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Photochemistry of substituted dibenzothiophene *S*-oxides and oxygenated bis-dibenzothiophenes

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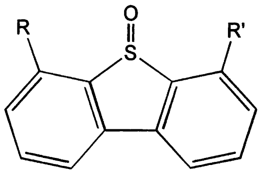
Substituted dibenzothiophene and bis-dibenzothiophene *S*-oxides were prepared and submitted to photolysis. The rate of deoxygenation of the molecules under photoirradiation was found to be highly dependent on their substitution pattern.

Keywords: dibenzothiophene *S*-oxides, photochemistry, deoxygenation, sensitisers

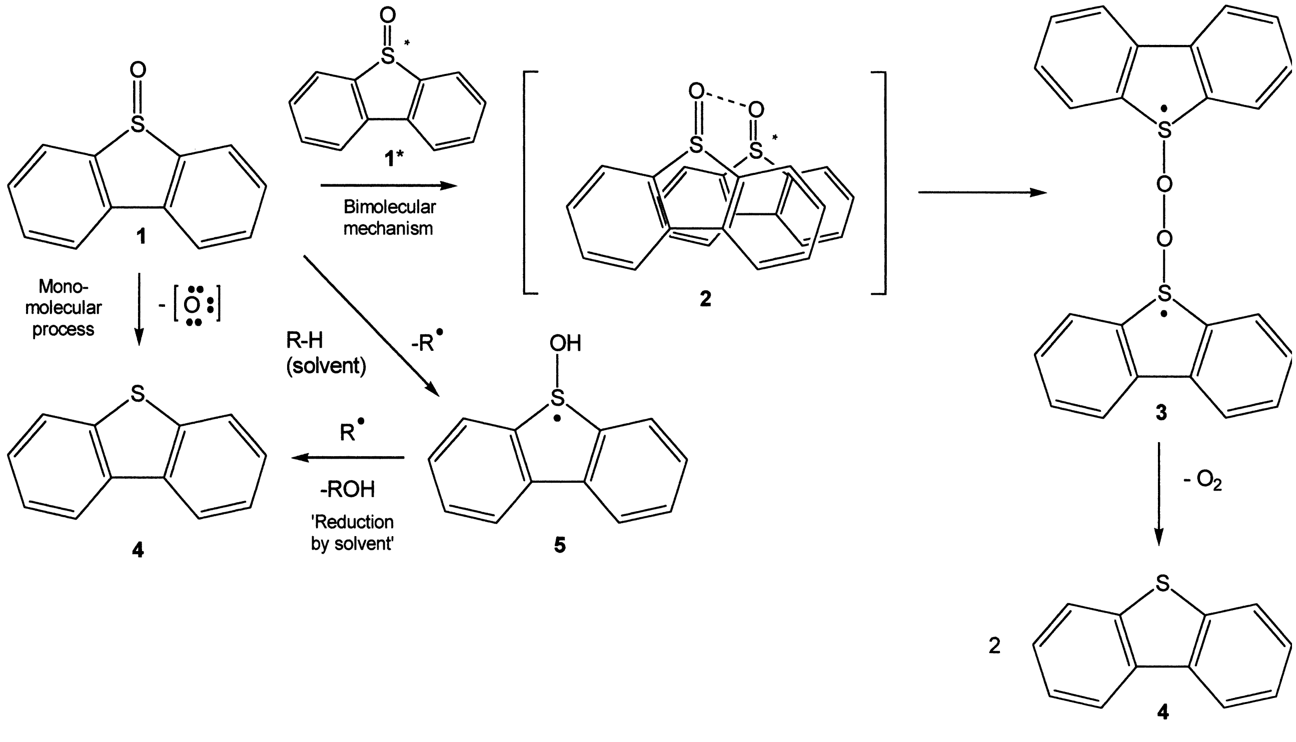
Upon photoirradiation, dibenzothiophene *S*-oxides can be deoxygenated. It has been a matter of debate, whether this photodeoxygenation is a mono- or a bimolecular process, a further possibility being a radical mechanism involving solvent molecules. Furthermore, the nature of the released oxygen has been under discussion. In a monomolecular process monoatomic oxygen [most likely $O(^3P)$] would be generated,[2–4] in the bimolecular process $O_2(^1\Delta_g)$.[5,6] If monoatomic oxygen were liberated in these cases, it has been remarked that this reaction would present a very interesting and clean way to produce a species which thus far has only been studied extensively in the gas phase.

The photodoxygenation has also been observed in simple, non-annelated thiophene *S*-oxides where, however, the outcome of the photoreaction is dependent on the nature of the substituents on the thiophene *S*-oxides.[8] In this communication, the synthesis and the photo-behaviour of 4-mono- and 4,6-disubstituted dibenzothiophene *S*-oxides as well as of a number of bisdibenzothiophenes, oxygenated at sulfur, are discussed with the aim of determining whether substitution at the vicinity of the sulfoxy-moiety with bulky substituents would have an effect on the photo-deoxygenation of the dibenzothiophene *S*-oxides.

For this purpose, 4-trimethylsilyldibenzothiophene *S*-oxide (**12**), 4,6-bis(trimethylsilyl)dibenzothiophene *S*-oxide (**15**) and 4,6-bis(2′,5′-dimethylphenyl)dibenzothiophene *S*-oxide (**18**) were prepared, either by lithiation of dibenzothiophene and reaction with chlorotrimethylsilane (for **12** and **15**) or by Suzuki coupling reaction of 4,6-diiododibenzothiophene with 2,5-dimethylphenylboronic acid and subsequent oxidation by *meta*-chloroperoxybenzoic acid of the dibenzothiophenes thus acquired.



