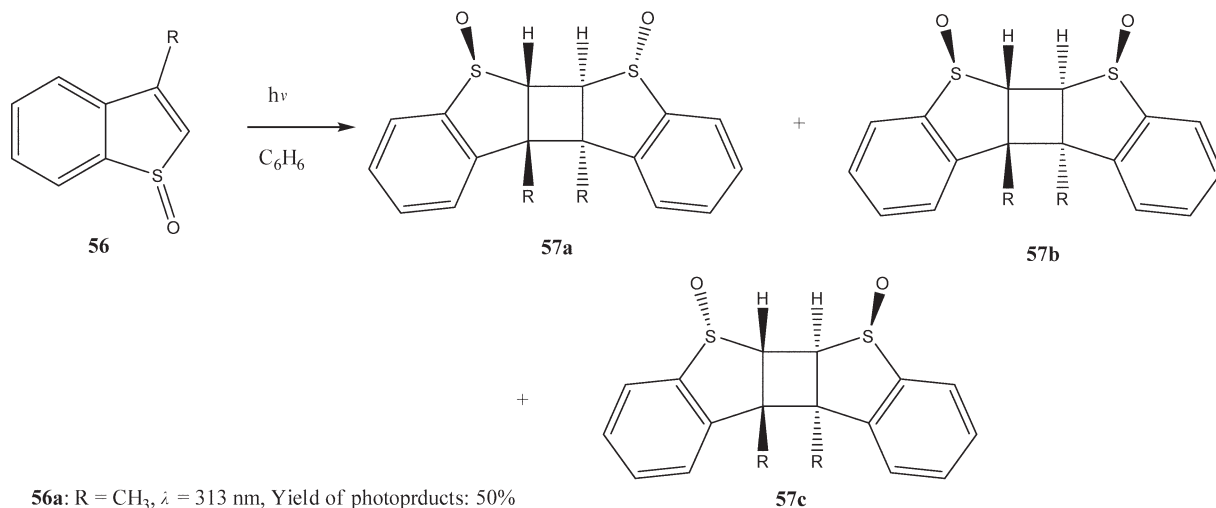
[ref. 34]

Scheme 16

positions C-2 and C-3 have been irradiated in benzene in the presence of benzophenone as a sensitizer. The outcome of the reaction depends heavily on the substitution pattern of the starting material. Halogenated, *ie.* brominated or chlorinated BTOs mostly gave an inseparable mixture of products. This has also been found in the photoirradiation of halogenated thiophene *S*-oxides, where a number of compounds was formed from irradiation of the starting material in CH_2Cl_2 in the

absence of an added photosensitizer. In these cases, however, the products could be separated and it was found that the C–X bond cleaves during the photoirradiation leading to halo-radicals which subsequently lead to the products. BTOs with alkyl- or aryl-substituents at C-3 photodimerise (Schemes 17 and 18), albeit often in low yield.

The dimers are *anti* head-to-head, exclusively. Thus, 3-Me-BTO **56a** gives three dimers, **57a–Me** (R = Me), **57b–Me**



