CHAPTER II

STEREOELECTRONIC EFFECTS IN OXIDATION OF DITHIOLANES
INTRODUCTION

This chapter is an outgrowth of our interest in the mechanistic investigations of photochemistry and photoelectron transfer oxidation studies of 1,3-dithiolanes. Some of the intermediates proposed could also be obtained by the reaction of singlet oxygen with dithiolanes. 1,3-Dithiolane constitutes an important functional group in organic chemistry, but its photochemistry remains underexplored. Broadly speaking, photolysis of 1,3-dithiolanes, in the absence of oxygen, lead to product(s) derived from initial C-S bond cleavage. The study showed the reluctance of 1,3-dithiolane to undergo photochemical change during irradiation under nitrogen atmosphere. Besides, in the literature, photodethioketalization of various 1,3-dithiolanes, in the presence of triplet sensitizers and molecular oxygen has been reported, for which no mechanistic suggestion was given.

Scheme - 1

The C-S bond in the 1,3-dithiolane molecule is the weakest bond (70 Kcal/mole). Therefore, it is prone to cleave first on irradiation. Eaton et al. have observed the breaking of C-S bond, leading to the biradical intermediate 2, during the photolysis of 2,2-bis (naphthylmethyl)-1,3-dithiolanes (Scheme-1). The biradical 2 has been shown to undergo
two reactions, resulting in the formation of either the olefin 3 or the thioketal 4. Though the existence of thioketal 4 was not proved by isolation, the formation of products 5 and 6 clearly indicated the intermediacy of 4.

While studying the photochemistry of cyclic mercaptols eg. 1,3-dithiolane 7, under various conditions, Berchtold et al. found the formation of various products eg. 9, 10, 11, 12, 13 and 14, as shown in Scheme-2. The formation of various products can be rationalised via the cleavage of C-S bond, resulting in the formation of intermediate diradical 8 and an unstable species 10.

Scheme-2
Thus, the examples involving photochemistry of 1,3-dithiolanes, are scarce in literature. However, the photooxidation of dialkyl sulphides has been studied extensively, especially by Foote group. It has been shown that dialkyl sulphides undergo sensitized photooxidation to give sulphoxides in a smooth reaction (Equation-1).

$$2 R_2 S + \text{O}_2 \xrightarrow{h\nu} 2 R_2 S - O$$

Equ. 1

The mechanism of $^1\text{O}_2$ oxidation of diethylsulphide has been extensively studied by Foote et al. and is known to be highly dependent on solvent proticity and temperature. In protic solvent a single intermediate, Zwitterion (persulphoxide) 19, has been proposed, whereas, the possibility of the involvement of two intermediates, persulphoxide 19 and cyclic sulphurane 20, has been suggested in aprotic solvent, based on the kinetics of trapping experiments (Equation-2).\(^{10-13}\)

$$R_2 S \xrightarrow[^1\text{O}_2]{} \left( \begin{array}{c} R_2 \text{SOO} \\ R_2 S \end{array} \right) \xrightarrow{R_2 S} 2R_2 S - O \xrightarrow{R_2 S} \left( \begin{array}{c} R_2 \text{SOO} \\ R_2 S \end{array} \right) \xrightarrow{R_2 S} 2R_2 S - O$$

Equ. 2

Thus, when diphenylsulphide, which is unreactive towards singlet oxygen, was added to diethylsulphide $^1\text{O}_2$ photooxidation reaction mixture in methanol, considerable amount of diphenylsulphoxide was produced along with diethylsulphoxide, which is consistent, as shown in Scheme-3, with the reactive intermediate persulphoxide 19.

**Scheme - 3**

$$\text{Et}_2 S \xrightarrow[^1\text{O}_2]{} \text{Et}_2 \text{SOO} \xrightarrow{\text{Et}_2 S} 2\text{Et}_2 \text{SO}$$

Thus, when diphenylsulphide, which is unreactive towards singlet oxygen, was added to diethylsulphide $^1\text{O}_2$ photooxidation reaction mixture in methanol, considerable amount of diphenylsulphoxide was produced along with diethylsulphoxide, which is consistent, as shown in Scheme-3, with the reactive intermediate persulphoxide 19.
In the background of the above literature on photochemistry of 1,3-dithiolanes, we became curious about the nature of reactive species involved during photooxidation studies. Thus, photooxygenation of 1,3-dithiolanes was examined with singlet oxygen.

