

## PHOTOFRAGMENTATION REACTIONS OF DITHIOLACTONES

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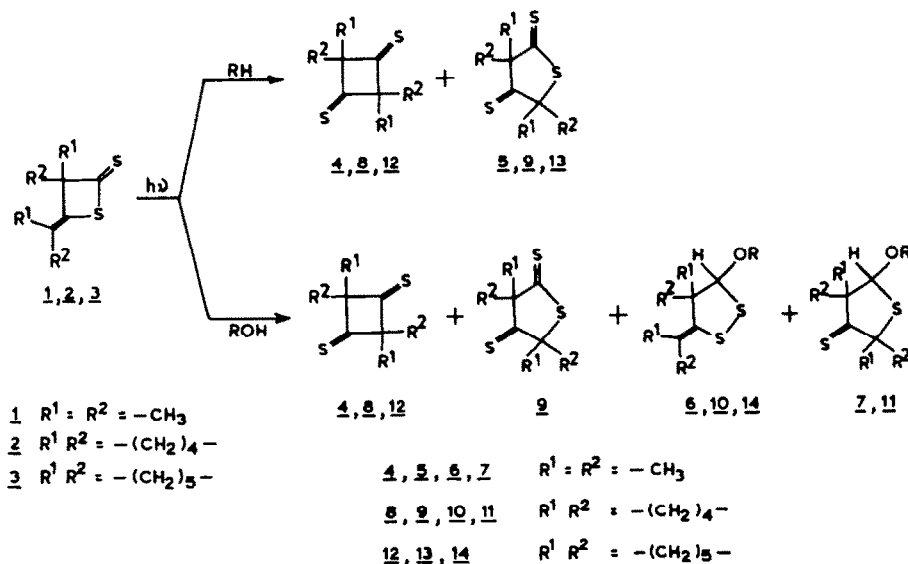
**Abstract**—The occurrence of Norrish type-I  $\alpha$ -cleavage has been established in  $\beta$ -dithiolactones, involving the  $n-\pi^*$  singlet state (diradical and carbene reactive intermediates). Concerted ring expansion to a thiocarbene from the excited state is suggested to be responsible for the formation, at least in part, of one of the cyclic thioacetals. Although this  $\alpha$ -cleavage process is similar to that of corresponding  $\beta$ -lactones, the behaviour of the resulting intermediates is different.

Early studies on the photochemistry of simple lactones and cyclic anhydrides illustrate the complexity of these reactions. The photochemistry of acid derivatives in general involves both  $\alpha$ -cleavage ( $\alpha$  to the carbonyl group) and  $\beta$ -cleavage (cleavage of the C-X bond) resulting in the loss of carbon monoxide and carbon dioxide and rearrangement.<sup>1</sup> Although a fair amount of understanding has been reached in the last several years regarding the photochemistry of carboxylic acid derivatives,<sup>2</sup> very little is known about thiocarboxylic acid derivatives. Photochemistry of dithioesters is virtually unknown. It is in this connection that we have investigated the photochemical behaviour of  $\beta$ -dithiolactones.<sup>3</sup> Interest in such systems also derives from our continued interest in the photofragmentation reactions of 1,3-cyclobutanedithiones.<sup>4</sup> Our hopes for observing the  $\alpha$ -cleavage process in dithiolactones were prompted by scattered reports wherein related systems are reported to do so. For example, trithiocarbonates,<sup>5</sup> O-ethyl S-benzyl xanthate<sup>6</sup> and the thiocarboxylic-O-esters<sup>7</sup> have been reported to undergo  $\alpha$ -cleavage (X-C=S). In the case of trithiocarbonates, elimination of carbon monosulfide and carbon disulfide has been observed whereas in the other two systems only

rearrangement is triggered by the  $\alpha$ -cleavage process. Neither in these systems nor during the photolysis of lactones and esters has the involvement of any carbene intermediate been reported. Results presented here on the photochemistry of dithiolactones illustrate that these undergo  $\alpha$ -cleavage similar to lactones but the behaviour of the resulting diradicals is unique.