56a: R = CH₃, λ = 313 nm, Yield of photoproducts: 50%

56a: R = CH₃, λ = 363 nm, benzophenone, Yield of photoproducts: 80%

56b: R = Ph, λ = 363 nm, Yield of photoproducts: 40%

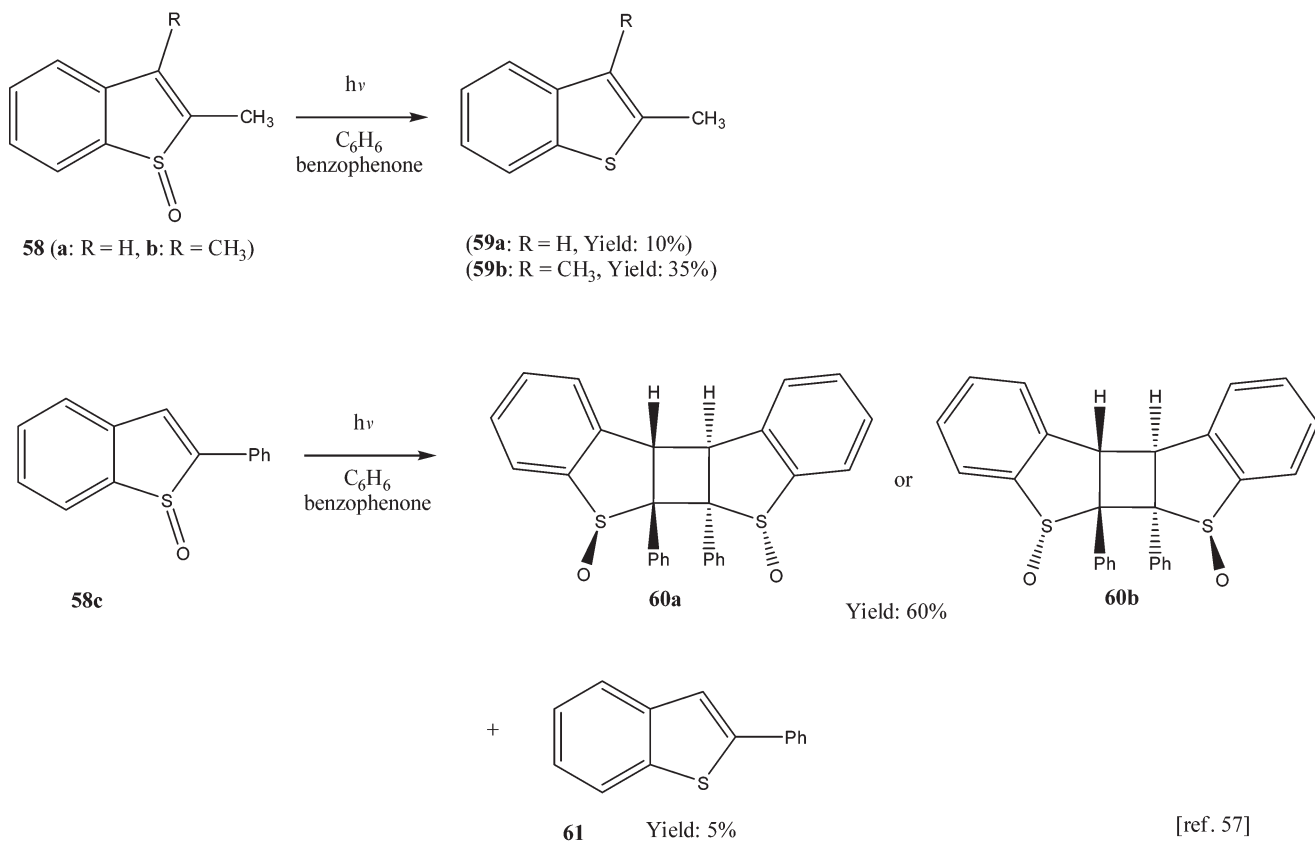
[ref. 57]

Scheme 17

(R = Me) and **57c-Me** (R = Me), in 50% combined yield upon photoirradiation in benzene at λ = 313 nm (Scheme 17). When benzophenone was added as a sensitizer, the photoirradiation of 3-Me-BTO **56a** at λ = 366 nm again results in the same dimers, albeit in higher yield. BTOs with alkyl- or aryl- substituents at C-2 undergo a photodeoxygenation in benzene (Scheme 18) upon irradiation at λ = 313 nm and at λ = 366 nm in the presence of benzophenone as a sensitizer. In the latter case, only very small amounts of a dimerisation product could be isolated upon photoirradiation of the 2-methylbenzo[*b*] thiophene *S*-oxide **58a**. 2-Phenylbenzo[*b*]thiophene *S*-oxide