Also, our recent interest in hydroperoxide-type intermediates e.g. (Scheme-7), which could also be obtained by singlet oxidation of dithiolanes, prompted us to examine the reaction of $^{1}O_2$ with 1,3-dithiolanes. This study describes a synthetically useful methodology for the preparation of 1,3-dithiolane-1-oxides under neutral and mild conditions and concludes that $^{1}O_2$ is certainly not the species involved during Takahashi dethioketalization. Notice that one of the possibility for dethioketalization could be via reaction of singlet oxygen with the thiol side species e.g., 4 or 10 (Scheme 1 & 2).

RESULTS AND DISCUSSION

The various 1,3-dithiolanes 23a,b and 1,3-dithianes 23c,d and 26 (Scheme-4) were prepared from corresponding ketones or aldehydes by reaction with 1,3-propanedithiol or 1,2-ethanedithiol in the presence of BF$_3$-etherate. Singlet oxidation was carried out in MeOH by $O_2$ bubbling and by using 350 nm lamp. Normally > 90% of dithiolane or dithiane was consumed during singlet oxidation, although the reaction was fast in the early stages of irradiation. Identical products were obtained with either Rose Bengal or Methylene Blue as sensitizers, ensuring the involvement of $^{1}O_2$. Although many variations in experimental conditions are possible as far as duration of irradiation, degree of $O_2$-saturation/agitation, solvent variation and concentration of substrate and photosensitizer are concerned, the above reaction conditions furnished synthetically useful yields of 1,3-dithiolane-1-oxides and 1,3-dithiane-1-oxides, as shown in Scheme-4.

The 1,3-dithiolane and 1,3-dithiane oxides were characterised by satisfactory IR, $^1$H-NMR and mass spectra. Characteristic features of the S-oxides in compound 2-phenyl-1,3-dithiane-1-oxide 27 are the strong absorption at 1040 cm$^{-1}$ in IR spectrum, complex multiplets at $\delta$ 2.15-2.9 (m, 5H), 3.4-3.8 (m, 1H), 4.5 (s, 1H), 7.35 (m, 5H, Ar) in $^1$H-NMR and in mass spectrum M$^+$ at 212 (100%). Similarly, in case of 1,4-dithiaspiro[4.4]nonane-1-oxide 24a and 1,4-dithiaspiro[4.5]decane-1-oxide 24b, characteristic features of the S-oxides are the strong absorption at 1040 cm$^{-1}$ in IR spectrum.
and complex multiplets between 1.6 and 3.8 δ in ¹H-NMR for the methylenes in dithiolane skeleton. Also, 1,5-dithiaspiro[5.4]decane-1-oxide 24c and 1,5-dithiaspiro[5.5]undecane-1-oxide 24d gave characteristic absorption band for S-oxide at 1040 cm⁻¹ in IR spectrum. Proton-NMR of compound 24c showed signals at δ 1.5-2.2 (m, 7H), 2.2-2.9 (m, 5H), 2.95-3.15 (m, 2H) and mass spectrum gave M⁺ at 190 (12%). Compound 24d gave ¹H-NMR signals at δ 1.0-2.1 (m, 10H), 2.1-2.58 (m, 4H), 2.6-3.1 (m, 2H) and mass spectrum gave M⁺ at 204 (20%). Interestingly, no di-S-oxides or sulphone was observed during singlet oxidation,¹⁵ and, surprisingly, no dethioketalization occurred either! Subsequently, we have examined the validity of 65% yield of 22b from 23b under reported experimental conditions with a 200W lamp⁴ (Scheme-5). However, we faced problems in reproducing these results and with repeated trials a maximum of only 10% dethioketalized product 22b could be observed by GLC.