### RESULTS

3-Mercapto-2,2,4-trimethyldithio-3-pentenoic acid  $\beta$ -thiolactone (**1**) and two related dithiolactones **2** and **3** were taken up for investigation. Dithiolactone **1** shows  $n-\pi^*$  (442 nm  $\epsilon$ : 16.0, methanol; 460 nm,  $\epsilon$ : 12, cyclohexane) and  $\pi-\pi^*$  (344 nm,  $\epsilon$ : 5700, methanol; 340 nm,  $\epsilon$ : 4500, cyclohexane) absorptions. Energy of  $S_1$  state is estimated to be  $\sim 55$  kcal mol<sup>-1</sup> from its absorption spectra. The triplet state is expected to have energy below 55 kcal mol<sup>-1</sup> but no measurements could be made. Selective excitation of the  $n-\pi^*$  band of **1-3** using Corning glass filters (CS-3.73; > 420 nm) in hydroxylic (alcohols and acetic acid) and hydrocarbon solvents (benzene and cyclohexane) gave the products shown in Table 1 and Scheme 1. Irradiation of **1** and **2** was carried out in a variety of



Scheme 1.

Table 1. Photolysis of the dithiolactones: yields of the products formed

Dithio- lactone	Solvent (RH or ROH)	Product yields*			
1	Cyclohexane	4 (60%)	5 (10%)	6 R = Me (80%)	7 R = Me (5%)
	Methanol	4 (< 5%)	—	6 R = Et (60%)	7 R = Et (5%)
	Ethanol	4 (< 5%)	—	6 R = Pr <sup>t</sup> (50%)	—
	i-Propanol	4 (< 5%)	—	6 R = Bu <sup>t</sup> (45%)	—
	t-Butanol	4 (< 5%)	—	6 R = Ac (60%)	—
	Acetic acid	4 (< 5%)	—	—	—
2	Benzene	8 (30%)	9 (10%)	10 R = Me (24%)	11 R = Me (5%)
	Methanol	8 (18%)	9 (7%)	10 R = Et (15%)	—
	Ethanol	8 (15%)	9 (7%)	10 R = Pr <sup>t</sup> (15%)	—
	i-Propanol	8 (10%)	9 (8%)	10 R = Bu <sup>t</sup> (20%)	—
	t-Butanol	8 (15%)	9 (10%)	10 R = Ac (15%)	—
	Acetic acid	8 (10%)	9 (10%)	—	—
3	Benzene	12 (30%)	13 (10%)	14 R = Me (60%)	—
	Methanol	12 (15%)	—	—	—

\*Product yields were estimated by <sup>1</sup>H-NMR integration

alcohols (methanol, ethanol, isopropanol, t-butanol), acetic acid, cyclohexane and benzene whereas 3 was excited only in methanol and benzene.

Excitation of 1 in benzene gave tetramethyl-1,3-cyclobutanedithione (4) and sulfur-containing product 5 (a secondary photoproduct formed only after accumulation of dithione 4). On the other hand, irradiation of 1 in hydroxylic solvents resulted in the formation of a solvent adduct 6 as the major product, a small amount of dithione 4 was also formed as a minor product. Both in methanol and in ethanol minor amounts of another adduct 7 accompanied the formation of 4 and 6. Products 4, 6 and 7 must therefore be formed directly from 1 as a study of products formed with time did not show the presence of any intermediates. Identification of all products was based on their spectral properties and comparison with authentic samples in some cases.<sup>4</sup>