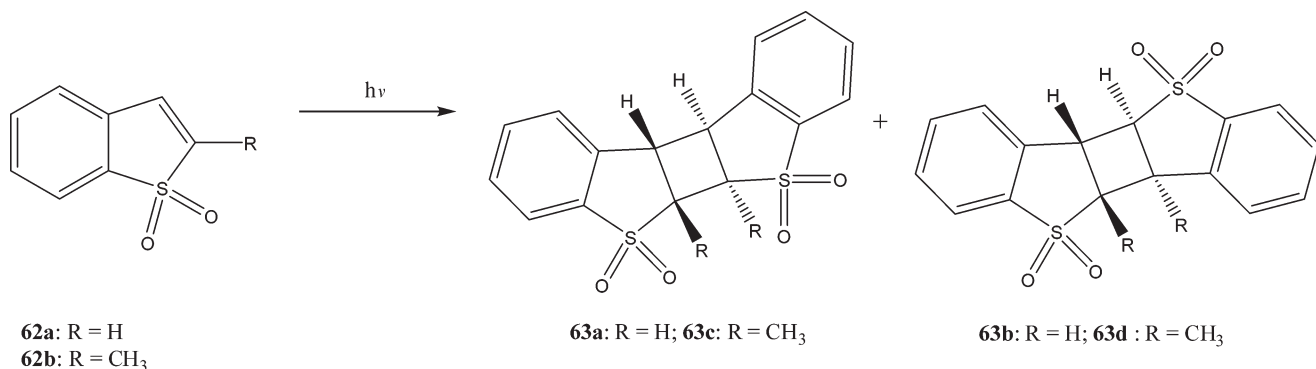
58c gave one dimer, with a structure of either **60a** or **60b** and the deoxygenated product **61** (Scheme 18).

It is interesting to note that benzo[*b*]thiophene *S,S*-dioxide (BTO₂, **62a**) also photodimerises.⁵⁸ Here, *anti* head to head (HH) and *anti* head to tail (HT) isomers are formed.⁵⁹ The photodimerisation of 2-methylbenzo[*b*]thiophene *S,S*-dioxide **62b** in benzene has been investigated in detail and it has been shown that the contribution of each isomer depends on the oxygen concentration in the photosolution. Thus, in oxygen free solution, the HH-isomer **63c** dominates (9:1), while in oxygenated solutions both isomers, **63c** and **63d**, are formed



[ref. 57]

Scheme 18



[ref. 60]

Scheme 19

equally (Scheme 19).⁶⁰ Plummer *et al.*⁶⁰ have suggested that the HH-isomer is formed *via* a triplet monomer, while the HT-isomer is created via an excimer. Other, substituted benzo[*b*]thiophene *S,S*-dioxides have been noted to photodimerise.⁶¹

Little is known of the photochemistry of unsubstituted BTO **58d** itself, as it is not easy to isolate in sufficient quantities and is not sufficiently inert in the dark. However, the photooxidation of BT itself may have been studied unwittingly a long time ago.^{37,62} Haines *et al.* noted that benzo[*b*]thiophene **58d** changes when kept for 6 months or longer in daylight. The authors reported that benzo[*b*]naphtho[1,2-*d*]thiophene **64** is formed within that time (Fig. 2), most likely by dimerisation of transient BTO and subsequent photoextrusion⁶³ of SO from the primary cycloadducts.

6. Photochemistry of thiophene *S*-oxides

The outcome of photoreactions of thiophene *S*-oxides depends greatly on the substitution pattern of the substrates. 2,3,4,5-Tetraphenylthiophene *S*-oxide **65a** is transformed into 2,3,4,5-tetraphenylfuran **66a** with 2,3,4,5-tetraphenylthiophene **67a** as a by product.⁶⁴ Upon photoirradiation, 2,5-di-*tert*-butylthiophene *S*-oxide **65b** leads mainly to 2,5-di-*tert*-butylfuran **66b** with bis(2,5-di-*tert*-butyl-3-furyl) disulfide (**68**, R¹ = R⁴ = Bu^t, R² = H) as a side product (Scheme 20).⁶⁴ Similar results have been found by Nakayama *et al.*⁶⁵ from the photolysis of 3,4-di-*tert*-butylthiophene *S*-oxide **65c** in degassed benzene where a mixture of 3,4-di-*tert*-butylthiophene (**67**, R¹ = H, R² = Bu^t), bis(3,4-di-*tert*-butyl-2-furyl) disulfide (**68**, R¹ = H, R² = R³ = Bu^t) and 3,4-di-*tert*-butylfuran (**66**, R¹ = R⁴ = H, R² = R³ = Bu^t) could be isolated (Scheme 20).