Scheme - 5
Recently, Masaki et al reported photo-oxygenation reaction of 2-(p-methyl phenyl)-1,3-thiane 30a or 2,2-di(p-methylphenyl)-1,3-thiane 30b under various conditions and by use of the different photoelectron-transfer sensizers such as 2,4,6-tri-(p-chlorophenyl) pyrylium perchlorate (TCPIClO₄), 9,10-dicyanoanthracene (DCA), Methylene Blue (MB) and (meso-TPP). When 30a was subjected to the photosensitized oxygenation reactions, p-methyl benzaldehyde 31, 2-(p-methylphenyl)-1,3-thiane-1-oxide 32a and small amount of 2-(p-methylphenyl)1,3-thiane-1,3-dioxide 33a were also obtained (Scheme-6).

Another unusual observation during our studies was the isolation of OH insertion product 29, besides 1,3-thiolane-1-oxide during the singlet oxidation of 2-ethyl-2-phenyl-1,3-thiolane 29 (Scheme-5). However, such OH-insertion products could not be observed with other substrates, even after repeated trials.

The tentative mechanism for this complex oxygenation process is shown in Scheme-7. Presumably, the formation of thiolane S-oxides and OH insertion products both could be rationalized via peroxysulfoxide 36, which could be formed either via a step-wise electron transfer process through a tight ion-pair 35 or via a concerted process. Based on detailed study by Foote et al. 36 could also be represented as thiadioxiranes 42 or H-bonded 43 with solvent MeOH. The reduction of 36/43 by 34 could result in the formation of S-oxides 37. On the other hand, Pummerer rearrangement of 36 via concerted 40 or step-wise 41 could lead to 38, which on further reduction with 34 could furnish OH insertion product.
39. The proposed mechanism explains the need for polar protic solvent (MeOH) and rationalizes the usually fast oxidation in the early stages of oxidation.

**Scheme 7**

In conclusion, an efficient methodology for the synthesis of 1,3-dithiolane-S-oxide via singlet oxidation of 1,3-dithiolane has been described. With one of the dithiolanes, an interesting OH-insertion product 39 has been obtained. No dethioketalization occurred during singlet oxidation of dithiolanes. Thus, during Takahashi’s dethioketalization (photolysis in the presence of O₂), singlet oxygen is certainly not involved.

In continuation, we have also examined the role of the size of reagent to ascertain whether stereoelectronic effect or steric effect is responsible for stereoselective oxidation of some of the optically active dithiolanes. It is commonly believed that the approach of oxidising agents e.g. NaIO₄, m-CPBA, etc., which are fairly bulky, is directed due to steric
reasons and hence, asymmetric S-oxides are obtained. The argument is based on the conformational preferences for dithiolanes. The examination of its model revealed that oxidation (Scheme-8) should preferentially take place at S-1' 44b' rather than S-3', since the molecule in its most stable conformation 44b', is sterically accessible to oxidation at S-1' rather than S-3', where approach of the reagent is inhibited due to the presence of C-2, C-1 and C-6 on the same side. Therefore, oxidation at S-1' takes place to give the more favoured equatorial sulfoxide.\(^2\) We were curious to know whether the above steric arguments are really true! Whether there could be any stereoelectronic reason for stereoselection. We argued that if bulky reagents are the reason for stereoselection, then with smaller oxidizing reagents such as singlet oxygen or radical cation/superoxide combination\(^1\) developed in our earlier studies, one should get a mixture of diastereomers. Following studies explore some of these mechanistic curiosities. Thus, oxidation of optically pure dithiolane 44a and 44b (Scheme-8) with small reagents e.g. singlet oxygen and radical cation-superoxide coupling method,\(^1\) was examined and product stereochemistry was compared with oxidations with bulky reagents e.g. NaIO₄, m-CPBA.\(^2\) These studies have relevance for various theories of stereoelectronic effect e.g. Cieplak effect,\(^2\) nucleophilic-electrophilic surface theory,\(^2\) etc. \(\pi\)-face selection during addition to trigonal carbon in olefins, carbonyls, enones, dienes, etc. or stereoselective additions (axial or equatorial) during S-oxide formation of dithiolanes are at the core of stereogenesis. While more obvious steric aspects of face selectivity was recognised early in 1952, popularly known as Cram's rule, the relevance of stereoelectronic effect was slow to come in organic chemistry. In due course, various theories of \(\pi\)-face stereoselection have come up in recent times. Most of these theories can be divided into two broad categories. The first group emphasizes the importance of ground state properties of starting materials, whereas the second group emphasizes the relevance of transition state properties. However, in these theories, the role of size of the reagent is rarely stressed especially, during oxidation of optically active dithiolanes, the stress on the bulkyness of the reagent is a popular reason. However, we have a suspicion for this type of explanation.