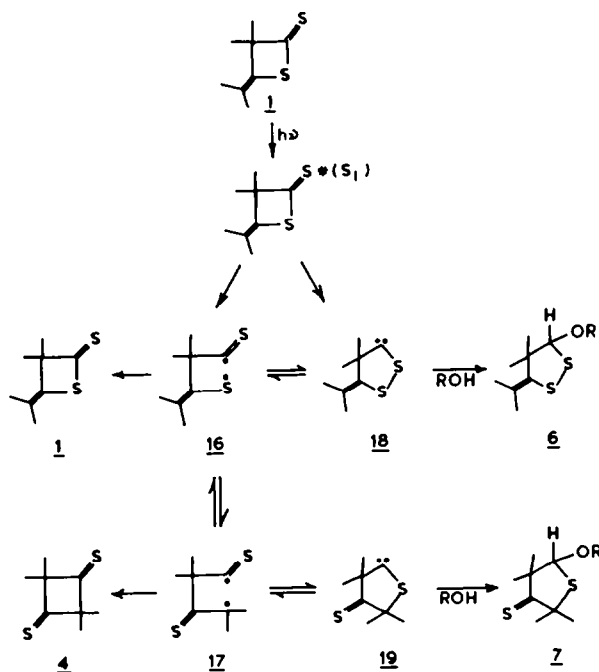
The photochemistry of 2 and 3 were closely similar to that of 1. Excitation of 2 and 3 in benzene and cyclohexane gave the corresponding 1,3-dithione (8 and 12 respectively) and sulfur incorporated products 9 and 13 respectively. Similarly excitation of 2 and 3 in hydroxylic solvents gave 1:1 solvent adducts 10 and 14 respectively as the major product. This was accompanied by the formation of 1,3-dithione (8 and 12) and sulfur incorporated products in minor amounts. Only during the excitation of 2 in methanol was yet another 1:1 methanol adduct formed, albeit, in small amounts.

Sensitization and quenching studies were conducted with dithiolactone 1 in order to identify the reactive state. We assume that these results can be applied to 2 and 3. As mentioned earlier, selective excitation of the  $n-\pi^*$  band of 1-3 resulted in the formation of products mentioned in Scheme 1 indicating the possible involvement of either a  $n-\pi^*$  singlet state ( $S_1$ ) or a triplet state ( $T_1$ ). Triplet sensitizers such as benzophenone ( $E_T \sim 69 \text{ kcal mol}^{-1}$ ), 4,4'-dibromodiphenyl ( $E_T \sim 66 \text{ kcal mol}^{-1}$ ) and fluorenone ( $E_T \sim 53 \text{ kcal mol}^{-1}$ ) did not sensitize these reactions. In agreement with these results, allo-ocimene, a triplet quencher ( $E_T \sim 47 \text{ kcal mol}^{-1}$ ) failed to quench these reactions. Based on these results we suggest that the products described in Scheme 1 originate from the lowest excited  $n-\pi^*$  singlet state.

## DISCUSSION

Photolysis of 1-3 in hydrocarbon solvents generally results in the formation of the corresponding 1,3-cyclobutanedithiones as the primary photoproduct. On the other hand, in protic solvents 1:1 solvent adducts are formed as major products. Both 1 and 2, in methanol, and 1 in ethanol give two 1:1 solvent adducts upon excitation whereas in other solvents only one adduct is obtained. 3 gives only one adduct even in methanol (Scheme 1 and Table 1). Since we infer from a time-dependant product study that sulfur-containing products (5, 9 and 13) are secondary photoproducts, our mechanistic discussion is limited to formation of 1,3-cyclobutanedithiones and solvent adducts (cyclic thioacetals).