Meanwhile, the oxidation of 3,4-di-*tert*-butylthiophene *S*-oxide **65c** with singlet oxygen provided 3,4-di-*tert*-butyl-5-hydroxy-2-furanone **70**, di-*tert*-butylmaleic anhydride **71** and 3,4-di-*tert*-butylthiophene **67b** (Scheme 21).⁶³

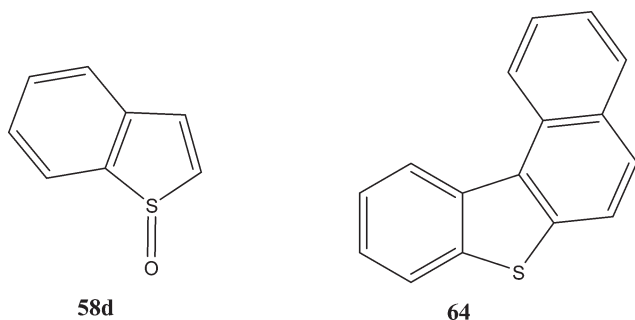


Fig. 2

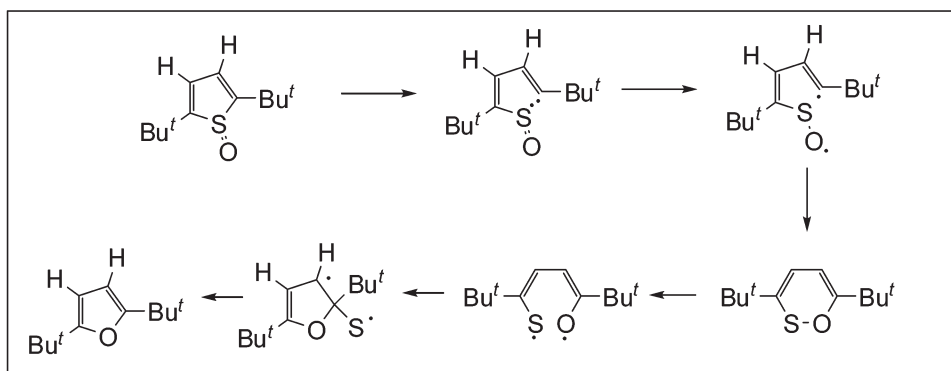
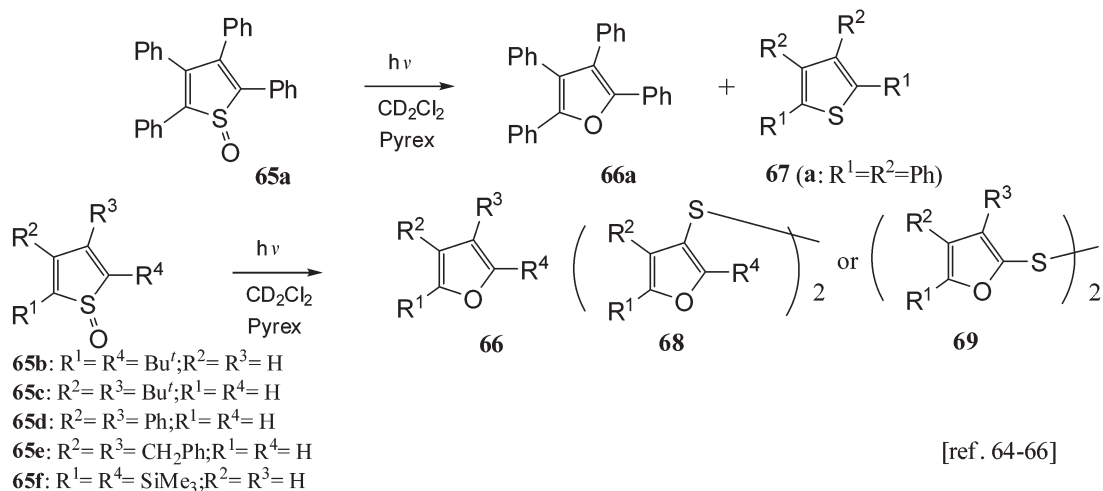
Proton-containing carbon substituents at C-2 and C-5 such as methyl groups are hydroxylated upon photoirradiation of thiophene *S*-oxides. Thus, 3,4-dibenzyl-2,5-dimethylthiophene *S*-oxide **65g** yields the hydroxymethyl substituted thiophene **67c** (Scheme 22). The ether **67d** is a minor product. In the presence of alcohols, the hydroxymethyl function is alkylated (Scheme 22).