The preparation of dithiolanes 44a,b and 46a,b was accomplished by standard procedure from respective ketones. Singlet oxidation of dithiolanes gave optically pure S-oxides,
even with fairly small oxidizing reagents, which should not exhibit any steric bias. This clearly establishes the fact that the reason for stereoselection in spiro-optically active dithiolanes is not steric, but stereoelectronic in nature.

Additionally, the photochemistry of optically active spiro-dithiolanes was studied with another small reagent i.e. superoxide under electron transfer conditions, using 1-cyano-naphthalene (CNN) as photoelectron acceptor. The photosensitized electron transfer oxidation was accomplished by irradiating the solution of 1,3-dithiolanes in the presence of 1-cyano-naphthalene in an oxygen saturated mixture of acetonitrile and water (3:1).

The dithiolanes of menthone 44a,b and camphor 46a,b were subjected to the same set of reactions of an electron transfer, as in Scheme-5. The spirothioketalized compounds 44a,b, and 46a,b were prepared by 1,2-ethanediithiol and 1,3-propanediithiol mediated by BF₄-etherate or an acid, as reported in 65-70% yield. Compound 5-isopropyl- 8-methyl-1,4-dithiospiro (4,5) decane 44a was oxidised by an electron transfer method (1-cyano-naphthalene-¹O₂) as per above procedure to give 65% yield of S-oxide 45a and 8% of dethiolized menthone. The structure of compound 45a was confirmed by spectral data and compared with authentic sample. Authentic sample of S-oxide was prepared by NaIO₄ (1.0 equ.) as per literature procedure. The spectroscopic and analytical data of compound 45a matched perfectly with that of authentic compound (NaIO₄). The optical rotation of 45a showed exclusively single regio- and stereo isomer [α]²₅° - 13.70, similar to product obtained by NaIO₄. IR spectrum of 45a gave the characteristic S-O stretching band at 1050 cm⁻¹, ¹H-NMR gave signals at δ 0.7-1.1 (m, 9H), 1.2-2.8 (m, 9H), 2.9-3.45 (m, 4H) and ¹³C-NMR at δ 86.54(s), 57.47(t), 52.19(t), 45.76(t), 34.66(d), 32.64(d), 31.55(d), 26.74(t), 26.09(t), 24.29(q), 22.41(q), 18.81(q).

Dithiane 44b on oxidation with 1-cyano-naphthalene in presence of oxygen (CH₃CN:H₂O) (electron transfer) and 1.0 equiv. of sodium metaperiodate (authentic) in methanol led, exclusively, to a single regio- and stereo-isomer 45b. Compound spiro [menthane-3,2'-m-dithiane]-1'-oxide 45b gave rotation [α]²₅° : + 20.612, IR spectrum of which showed the characteristic S-O stretching band at 1040 cm⁻¹ and ¹H-NMR spectrum.
demonstrated a downfield shift of the C-6’ protons at δ ~ 3.0 and 13C-NMR at δ 68.87(s), 44.73(t), 44.34(t), 34.11(t), 29.53(d), 28.99(t), 26.72(d), 25.25(d), 24.05(t), 23.35(t), 21.80(q), 20.92(q), 18.83(q). Mass spectrum indicated M⁺ at 260 (15%).