Through triplet sensitization and quenching studies of 1 it is inferred that the reactive state is the excited singlet ( $n-\pi^*$ ,  $S_1$ ) state. Formation of products shown in Scheme 1 can be accounted for by invoking  $\alpha$ -cleavage (C-S bond) as the primary photoprocess in the  $S_1$  state. Thiocarbene as an intermediate is suggested by the formation of cyclic thioacetals while irradiations of 1-3 were conducted in alcoholic solvents. Formation of two types of cyclic thioacetals clearly calls for the involvement of two thiocarbenes 18 and 19 shown in Scheme 2. Although, one could conceive of a totally concerted pathway for the formation of thiocarbene 18 from the excited state of  $\beta$ -dithiolactone, involvement of thiocarbene 19 requires the presence of an intermediate possibly a diradical. Presence of a diradical is further supported by the formation of 1,3-cyclobutanedithiones. Assuming that diradicals are the precursors for the thiocarbenes 18 and 19, formation of two cyclic thioacetals and 1,3-cyclobutanedithione indicate that the initially formed diradical 16 through  $\alpha$ -cleavage process also exists in the other conformeric form 17. We believe that thiocarbenes 18 and 19 are in equilibrium with the diradicals 16 and 17. In the absence of suitable trapping agents this would imply that thiocarbene would revert to the diradical. This postulate is necessitated by the fact that we have failed to isolate any carbene-derived products while irradiations were conducted in hydrocarbon solvents. Thus we conclude that diradicals are formed as intermediates during the



Scheme 2.

$\alpha$ -cleavage process of  $\beta$ -dithiolactones and these undergo either ring expansion to thiocarbene or close to 1,3-cyclobutanedithione. It is interesting to note the same diradicals **16** and **17** generated from the corresponding 1,3-cyclobutanedithiones behave similarly.<sup>4</sup>

The behaviour of  $\beta$ -dithiolactones **1-3** studied here is different from that of  $\beta$ -lactones. Photochemical behaviour of the oxygen analogue of **1** (2,2,4,4-tetramethyl-3-hydroxy-3-pentenoic acid  $\beta$ -lactone) has been reported.<sup>8</sup> Excitation of **1** (O in place of S) to singlet  $n-\pi^*$  state results in the  $\alpha$ -cleavage but the behaviour of the resulting diradical is totally different from that of **16** and **17**. Diradicals from  $\beta$ -lactone either lose carbon monoxide to yield cyclopropanone or fragment to ketene. Neither of these processes are observed with  $\beta$ -dithiolactones. Enhancement of ring expansion over dethiocarbonylation and  $\beta$ -cleavage in **1-3** can be understood on the basis of stabilization of the thiocarbene intermediate and/or inhibition of competing reactions from the biradical intermediate. The large size of the sulfur 3p orbital and the resonance stabilization of thiocarbenes by adjacent sulfur might be expected to favour the ring expansion over dethiocarbonylation and  $\beta$ -cleavage.

At this stage, the presence of diradical and carbene as intermediates appears to be secure from our product study. Formation of such intermediates must arise from the  $\alpha$ -cleavage process. One can visualize the formation of diradical and carbene intermediates through either of the following pathways: (a)  $\alpha$ -cleavage of dithiolactones gives rise to the diradical **16** and this in turn undergoes ring expansion to thiocarbene **18** and establishes an equilibrium with diradical **17** and carbene **19** (diradical **16** is the primary intermediate); (b) thiocarbene **18** is formed directly from the excited state of  $\beta$ -dithiolactones through a concerted process and this rearranges to