Oxidisable additives to the photo-solution suppress the above reactions. Thus, photoirradiation of thiophene *S*-oxides in the presence of amines yields thiophenes directly,⁶⁴ where the fate of the amines could not be determined. Photoirradiation of thiophene *S*-oxide in the presence of the thiophenol **72** also gives the respective thiophenes, but here the disulfide **73** can be isolated as the oxidation product (Scheme 23).⁶⁴ Jenks *et al.* have also studied the photolysis of 3,4-diphenylthiophene *S*-oxide **65d**, 3,4-dibenzylthiophene *S*-oxide **65e** and 2,5-bis(trimethylsilyl)thiophene *S*-oxide **65f**.⁶⁵ While **65d** and **65e** gave the respective furans in moderate yield, 2,5-di-*tert*-butylthiophene *S*-oxide **65f** was deoxygenated exclusively to give the thiophene. The photolytic deoxygenation has been carried out in the presence of 2-methylbutane **40** to probe for O(³P) formation. Here, Jenks *et al.* have found hydroxylation selectivity for the 3°, 2° and 1° positions of the alkane to be 3.0:1.7:1.0, respectively, which is similar to the one found in the photolytic deoxygenation of DBTO, indicative of O(³P) formation in the process (Scheme 23).⁶⁶

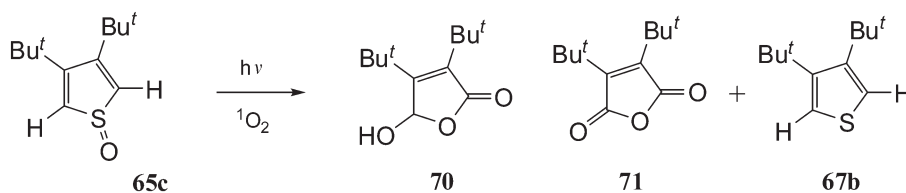
7. Electrochemical oxidation and reduction of thiophenes, thiophene *S*-oxides and related compounds

Bongini *et al.* have noted that thiophene *S*-oxides can both be oxidised and reduced at relatively mild potentials.⁶⁷ Preparatively, electrochemical reduction of thiophene *S*-oxides has been shown to lead to the respective thiophenes (Scheme 24).⁶⁸

The outcome of the electrochemical oxidation is dependent upon the substitution pattern of the thiophene *S*-oxide. It has been shown that in acetonitrile, tetraphenylthiophene *S*-oxide **65a** reverts to dibenzoylstilbene **74** at 2.1V vs. SCE (Pt-electrode, Bu₄NPF₆ as electrolyte) and to a mixture of the latter and the unstable sulfenic acid **75** (*x* = 0) at 1.6V versus SCE (Scheme 25).⁶⁹ Sonoirradiation of **65a** at both 40 kHz and 850 kHz leads to a 10-fold increase in oxidation current with loss of definition of the two oxidation waves. No new products have been isolated from the sonoelectrooxidation as compared to the 'silent electrooxidation', but the formation of such products in small amounts cannot be excluded.⁷⁰ Thus, oxidation products have been reported in high intensity aquasonolysis of benzo[*b*]thiophene due to reaction of benzo[*b*]thiophene with



Scheme 20



Scheme 21

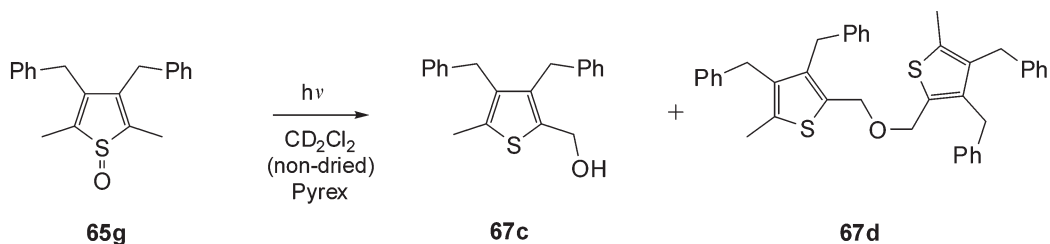
OH radicals.⁷¹ Oxidation products of thiophenes themselves have not yet been found under aquasonolysis conditions,⁷² where it is known that the rate constant of the reaction thiophenes with atmospheric OH radicals is lower than that of benzo[*b*]thiophene.⁷³