**Scheme - 8**

Subsequently, we prepared dithiane of camphor, 46a,b, which were subjected to oxidation with (I-CN/\(^{18}\)O₂ at 350, CH₃CN:HO) for 20 minutes, but it led to the polymeric product (white ppt.). Oxidation using sensitizer procedure (Rose Bengal-\(^{18}\)O₂, CH₃CN:HO)\(^{16}\) also failed to give the desired product. We concluded that camphor dithiane products under photolytic condition may not be stable.
CONCLUSIONS

1,3-Dithiolanes constitute an important functional group in organic chemistry. While studying the photochemical behaviour of this functional group, we developed two new routes for dithiolane S-oxide formation, both of which are neutral and mild reaction conditions. These methods should complement conventional oxidising methods like oxidation with peroxides (m-CPBA, NaIO₄).

The oxidation of optically active dithiolane clearly establishes the fact that the reason for stereoselection in optically active spiro-dithiolanes is not steric (earlier presumption), but stereoelectronic in nature. We presume that there are hidden stereoelectronic parameters via σ-bond interactions and their combinatorial effect, etc. for stereoselective oxidations.
EXPERIMENTAL

General procedure for protection of aldehyde and ketone by 1,2-Ethanedithiol or 1,3-Propanedithiol(I): A solution of aldehyde or ketone (10 mmol) in dichloromethane (15 ml) was stirred under protection of guard tube (CaCl₂) at room temperature. To the stirring solution, 1,2-ethanedithiol (15 mmol) or 1,3-propanedithiol (15 mmol) and catalytic amount of BF₃-etherate were added successively. After following the progress of the reaction by TLC, dichloromethane layer was washed with dilute aqueous solution of potassium hydroxide (5%) (3x10 ml) to remove excess 1,2-ethanedithiol or 1,3-propanedithiol, followed by water washings (2x20 ml), solvent was dried over anhydrous Na₂SO₄. Solvent was evaporated and thioketals were purified by silica gel column chromatography.

Following this procedure, the quantities (mol) of reactants used and the various thioketals prepared are given below:

**1,4-Dithiaspiro [4.4] nonane (23a):**

- Cyclopentanone : 0.84g (10 mmol).
- 1,2-Ethanedithiol : 1.4g (15 mmol).

The crude product was purified by silica gel column chromatography using pet.ether as eluent (1.36g, 85%): (b.p. = 90°C/5mm, Lit. b.p.²⁶ = 89°C/5mm).

**1,4-Dithiaspiro [4.5] decane (23b):**

- Cyclohexanone : 0.98g (10 mmol).
- 1,2-Ethanedithiol : 1.4g (15 mmol).

The crude product was purified by silica gel column chromatography using pet.ether as eluent (1.4g, 82%): (b.p. = 110°C/5mm, Lit. b.p.²⁶ = 107°C/5mm).

**1,5-Dithiaspiro [5.4] decane (23c):**

23c was prepared as per the procedure described for I.

- b.p. : 100°C/0.1mm (Lit.²⁶ 86-87°C/0.05mm).
- ¹H-NMR (80 MHz) : δ 1.64-1.86 (m, 6H), 1.88-2.23 (m, 4H), 2.75-2.98 (m, 4H).
1,5-Dithiaspiro [5.5] undecane (23d):

23d was prepared as per the procedure described for I and the product was purified by chromatography (2% EtOAc:pet.ether) to afford 85% yield.

$^1$H-NMR (80 MHz) : δ 1.52-1.88 (m, 8H), 1.89-2.19 (m, 4H), 2.75-3 (m, 4H).

2-Phenyl-1,3-dithiane (26):

m.p. : 73°C.

$^1$H-NMR (90 MHz) : δ 1.64-2.34 (m, 2H), 2.73-3.38 (m, 4H), 5.15 (s, 1H), 7.15-7.6 (m, 5H).

Typical procedure for singlet oxygen oxidation of 2-substituted-1,3-dithiolanes to 1,3-dithiolane-1-oxides (II): The solution of 1,3-dithiolanes (1 mmol) in methanol with photosensitizer (either Rose Bengal or Methylene Blue) (0.5 mmol) in pyrex vessel was irradiated with 200W Hanovia lamp for 4-5 h. under continuous oxygen agitations. The ambient temperature was maintained at (+, 2°C) by continuous water circulation. The progress of the reaction was monitored by GLC. After the completion of reaction, solvent was concentrated and residue was purified by silica gel column chromatography to furnish 1,3-dithiolane-1-oxides.