the diradical **17** (thiocarbene **18** is the primary intermediate) and (c) excited  $\beta$ -dithiolactone undergoes  $\alpha$ -cleavage to the diradical **16** and rearranges to thiocarbene **18** simultaneously (both diradical **16** and thiocarbene **18** are primary intermediates). Our results support the occurrence of concerted rearrangement of  $\beta$ -dithiolactone to thiocarbene **18** at least partly. Excitation of **1** and **2** in protic solvents other than in methanol gives cyclic thioacetals corresponding to thiocarbene **18** as the only adduct, the other adduct being completely absent. Even in methanol, the adduct corresponding to **19** is formed only as a minor product. Further,  $\beta$ -dithiolactone **3** gives only one adduct, i.e. the one corresponding to thiocarbene **18**. These results imply that either thiocarbene **19** is trapped inefficiently by protic solvents or that the equilibrium is not in its favour. Through independent study, by generating these diradicals and carbenes (**16-19**) from 1,3-cyclobutanedithiones,<sup>4</sup> we have shown that at least in the case of **1**, the resulting thiocarbenes **18** and **19** can be trapped efficiently by protic solvents and that the diradicals **16** and **17** undergo ring expansion to thiocarbene equally efficiently. Therefore, the poor yield of cyclic thioacetals corresponding to **19** can be attributed neither to the inefficiency of ring expansion of diradical **17** nor to the inefficiency of trapping of thiocarbene **19** by protic solvents. Hence we speculate that thiocarbene **18** is produced directly from excited  $\beta$ -dithiolactone and this is trapped by protic solvents very efficiently to give cyclic thioacetal before it can either rearrange to the diradical **16** or establish an equilibrium with thiocarbene **19**. This speculation further rationalizes the poor yield (< 5% of **1**) of 1,3-cyclobutanedithiones while irradiations are conducted in protic solvents, although this is the only primary photoproduct in hydrocarbon solvents; under conditions where thiocarbene **18** is not trapped it

establishes an equilibrium with **16** and **17** and the latter diradical (**17**) closes to the observed product—1,3-cyclobutanedithione. Such type of concerted ring expansion to oxacarbene has been suggested earlier,<sup>9</sup> however, the question of the concertedness of oxacarbene formation from cyclobutanones is incompletely resolved. Although our results favour the occurrence of concerted rearrangement to thiocarbene in the excited state of  $\beta$ -dithiolactone, formation of thiocarbene through diradicals is not completely ruled out.

In summary, we have established the occurrence of Norrish type-I  $\alpha$ -cleavage in  $\beta$ -dithiolactones. Norrish type-I  $\alpha$ -cleavage is rarely reported in thio-carbonyl systems. It is now clear that diradicals and carbenes are intermediates in the product formation through  $\alpha$ -cleavage. It remains to be established whether diradicals arise from thiocarbenes formed in a concerted process or are themselves primary intermediates in the formation of thiocarbenes.

## EXPERIMENTAL

### Spectral data

UV-Visible absorption spectra were recorded on a Shimadzu UV-180 double beam spectrophotometer. IR data were obtained using Perkin-Elmer Model 730 infrared spectrometer. Varian T-60 and Bruker HW-270 FT NMR spectrometers were used for recording <sup>1</sup>H and <sup>13</sup>C NMR spectra, respectively. Mass spectral data were kindly provided by Prof. N. J. Turro and M. Mirbach.

### Chemicals

Benzene, cyclohexane, alcohols and acetic acid (BDH Chemicals) were once distilled prior to use. Sensitizers benzophenone, 4,4'-dibromobiphenyl and fluorenone were Aldrich samples and twice recrystallized before use. Quencher allocimene, Aldrich sample, was twice distilled before use. Tetramethyl-1,3-cyclobutanedione, dispiro[5.1.5.1]tetradecane-7,14-dione and dispiro[4.1.4.1]dodecane-6,12-dione were prepared by reported procedures.<sup>10</sup> 2,2,4,4-Tetramethyl-1,3-cyclobutanedithione (**4**) and dispiro[5.1.5.1]tetradecane-7,14-dithione (**12**) were prepared by refluxing pyridine solution of the corresponding dione with phosphorus pentasulfide following the literature reports.<sup>11</sup>