12 R = Me_3Si, R' =H
15 R = R' = Me_3Si
18 R = R' = 2,5-$Me_2C_6H_3$
19 R = R' = Me



Scheme 1 Possible mechanisms for the photochemical deoxygenation of dibenzothiophene *S*-oxide.

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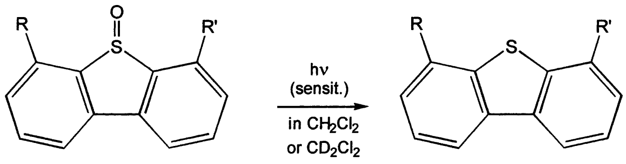
The dibenzothiophene *S*-oxides were photoirradiated in CH_2Cl_2 or in CD_2Cl_2 by using a 1kW high pressure mercury lamp. The reactions were monitored by ^{1}H NMR spectroscopy. At the end of the reaction, representative samples were purified by chromatography. The standard dibenzothiophene S-oxides, dibenzothiophene *S*-oxide (**1**) itself and 4,6-dimethyldibenzothiophene *S*-oxide (**19**) deoxygenate smoothly to give dibenzothiophene and 4,6-dimethyldibenzothiophene under these conditions. 4,6-Bistrimethylsilyldibenzothiophene *S*-oxide (**15**), however, does not photodeoxygenate at all. Initially, this was thought to indicate that a bimolecular process is involved in the photodeoxygenation, which would be hindered by sterically exacting groups at C-4 and C-6 of the dibenzothiophene *S*-oxide. In subsequent experiments, however, it could be observed that the equally bulkily substituted 4,6-bis-(2′,5′-dimethylphenyl)dibenzothiophene *S*-oxide (**18**) deoxygenates efficiently. On the other hand, 4-trimethylsilyldibenzothiophene *S*-oxide (**12**), a molecule with only one sterically demanding substituent, rather than with two as in **18**, shows a much reduced rate of deoxygenation when compared either to dibenzothiophene *S*-oxide (**1**), to 4,6-dimethyldibenzothiophene S-oxide (**19**), or to **18**.

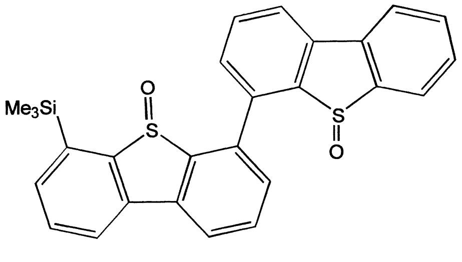


Scheme 2 Photodeoxygenation of dibenzothiophene *S*-oxides.

Photosensitisers were then added to solutions of 4-trimethylsilyldibenzothiophene *S*-oxide (**12**) and 4,6-bis(trimethylsilyl) dibenzothiophene *S*-oxide (**15**). The addition of 10mol% naphthalene to **12** gave a marked increase of reaction rate when compared to the non-sensitised reaction and the addition of 10mol% benzophenone gave an even greater increase in reaction rate. When 10mol% benzophenone was added to **15**, also **15** photodeoxygenated smoothly, at a rate comparable to that of **12**.

This in itself shows that the reluctance of 4,6-bis-(trimethylsilyl)dibenzothiophene *S*-oxide (**15**) to deoxygenate in a non-sensitised reaction may not involve an inability to form a dimeric structure necessary for the deoxygenation, but may be either caused by an ineffective intersystem crossing or due to the short lifetime of the triplet state itself. Interestingly, when 10mol% 4,6-dimethyldibenzothiophene was added to **12**, again a rate acceleration, similar to that observed with naphthalene added as sensitiser, was noted when compared to the non-sensitised irradiation, which indicates that the photodeoxygenation of certain dibenzothiophene *S*-oxides is self-catalysing. This has been seen in the photoirradiation of some monomeric thiophene *S*-oxides, such as 2,3,4,5-tetramethylthiophene *S*-oxide, and of thienylthiophene *S*-oxides.[9] Also, the addition of 4,6-dimethylbenzothiophene to 4,6-bis-(trimethylsilyl)-benzothiophene *S*-oxide (**15**) led to deoxygenation of the dibenzothiophene *S*-oxide, which is unreactive in the absence of additive (see above).

When the oxygenated dibenzothiophene-dimers **22** and **23** were photoirradiated under the same conditions, the rates of deoxygenation were remarkably different. While the deoxygenation of **23** was complete within 4h, the photodeoxygenation of **22** took 19h hours to complete. Here, a contributing factor may be the catalytic effect of the (non-oxidised) thiophene unit in **23**.



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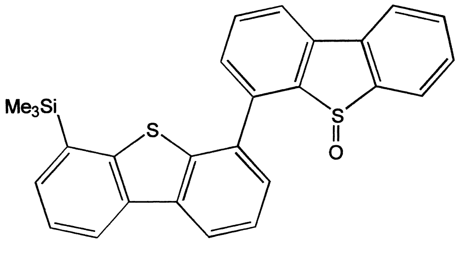

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Techniques used: IR, ^{1}H NMR, ^{13}C NMR, LRMS, HRMS, UV-VIS, column chromatography, HPLC, photo-irradiation

References: 17

Schemes: 6

Figures: 4 (reaction/time plots: 3)

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