1,4-Dithiaspiro [4.4] nonane-1-oxide (24a):

Yield : 80%.

b.p. : 118-120°C/0.05mm (Lit.$^3$ 122°C/0.05mm).

IR (Neat) : cm$^{-1}$ 1040(s), 1250(m), 3000(m).

$^1$H-NMR (80 MHz) : δ 1.8-2.0 (m, 7H), 2.6 (m, 1H), 3.1-3.8 (m, 4H).

MS : m/z 176 (M$^+$, 42%), 159(10), 149(12), 77(54), 71(26), 67(100).

1,4-Dithiaspiro [4.5] decane-1-oxide (24b):

Yield : 75%.

m.p. : 87°C (Lit.$^3$ 83-85°C).

IR (Nujol) : cm$^{-1}$ 1040(s), 1220(m).

$^1$H-NMR (80 MHz) : δ 1.6-2.1 (m, 10H), 3.1-3.6 (m, 4H).
MS : m/z 190 (M⁺, 38%), 178(8), 153(16), 146(52), 114(24), 98(48), 81(92), 71(100), 55(73).

1,5-Dithiaspiro [5.4] decane-1-oxide (24c):
IR (CHCl₃) : cm⁻¹ 2920(s), 1040(vs), 800(s).
¹H-NMR : δ 1.5-2.2 (m, 7H), 2.2-2.9 (m, 5H), 2.95-3.15 (m, 2H).
MS : m/z 190 (M⁺, 12%), 174(40), 121(70), 68(100).

1,5-Dithiaspiro [5.5] undecane-1-oxide (24d):
IR (CHCl₃) : cm⁻¹ 2910(s), 1440(m), 1030(vs).
¹H-NMR (80 MHz) : δ 1.0-2.1 (m, 10H), 2.1-2.58 (m, 4H), 2.6-3.1 (m, 2H).
MS : m/z 204 (M⁺, 20%), 188(18), 168(60), 153(55), 121(100).

2-PhenyI-1,3-dithiane-1-oxide (27):
m.p. : 141°C.
IR (CHCl₃) : cm⁻¹ 2960(m), 1460(m), 1040(vs), 750(m), 695(w).
¹H-NMR (80 MHz) : δ 2.15-2.9 (m, 5H), 3.4-3.8 (m, 1H), 4.5 (s, 1H), 7.35 (bs, 5H, Ar).
MS : m/z 212 (M⁺, 100%), 196(8), 163(32), 121(48), 90(70).

5-Isopropyl-8-methyl-1,4-dithiaspiro [4,5] decane (44a): 44a was prepared as per the procedure described for I. The product was eluted using 3% acetone in pet.ether during silica gel column chromatography.
¹H-NMR (90 MHz) : δ 0.78-1.04 (m, 9H), 1.1-1.86 (m, 7H), 2.06-2.58 (m, 2H), 3.24 (s, 4H).
MS : m/z 230 (M⁺, 32%), 202(20), 102(100).

Spiro [Methane-3,2'-m-dithiane]/Menthone trimethylene mercaptole (44b): A mixture of 1.0g (6.49 mmol) of menthone and 0.70g (6.4g mmol) of 1,3-propanedithiol was cooled in an ice bath and a stream of hydrogen chloride was passed through the solution till the reaction was complete (~ 5 h.). Excess HCl was then removed in a vacuum desiccator over NaOH and the mixture was dissolved in ether, washed with 5% NaOH solution, water, brine and dried over Na₂SO₄. After removal of ether, the residual oil was chromatographed (30% EtoAC-pet.ether) to give the pure 44b as crystalline product in 70-75% yield.
m.p. : 41-42°C.

IR (CHCl₃) : cm⁻¹ 2980(m), 1450(m), 1400(s), 1230(m).