### Synthesis of 3-Mercapto-2,2,4-trimethyldithio-3-pentenoic acid $\beta$ -thiolactone (**1**)

A solution of 5 g of dithione **4** and 0.2 g of sodium methoxide in 25 ml of benzene was refluxed for 15–20 min on a steam bath. Completion of the reaction was indicated by the colour change from red to orange. The soln was acidified with formic acid and washed thoroughly with water. Benzene was distilled off and the orange liquid that remained was passed through a column (silica gel, hexane) to give 4 g (80%) of **1**. UV-visible (cyclohexane): 244(3800), 340(4500), 460 nm (**12**); IR (Neat): 1235, 1160, 1070, 865, 825  $\text{cm}^{-1}$ ; <sup>1</sup>H-NMR (CCl<sub>4</sub>):  $\delta$  1.41(s, 6H), 1.70(s, 3H), 1.86(s, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  19.98(q), 21.82(q), 25.25(q), 74.16(s), 122.27(s), 131.18(s), 242.90(s); Calc. for C<sub>8</sub>H<sub>12</sub>S<sub>2</sub>: C, 55.78; H, 7.02. Found: C, 55.65; H, 7.26%; Found, 172.0377; Calc for C<sub>8</sub>H<sub>12</sub>S<sub>2</sub> 172.0380.

### Synthesis of dithiolactone **2**

A pyridine soln (30 ml) of dispiro[4.1.4.1]dodecane-6,12-dione (5 g, 0.026 mole) and phosphorous pentasulfide (10 g, 0.045 mole) was refluxed for 2 h. Then the reaction mixture was poured into water and extracted with ether. Product obtained after evaporation of the solvent was purified by column chromatography (silica gel, hexane/benzene). An orange coloured liquid was obtained; UV (benzene): 270(12,750), 350(9450), 410 nm (shoulder);

IR (Neat): 1250, 1175, 1150, 980, 855  $\text{cm}^{-1}$ ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  1.68–1.97 (broad multiplet, 8H), 2.05–2.39 (broad multiplet, 8H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  25.99(t), 26.87(t), 27.79(t), 30.46(t), 32.57(t), 38.27(t), 84.61(s), 126.22(s), 131.77(s), 245.72(s); Calc. for C<sub>12</sub>H<sub>16</sub>S<sub>2</sub>: C, 64.22; H, 7.19. Found: C, 63.90; H, 6.96%; Found, 224.0692. Calc. for C<sub>12</sub>H<sub>16</sub>S<sub>2</sub> 224.0694.

### Synthesis of dithiolactone **3**

A benzene soln of 5 g of dispiro[5.1.5.1]tetradecane-7,14-dithione (**12**) and 0.5 g of sodium methoxide was refluxed for 15–20 min by which time the thione colour completely faded and the solution turned into orange colour. The soln was washed with water, dried over anhydrous sodium sulfate and evaporated to give orange solid (yield ~90%; mp 72°). UV-visible (CHCl<sub>3</sub>): 246(4800), 353(7000), 463 nm (**42**); IR (Nujol): 1180, 1120, 930, 835  $\text{cm}^{-1}$ ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  1.57–2.02 (broad multiplet, 18H), 2.18–2.27 (broad multiplet, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  21.10(t), 25.37(t), 26.25(t), 27.41(t), 27.49(t), 30.77(t), 33.24(t), 34.04(t), 76.64(s), 126.30(s), 129.98(s), 242.66(s); Calc. for C<sub>14</sub>H<sub>20</sub>S<sub>2</sub>: C, 66.61; H, 7.99. Found: C, 66.91; H, 8.40%; Found 252.1003. Calc. for C<sub>14</sub>H<sub>20</sub>S<sub>2</sub> 252.1006.

### General irradiation procedure

A 0.02 M solution of the dithiolactone in alcohols, acetic acid, cyclohexane or benzene (50 ml) was de-aerated by bubbling N<sub>2</sub> through the solution for 30 min. The above solution in a Pyrex vessel sealed with rubber cork was irradiated using a 450W medium pressure mercury lamp. Progress of the reaction was followed by TLC and after about 50–75% completion, solvent was evaporated off (in the case of acetic acid poured into water and extracted with ether) and the products were isolated by repetitive column and TLC (silica gel, hexane/benzene). Products were identified to be of three types based on their spectral properties (UV, IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, mass spectra and elemental analysis)—cyclobutanedithiones, sulfur incorporated products and solvent adducts (Scheme 1). Product yields are represented in Table 1. Large scale irradiations were conducted using Ace Glass Inc's immersion well reactor. About 300 ml of 0.02 M solution of dithiolactone was irradiated while nitrogen gas was continuously bubbled through the solution. Isolation of products was done as before.