Upon electrooxidation, thiophenes⁷⁴ and benzo[*b*]thiophenes⁷⁵ often polymerise. Dibenzothiophenes, especially, electron-donor substituted derivatives, can form stable radical cations.⁷⁶ Nevertheless, in hydroxy-containing solvents, the sulfur moiety of the thiophene unit can be oxygenated under electrooxidative conditions. An over-oxidation of electrochemically produced oligothiophenes has been noted when the polymerisation is conducted in an aqueous medium.⁷⁷ Dibenzothiophene has been oxidised to dibenzothiophene *S*-oxide at Pt electrodes in sulfate and perchlorate solutions.⁷⁸ Also, recyclable oxidation catalysts doped on electrode surfaces oxygenate the sulfur in thiophenes and dibenzothiophenes. Thiophene has been oxidised electrochemically at PbO₂

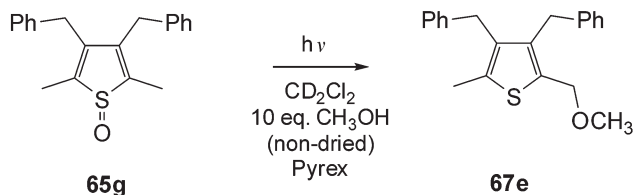
electrodes, where carboxylic acids were isolated as final products.⁷⁹ These reactions are thought to proceed *via* thiophene *S*-oxide and thiophene *S,S*-dioxide intermediates and a subsequent SO extrusion mechanism much like the one detailed in Scheme 25. Recently, an electrooxidative process has been used in the removal of dibenzothiophenes from gasoline. Thus, 5 wt% CeO₂ on C particle electrodes were used as anodes with aqueous cerium nitrate solution as electrolyte.⁸⁰ The products, which were assumed to be sulfones and/or sulfoxides, but which were not identified experimentally, were removed with DMF by liquid-liquid extraction from the remaining oil.⁸⁰ Alternatively, a β -PbO₂ on C anode was used with aqueous NaOH as anolyte.⁸¹

8. Conclusion

Photooxygenation of thiophenes, benzo[*b*]thiophenes and dibenzothiophenes presents an interesting platform for the desulfurisation of sulfur-contaminated matrices. While the

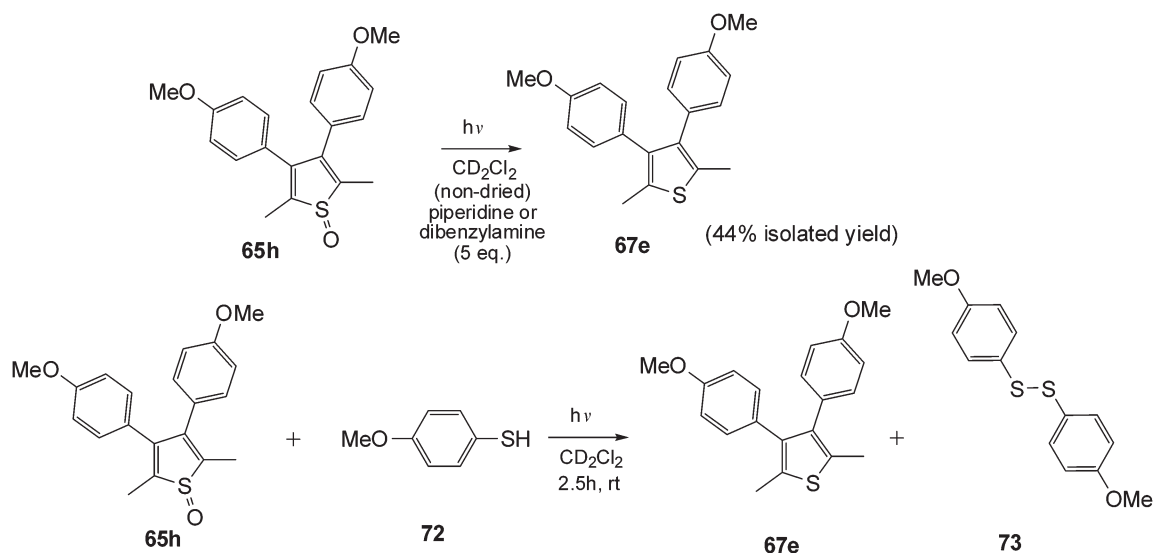


Irradiation with a mercury high pressure lamp (100 Watt); for $c = 0.16$ M in **65g**: **67c** (7%); **67d** (70%)
 for $c = 0.016$ M in **65g**: **67c** (35%); **67d** (35%)