¹H-NMR (80 MHz) : δ 0.85-1.0 (3d, J=5.5Hz, 3CH₃), 1.0-2.2 (m, 9H), 2.3-3.4 (m, 6H).

MS : m/z 244 (M⁺, 23%), 201(11), 170(17), 159(42), 137(30), 128(7), 114(9), 106(19), 95(31), 85(9), 81(34), 77(17), 67(23), 55(41), 43(75), 41(100).

Camphor ethylene mercaptol (46a): 46a was prepared as per the procedure described for 44b. The product was eluted using 3% acetone in pet.ether during silica gel column chromatography.

¹H-NMR (90 MHz) : δ 0.9 (s, 3H), 1.0(s, 3H), 1.1-2.56 (m, 7H), 2.9-3.4 (m, 4H).

MS : m/z 228 (M⁺, 40%), 200(68), 185(10), 118(100).

Spiro [camphane-2,2'-dithiane]/camphor trimethylene mercaptol (46b): 46b was prepared as per the procedure described for 44b and the product was purified by chromatography using pet.ether:ethyl acetate (98:2) to afford 70-80% of the pure dithiane.

IR (CHCl₃) : cm⁻¹ 2980(s), 1480(w), 1460(m), 1400(s), 1225(s).

¹H-NMR (80 MHz) : δ 0.9 (s, 3H, CH₃), 1.1 (s, 3H, CH₃), 1.2 (s, 3H, CH₃), 1.3-2.4 (m, 7H), 2.5-3.4 (m, 6H).

MS : m/z 258 (M⁺, 67%), 240(6), 225(2), 167(35), 123(81), 93(94), 91(100).

Authentic (NaIO₃): Spiro [Menthane-3,2'-m-dithiane]-1'-oxide (45b): To a solution of 1.0g (4.098 mmol) of menthone trimethylene mercaptol 44b in 70 ml of MeOH was added dropwise, a solution of 0.96g (4.482 mmol) of NaIO₃ in 20 ml of water at -10°C. The mixture was maintained at this temperature with stirring until the reaction was complete (7-8 h.). Sodium iodate was then filtered off and methanol was removed in vacuo followed by the extraction of the aqueous phase with chloroform. The chloroform extract was washed with brine, worked up and chromatographed (40% EtOAc/PhH) to afford 0.90g (84%) of the pure white crystalline solid product.
Photochemical Route:

Spiro [Menthane-3,2'-m-dithiane]-1'-oxide (45b): The solution of menthene trimethylene mercaptole 800 mg (3.27 mmol) with 1-cyanonaphthalene (CNN) 250 mg (1.63 mmol) in an oxygen saturated mixture of CH$_3$CN:H$_2$O (3:1, 187 ml : 62 ml) in a pyrex vessel was irradiated (Rayonet Photoreactor, 350 nm) for 12-15 h. Oxygen bubbling was repeated intermittently (every 90 min.) during photolysis. Progress of the reaction was monitored by TLC and GLC. Normally, 85-90% of reactants were consumed. Acetonitrile was removed under vacuum, water (20 ml) was added and the aqueous layer was extracted with dichloromethane (3x25 ml), washed with water (2x20 ml) and brine solution (2x20 ml). It was then dried over anhydrous sodium sulphate. Removal of solvent led to a residue which was purified by silica gel column chromatography using pet.ether:2% acetone first eluted menthone 10% and elution with pet.ether:10% acetone gave S-oxide 45b in 70% yield (600 mg) even 4-6% starting material was also recovered.

m.p. : 135-136°C (Lit. 135-137°C).

$[\alpha]_{D}^{25}$ : +20.612 [C = 0.0049, CHCl$_3$] (Authentic NaI$_4$). 
+20.477 [C = 0.0050, CHCl$_3$] (Photochemical).

IR (Nujol) : cm$^{-1}$ 2980(s), 2880(m), 1470(s), 1040(vs).

$^1$H-NMR (90 MHz) : $\delta$ 0.84 (d, J=6.5 Hz, CH$_3$), 0.86 (d, J=6.5 Hz, CH$_3$), 0.92 (d, J=6.5 Hz, CH$_3$), 2.4-3.4 (m, 24H).