### Identification of products

Products obtained upon irradiation of **1–3** are shown in Scheme 1. Irradiation of **1** in cyclohexane gave the corresponding dithione **4** and sulphur containing product **5**. On the other hand, irradiation of **1** in alcohols and acetic acid gave a 1:1 adduct-cyclic thioacetal in each case as the major product. Minor amounts of dithione **4** was also formed. However, careful investigation revealed that sulphur-containing product is a secondary photolysis product in the case of **1**. We assume that this might also be true in the case of **2** and **3**. Sulphur-containing products are also formed on irradiation of 1,3-cyclobutanedithiones and the spectral data are available in the literature.<sup>4</sup> Corresponding 1,3-cyclobutanedithione as one of the products was identified by comparison with authentic samples. The spectral properties (UV, IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and mass spectra) of isolated products were identical in all respects with authentic samples synthesized by reported procedures. Spectral data for these are already reported.<sup>11</sup>

3-Mercapto-2,2,4-trimethyldithio-3-pentenoic acid  $\beta$ -thiolactone (**1**) was irradiated in a variety of solvents in order to trap the carbene intermediates. Spectral data for these adducts are similar. Herein we provide spectral data for only two such adducts, namely methanol (**6**, R = CH<sub>3</sub>) and acetic acid (**6**, R = CO-CH<sub>3</sub>) adducts which serve as typical examples. In methanol and ethanol, in addition to **6**, minor amounts (< 5%) of another adduct is also formed

and only  $^1\text{H-NMR}$  spectral data could be provided for these owing to the difficulty in obtaining pure materials.

**Spectral data for 6 (R = Me).** UV (Cyclohexane): 250(4300), 345 nm (300); IR (Neat): 1450, 1360, 1190, 1090, 730  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.34(s, 3H), 1.43(s, 3H), 1.85(s, 3H), 1.89(s, 3H), 3.49(s, 3H), 4.61(s, 1H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  21.55(q), 23.13(q), 26.48(q), 26.83(q), 51.49(s), 58.29(q), 105.79(d), 123.53(s), 137.09(s); Mass Spectra *m/e* at 204 ( $\text{M}^+$  ion), 172, 141, 139, 128, 108, 96, 86, 81, 71, 59; Calc. for  $\text{C}_9\text{H}_{16}\text{S}_2\text{O}$ : C, 52.45; H, 7.84. Found: C, 52.77; H, 7.70%.

**Spectral Data for 6 (R = COCH<sub>3</sub>).** IR (Neat): 1750, 1460, 1370, 1220, 1025, 980, 920  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.36(s, 3H), 1.46(s, 3H), 1.88(s, 3H), 1.91(s, 3H), 2.15(s, 3H), 5.86(s, 1H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  21.05(q), 21.39(q), 23.49(q), 26.91(q), 27.09(q), 52.17(s), 93.65(d), 123.45(s), 137.33(s), 169.98(s); Mass Spectra (70 eV) *m/e* 232 ( $\text{M}^+$  ion); precise mass: found, 232.0574. Calc. for  $\text{C}_{10}\text{H}_{16}\text{S}_2\text{O}_2$ , 232.0576; Calc. for  $\text{C}_{10}\text{H}_{16}\text{S}_2\text{O}_2$ : C, 51.72; H, 6.89. Found: C, 52.22; H, 6.47%.

**Spectral Data for 7 (R = Me).**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.35(s, 3H), 1.39(s, 3H), 1.59(s, 6H), 3.35(s, 3H), 4.81(s, 1H).