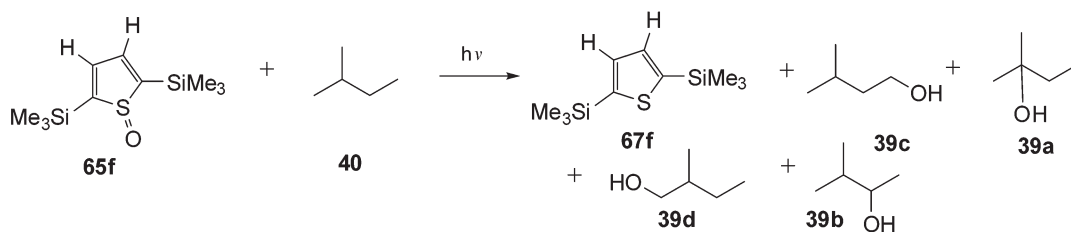


[ref. 64]

Scheme 22

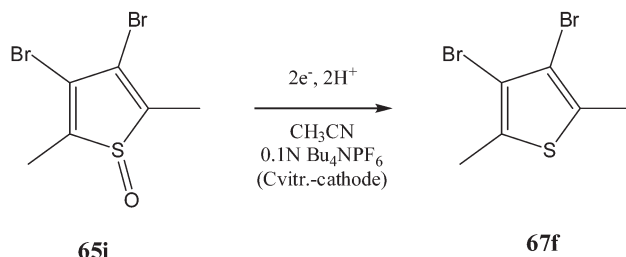


[ref. 64]



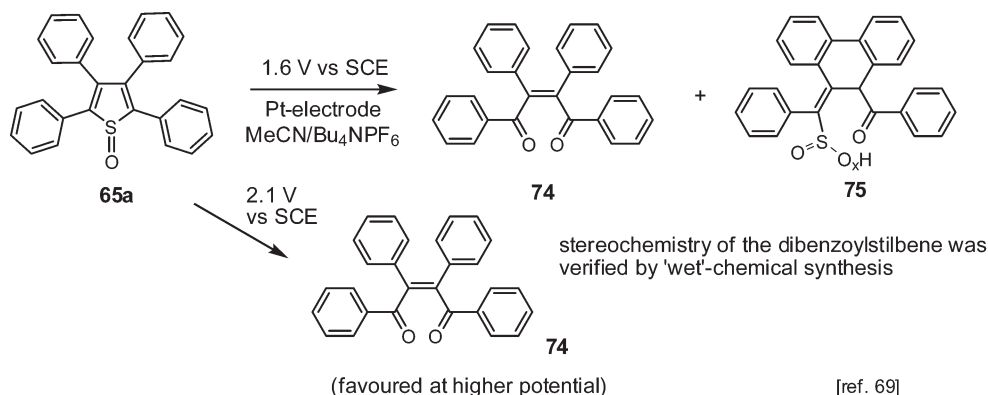
[ref. 66]

Scheme 23



[ref. 68]

Scheme 24



[ref. 69]

Scheme 25

S-oxides and S,S-dioxides of these contaminants can be removed by extraction, they themselves exhibit interesting photobehaviour, often leading to extrusion of the sulfur moiety from the heterocycle. These reactions are complicated by the fact that thiophene S-oxides and analogs can also undergo photoreduction leading to the starting thiophenes. The deoxygenation can be accompanied by oxidation of a small part of the matrix. Though dibenzothiophene-S-oxides are generally inert towards photodeoxygenation at wavelengths above $\lambda > 230$ nm in the absence of a photosensitizer, it might be noted that oligomers and polymers with thiophene S-oxide or dibenzothiophene S-oxide units, can serve as building blocks for materials with interesting electronic characteristics,⁸² but may exhibit potentially low photochemical stability and should be examined carefully in that regard.

While the thiophene unit can only be oxygenated electrochemically under certain conditions, further electrooxidation of the oxygenated species such as thiophene S-oxides can lead to sulfur extrusion. Within the context of a complementary removal method of dibenzothiophenes and analogs from fossil fuels, a further investigation into the oxidation of thiophenes by photochemical and electrochemical methods is warranted. In particular, a combined photoelectrochemical approach would lend itself to an interesting continuation of studies in this field.

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