$^{13}$C-NMR (200 MHz) : $\delta$ 68.87(s), 44.73(t), 44.34(t), 34.11(t), 29.53(d), 28.99(t), 26.72(d), 25.25(d), 24.05(t), 23.35(t), 21.80(q), 20.92(q), 18.83(q).

MS : m/z 260 (M$^+$, 15%), 244(6), 137(23), 123(100), 95(56), 81(58).

Analysis : C$_{13}$H$_2$S$_2$O: Calculated : C, 60; H, 9.23; S, 24.61.

Found : C, 59.80; H, 9.15; S, 24.40.

Electron transfer method (45a):

5-Isopropyl-8-methyl-1,4-dithiaspiro (4,5)decane : 500 mg (2.03 mmol).

Cyanonaphthalene : 166 mg (1.13 mmol).
**45a** was prepared as per the procedure described for **45b**. The product was purified by column chromatography. The use of pet.ether:acetone (98:2) yielded menthone (8%), pet.ether:acetone (93:7) gave 350 mg of S-oxide (65%) and starting material recovered was (5%).

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<tr>
<td>Yield</td>
<td>78% (250 mg)</td>
</tr>
<tr>
<td>m.p.</td>
<td>85°C</td>
</tr>
<tr>
<td>[α]_D^25</td>
<td>-13.70 (C = 0.026, CHCl₃) (Authentic NaIO₄)</td>
</tr>
<tr>
<td></td>
<td>-13.682 (C = 0.0265, CHCl₃) (Photochemical)</td>
</tr>
<tr>
<td>IR (Nujol)</td>
<td>cm⁻¹ 2980(s), 2860(m), 1470(s), 1050(vs).</td>
</tr>
<tr>
<td>'H-NMR (90 MHz)</td>
<td>δ 0.7-1.1 (m, 9H), 1.2-2.8 (m, 9H), 2.9-3.45 (m, 4H).</td>
</tr>
<tr>
<td>'C-NMR (200 MHz)</td>
<td>δ 86.54(s), 57.47(t), 52.19(t), 45.76(t), 34.66(d), 32.64(d), 31.55(d), 26.74(t), 26.09(t), 24.29(q), 22.41(q), 18.81(q).</td>
</tr>
<tr>
<td>MS</td>
<td>m/z 246 (M⁺, 27%), 228(10), 137(100), 95(37), 81(35).</td>
</tr>
<tr>
<td>Analysis</td>
<td>C₁₁H₂₂S₂O: Calculated: C, 58.53; H, 8.94; S, 26.01. Found: C, 58.41; H, 8.73; S, 25.78.</td>
</tr>
</tbody>
</table>

**Spiro [Camphane-2,2'-m-dithiane]-1'-oxide (47b):** To a solution of 1.0 mmol of dithiane **46b** in 15 ml of methanol was added dropwise a solution of NaIO₄ (1.0 mmol) in 5 ml water at -10°C. The mixture was maintained at -10°C with stirring until the completion of reaction (7-8 h.). Sodium iodate was then filtered off and methanol was removed in vacuo (< 40°C). The residue was extracted with chloroform 3-4 times, the extracts were combined, worked up and chromatographed (60% EtOAc-hexane) to afford 70-80% of the pure sulfoxide **47b**.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.p.</td>
<td>107-109°C</td>
</tr>
<tr>
<td>[α]_D^25</td>
<td>+ 132.4 [C = 1.0, CHCl₃].</td>
</tr>
<tr>
<td>IR (CHCl₃)</td>
<td>cm⁻¹ 1030.</td>
</tr>
<tr>
<td>'H-NMR</td>
<td>δ 0.75 (s, 3H, CH₃), 0.88 (s, 3H, CH₃), 0.94 (s, 3H, CH₃), 1.2-3 (m, 7H), 3.0-3.9 (m, 6H).</td>
</tr>
<tr>
<td>MS</td>
<td>m/z 258 (M⁺, 5%), 239(7), 183(12), 107(67), 91(100).</td>
</tr>
</tbody>
</table>
REFERENCES