**Spectral Data for 7 (R = Et).**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.10(t, 3H), 1.34(s, 3H), 1.40(s, 3H), 1.59(s, 6H), 3.60(dq, 1H), 3.85(dq, 1H), 4.89(s, 1H).

Similar to 1, dithiolactone 2 was also irradiated in a variety of alcohols (methanol, ethanol, iso-propanol, *t*-butanol) and acetic acid in order to trap the suspected carbene intermediates. As expected solvent adducts were obtained and one of them in major amounts. The yields of these adducts are listed in Table 1. Spectral data for all such adducts (10) were similar and as a typical example data for two such adducts (methanol and acetic acid) are provided. The other adduct suspected to be 11 was formed in too small amounts and could not be obtained in pure form for full spectral characterization.

**Spectral Data for 10 (R = Me).** UV ( $\text{CCl}_4$ ): 263(5000), 320 nm (250); IR (Neat): 1440, 1110  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.54–1.92 (broad multiplet, 10H), 2.17–2.24 (m, 2H), 2.30 (t, 2H), 2.42 (t, 2H), 3.47 (s, 3H), 4.60 (s, 1H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  25.85(t), 26.41(t), 28.13(t), 30.93(t), 31.49(t), 36.49(t), 36.40(t), 40.00(t), 57.62(q), 64.65(s), 103.37(d), 132.78(s), 135.33(s); Mass Spectra (70 eV)  $\text{M}^+$  ion at *m/e* 256.

**Spectral data for 10 (R = COCH<sub>3</sub>).** IR (Neat): 1750, 1445, 1365, 1210, 1050  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.57–1.95 (broad multiplet, 12H), 2.13(s, 3H), 2.26–2.35(m, 2H), 2.43–2.48(m, 2H), 5.86(s, 1H).

Direct excitation of 3 was conducted only in methanol and benzene. In methanol, a cyclic adduct 14 (R = CH<sub>3</sub>) and cyclobutanedithione 12 were obtained as primary products. No other solvent adducts were obtained. Spectral data for the adduct 14 (R = CH<sub>3</sub>) are: UV ( $\text{CHCl}_3$ ): 338 nm (weak  $n\text{-}\sigma^*$  band characteristic of disulfide); IR (Neat): 1440, 1220, 1090  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.50–1.67 (broad peak, 6H), 1.70–1.90 (broad multiplet, 10H), 1.93–2.08 (m, 2H), 2.30–2.47 (m, 2H), 3.48 (s, 3H), 5.12 (s, 1H).

Full spectral details were obtained for solvent adduct 6 based on which the structures were assigned. Spectral

features of adduct 10 (R = Me) and 14 (R = CH<sub>3</sub>) obtained from the irradiation of dithiolactone 2 and 3 respectively are closely similar.  $^{13}\text{C-NMR}$  and mass spectral data for 14 (R = CH<sub>3</sub>) could not be obtained.

#### Sensitization and quenching studies

Sensitization and quenching studies were carried out only with dithiolactone 1. Benzophenone, 4,4'-dibromobiphenyl and fluorenone were used as sensitizers. In a typical experiment, a solution of dithiolactone (1) (100 mg) and sensitizer (100 mg) in cyclohexane or methanol (25 ml) was irradiated in a pyrex tube using Rayonet RPR 3000 Å mercury lamp. Under this condition > 90% of the incident light was absorbed by the sensitizer. Analysis of the irradiation mixture by  $^1\text{H-NMR}$  spectroscopy revealed the absence of all the products.

Quenching studies were carried out using allo-ocimene as quencher. This was conducted in a merry-go-round apparatus with solutions varying in quencher concentration (0.00–0.03 M) and fixed dithiolactone concentration (0.02 M). The progress of the reaction was followed by UV-visible absorption spectroscopy (disappearance of dithiolactone). No quenching was observed.

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